Xenobiotic Chemicals with Pollution Potential

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KEYWORDS

Biodegradation, chlorinated compounds, environmental fate, persistence, risk assessment, toxicity

Abstract. Xenobiotic compounds are chemicals which are foreign to the biosphere. More specifically, they are chemicals having structural moieties or groups which are not found in natural products. Over five million chemical compounds are now known and industry produces about one hundred and fifty million tons of chemicals annually. Portions of these chemical products enter the environment and become pollutants when they exert an undesirable effect there. The type and magnitude of the undesirable toxic effects depends chiefly (as illustrated by the following relationship) on the intrinsic toxicity of the compound on the one hand and on the available concentration on the other:

$$\text{Effect} = \text{Toxicity} \times \text{Concentration}$$

The concentration of chemicals depends on loading (input), distribution and reactivity (behaviour) in various environmental compartments. The chemicals, depending on their fate in air, water, soil or sediment, may thus become available in different concentrations to organisms in different environmental subcompartments. Microorganisms play a key role in the biogeochemical cycles that occur in the environment. In these cycles, molecules of biological origin are being recycled by the respiratory process of microorganisms. Microorganisms also play an important part in the degradation of many man-made molecules. Some xenobiotic molecules, however, appear to be resistant to microbial attack.

XENOBIOTIC COMPOUNDS

Terminology

The term "xenobiotic" (stranger to life) is derived from the Greek words *xenos* (ξένος): a stranger, foreign, strange; and *bios* (βιος): life, or course of life. For the environmental chemist xenobiotic usually implies "foreign to the biosphere".

Unfortunately for the proper application of the term, *xenos* does not only mean foreign but also a foreigner who is to be met and welcomed (as, for instance, a stranger to an inn). The qualities of "foreign-ness yet friendliness" appear in the linguistically related expression "xenobiosis" which is a form of communal life in which two colonies of different species live together on friendly terms but do not rear their young in common, as in the case of certain species of ants (Webster, 1977). While many xenobiotic compounds appear to be perfectly harmless after entering the biosphere, others are not always on friendly terms with life, as the original Greek meaning implies.

Another term which is often used synonymously with "xenobiotic" is "anthropogenic" since it appears to be a scientific term for man-made. In Greek, *anthropos* (ἄνθρωπος) means man, human, and *gignesthai* (γίγνεσθαι) to become, be born. However, strictly speaking "anthropogenic" does not mean man-made but man-making—the origin of man—as is evident in anthropogenesis (the study of man's origin and development). Similarly, terms such as "mutagenic" or "carcinogenic" refer to agents which originate mutations or carcinomas.

On the other hand, the term "biogenic" (of biological origin, produced by the biosphere), which is of similar linguistic construction as "anthropogenic", is commonly accepted by the scientific community.

Adjectives which are used more or less interchangeably with "xenobiotic" or "anthropogenic" are: "man-made", "synthetic", "environmental", "alien" and "pollutant". Most often the full term includes "chemical" or "compound" as for example in "environmental chemicals" or "pollutant compounds". The word "chemical" itself somehow seems to imply unnaturalness since organic substances referred to in their context as natural compounds (e.g. vitamins, proteins, humic acids) are seldom spoken of as "chemicals".

Other terminology emphasizes certain undesirable aspects of xenobiotic

Table 1
Chemicals of environmental concern: Terminology

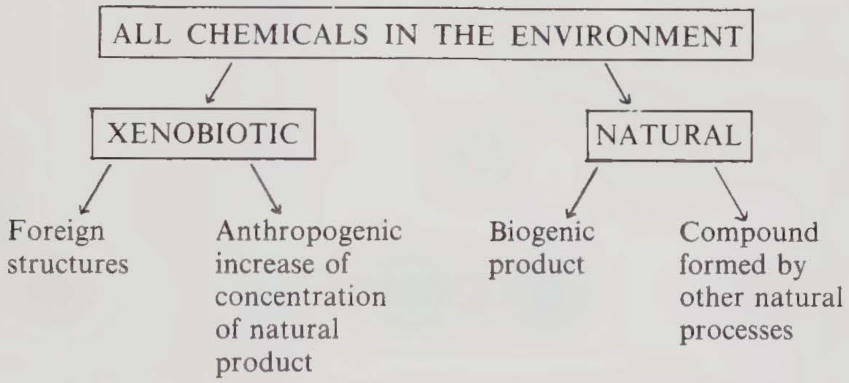
Characteristic of compound	Name (adjective)
Foreign to the biosphere	Xenobiotic, alien
Produced (released) by man	Anthropogenic, man-made, synthetic
Effect on the environment and/or on man	
—toxic	Environmental toxicant, TOS (toxic organic substance)
—non-degradable	Recalcitrant, persistent
—overall undesirable effects—implied	Environmental pollutant
—proven	

compounds: "recalcitrant" or "persistent" compounds do not degrade readily, and the terms "toxic chemicals", "environmental toxicants" or TOS (toxic organic substances) stress their harmful effect on biological organisms (Table 1).

Since 1828, when Friedrich Wöhler synthesized urea (Kerstein, 1962) we have known that, strictly speaking, the terms "anthropogenic", "man-made" and "synthetic" cannot be used synonymously with xenobiotic or alien compounds. By now many natural compounds have been synthesized and they are identical with their biosynthetic sister molecules in function and behaviour. The synthesis of biologically important molecules such as vitamins, hormones and amino acids are examples.[1] Kolbe, a student of Wöhler, first used the term *Synthese* (synthesis) in his report on the preparation of acetic acid.

Definitions and Classifications

All possible chemical compounds[2] found in the environment can be classified into those which would be there without the presence of man (natural products) and those which have been added by man (xenobiotic compounds).



A natural compound may be the product of living organisms (the biosphere) or may be formed by other natural processes. The important fact is that they have been long-time components of the ecosphere (or at least some environmental compartment) and biological organisms, particularly microorganisms, were exposed to them and able to adapt to their presence.

Xenobiotic compounds are substances which are normally absent from the ecosphere and are introduced by man, often by industrial processes involving synthetic chemicals. Of particular interest are xenobiotic compounds which have "unnatural" structural features. Thus in one sense "xenobiotic" refers to a compound which biological organisms in the biosphere have not been exposed to in evolutionary history (a definition centred on biological organisms) and in the other sense refers to structural features which are not commonly found in natural products (a definition centred on the compound). A special case is the anthropogenic increase of natural compounds to xenobiotic levels. A xenobiotic compound, thus, can be defined either as a chemical substance which is not produced by any natural enzymatic process or as a compound having "unnatural" structural features. Compounds which are released into the environment by the action of man and which occur in an environmental compartment in concentrations significantly higher than without man's interference reach "xenobiotic levels".

The difficulty in classifying a chemical as xenobiotic is highlighted in Tables 2 and 3 where chemical compounds which can enter the environment as pollutants are classified according to their origin. From the information given in these tables it becomes evident that a proper definition of "xenobiotic compound" is difficult when natural origin, diagenetic processes, erosion, forest fires, oil seepage, photochemical conversions and other processes are considered.

As with the definition of a weed (a plant out of place: a rose in a wheat field is, strictly speaking, a weed), a xenobiotic compound can be defined as a "chemical out of place in the biotic world". This chemical can be undesirable as such (the "wrong chemical", e.g. TCDD), it can be present in undesirable amounts (the "wrong concentration", e.g. the essential element phosphorus as phosphate in too high concentrations causes eutrophication) or it can be in the "wrong place" (e.g. NaCl in lake water rather than in the ocean, or ozone in the lower atmosphere rather than in the upper). Xenobiotic compounds are those compounds that are released in any compartment of the environment by the action of man and thereby occur in a concentration in this or another compartment of the environment that is higher than "natural". Examples of this can readily be cited from the presence of heavy metals in parts of the environment. Many metals are reasonably abundant in the earth's crust and are more mobilized by erosion. For some of these metals, however, mining, smelting and use have dramatically increased natural background levels in certain environmental subcompartments. Figure 1 shows the relation between natural and anthropogenic origin of

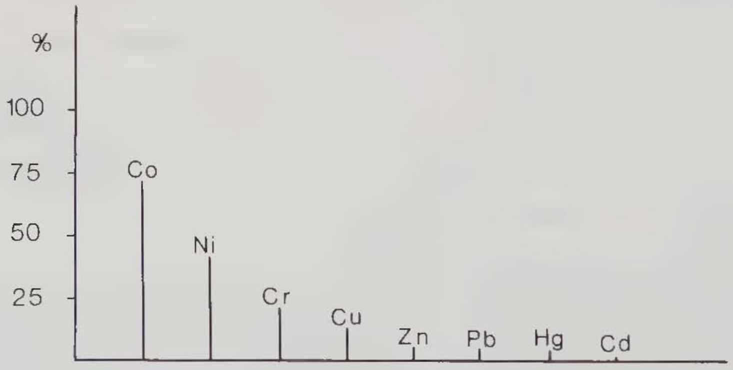


Fig. 1. Metals in Rhine river sediments. Figure shows percentage of *natural* origin for eight metals. The rest to 100% are of anthropogenic origin.

Table 2
Classification of natural products which are of interest in pollution studies

		Entry into the environment[a]	
Source of natural product	Examples of compounds	Natural release	Anthropogenic assistance
Of biological origin			
ANIMAL	Cell constituents, toxins	Excretion, death and decay of organism	Bio-industry, agriculture, municipal (biological) waste
PLANT	Primary and secondary plant products, terpenes, alkaloids		
MICROORGANISMS	Antibiotics, mycotoxins, odorous compounds in drinking water		
From secondary reaction			
DIAGENESIS	Organic compounds in sediments, oil	Oil seepage	Oil spill
HUMIFICATION	Humic and fulvic acids in soil, ocean *Gelbstoff*	In soil and water	Composting
PHOTOREACTION	"Blue haze" over tropical forests	From natural terpenes	
THERMAL REACTION	Polycyclic aromatic hydrocarbons from fire	Forest fires	Agricultural burning, incineration
Of geological origin			
EROSION	Minerals, heavy metals	Natural erosion	Mining, geophysical modification
VOLCANIC ACTION	CH_4, SO_2, CO, particulate matter, CS_2	Eruptions	

[a] Entry into the environment is defined as first appearance of a structural entity in any freely accessible environmental compartment outside living organisms

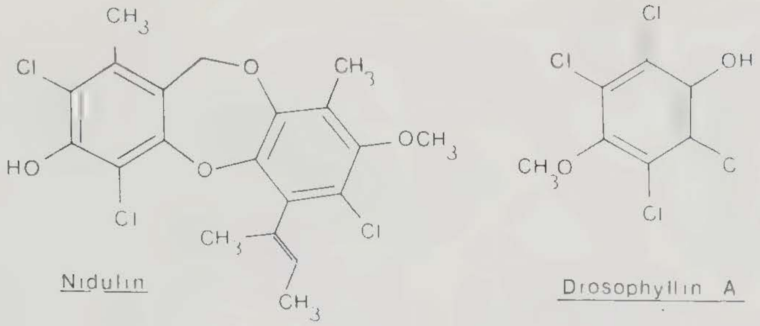
Table 3
Classification of xenobiotic compounds which are of interest in pollution studies

Type of product	Examples	
Synthetic compound of use	Pesticides, plasticizers, dyes, explosives, detergents, additives, polymers, intermediates	
Inadvertently formed waste- and by-products	Industrial waste water, car exhaust, products of incineration	CO, SO_2, NO_x, metals, particulate matter, PAH, by-products
	Chlorination of drinking water	chloroform, chlorophenols
Environmental transformation products of xenobiotic (industrial) compounds	DDE, photomirex, 2,4-dichlorophenol, 3,4-dichloroaniline, benzo(a)pyrene quinones	

some metals in Rhine river sediments (Korte, 1980). The effects of such increases in concentration have been dramatized by the catastrophic incidences in Japan of what are known as Minimata disease (mercury) and Itai-Itai disease (cadmium). Another example of a "natural product" which can become xenobiotic is oil when it is spilled into the environment by tanker or drilling accidents.

Finally, a definition of "environmental chemicals" as given by the German Environmental Programme in 1971 (Schmidt-Bleek and Wagenknecht, 1979) describes them as being substances which enter the environment through human activities and which can appear in such concentrations that they can become hazardous to living things, in particular to man himself. Among these substances are chemical elements and/or compounds of organic and inorganic nature, of natural and/or synthetic origin. The human activities may be direct or indirect, deliberate or accidental. The term "living things" encompasses human beings and their environment, including animals, plants and microorganisms.

Curiosity and the urge to create chemicals with useful practical applications have induced chemists in university and industrial laboratories to synthesize a vast array of organic chemicals: dyes and drugs, explosives, additives, pesticides, detergents and many others. In the search for unique properties—such as thermal stability or biological activity—many different structural features were explored, including atoms or functional groups rarely or never found in naturally occurring substances. Silicones, nitro- or trifluoromethyl (CF_{3-}), substituted aromatic rings and compounds with multiple halogen substitution are examples. Thus, xenobiotic compounds were created and industrial production and contamination of the biosphere was only the next step.



Nidulin

Drosophyllin A

Fig. 2. Two antibiotics with chlorinated aromatic ring features.

For many environmental scientists halogenated, particularly polychlorinated organic chemicals, are the most readily recognizable xenobiotic compounds. Yet several hundred naturally occurring organic chlorine compounds are known (Fowden, 1968; Faulkner, 1980) and, undoubtedly, many more will be discovered in the future. The structures of two chloroaromatic antibiotic products of microbial origin are depicted in Fig. 2.

During the last few years it has become evident that even some chemicals which are considered "typical" industrial organochlorine compounds also have significant natural sources (Pearson and McConnell, 1975). Examples are carbon tetrachloride, methyl chloride, chloroform and bromoform. As a curiosity, the occurrence of fluorocarbons in minerals may also be mentioned (Kranz, 1966).

Recent evidence further suggests that typical persistent chlorinated aromatic compounds can be formed by a natural process such as fire (Dow, 1978). Polychlorobenzenes, for instance, were found on the fly ash from installations burning coal (a natural product) (Olie and Hutzinger, 1980) and, theoretically, even the classical persistent pollutants—polychlorinated biphenyls (PCBs)—may be formed from such chlorobenzenes by photochemical reaction (Fig. 3; Choudhry *et al.*, 1979).

On the other hand, some synthetic compounds which resemble natural (even essential) products closely, are truly xenobiotic at least by one definition (they do not occur in the biosphere). Examples are: certain sugars and amino acids, antimetabolites, nucleic acid derivatives and analogues.

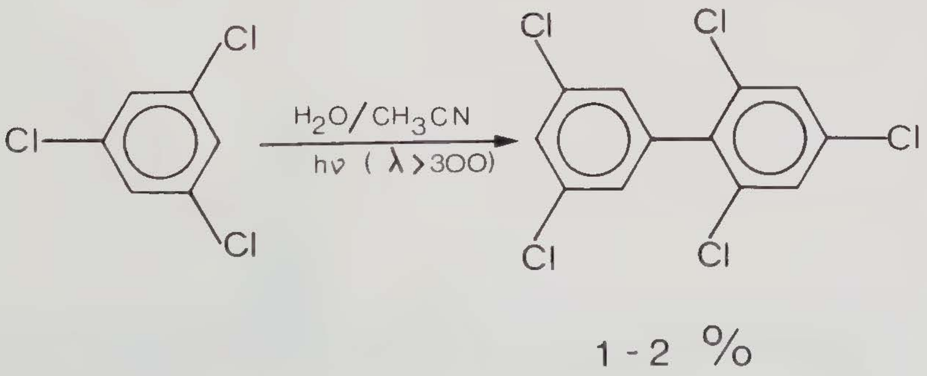
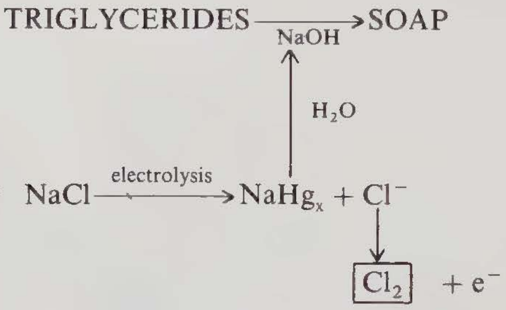


Fig. 3. Photochemical generation of chlorobiphenyl from trichlorobenzene.

Some Examples: Polychlorinated Compounds

The first large-scale use of chemicals was in the textile (cotton) and glass industries in the nineteenth century where sodium carbonate and other alkalis were necessary bulk ingredients, additives or preparation aids. The Leblanc and Solvay processes for the production of soda were developed in this period. With the advent of industrial electrolysis, sodium hydroxide, for which increasing demand existed from soap manufacturers, was prepared on a large scale. Chlorine is a second product in the electrolysis of sodium chloride and industrial uses had to be found for the excess chlorine so produced. Thus the first step in the development of organochlorine chemicals was made.



The first preparations of organochlorine compounds, however, were not dependent on the availability of elemental chlorine. Ethyl chloride, probably the first organochloride compound ever made, was obtained in solution in about 1440 when "spirit of salt" (HCl) was allowed to react with "spirit of wine" (ethanol) in a closed bottle for one month. It was not until much later, of course, that the structure of this "sweet spirit of salt" was determined (Kirk and Othmer, 1949).

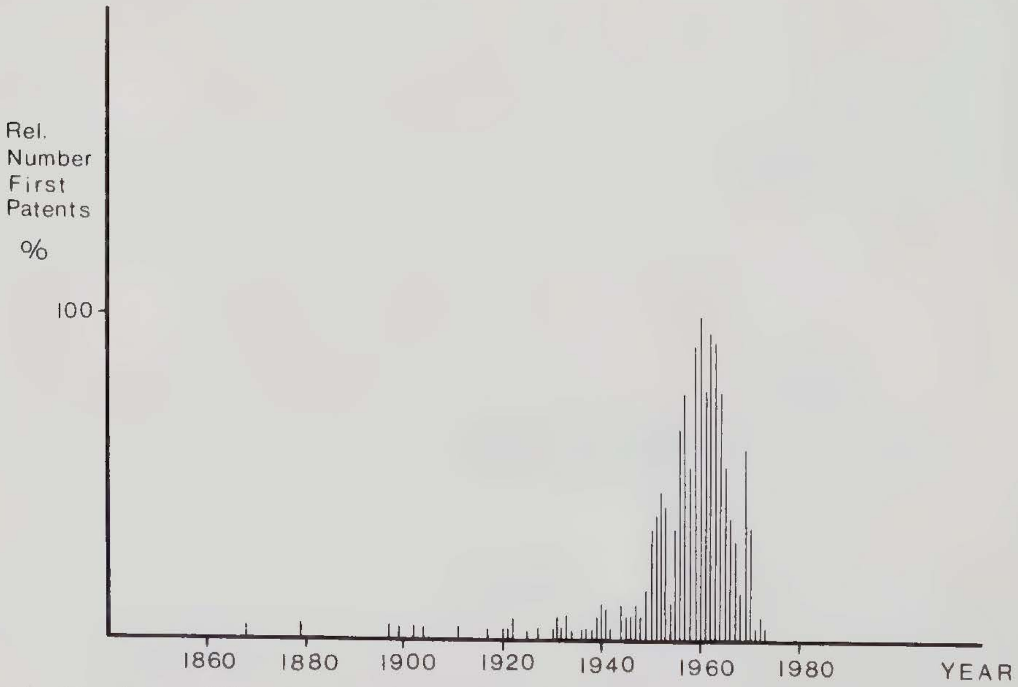


Fig. 4. Numbers of first patents for organochlorine compounds (Windholz, 1976).

Although some industrial interest existed in organochlorine compounds in the mid nineteenth century, as is evident from the granting of patents for such compounds, it was not until about 1940 that the number of new organochlorine compounds of apparent industrial value increased (Fig. 4). The development of most organochlorine insecticides occurred in this period. Interestingly, there was a steady decrease of patents for organochlorine compounds from about 1960 to 1975, the last year recorded in the Merck Index (Windholz, 1976). As is evident from Table 4 and Fig. 5 the total amounts of organochlorine compounds produced also show a similar trend. Because of desirable properties such as thermal stability and high dielectric constants the production and use of PCBs increased worldwide up until about 1970. By this time reports on their ubiquitous presence in the environment and their possible harmful effects caused voluntary restriction by industry to "contained use only". Several years later, manufacture and use was prohibited in many industrialized countries (Fig. 5). A total PCB budget in the USA, however, revealed that most of the PCB produced in that country was either still in use or deposited in landfills, thus threatening further contamination of the environment.

The year of first synthesis, first patent and first industrial production, together with production figures and use for a number of important organochlorine compounds are given in Table 4. Interestingly, for some compounds almost a century passed between first synthesis and industrial application, whereas for others first synthesis, patent and production occurred almost in the same year. Acute toxicity (LD_{50}) is not the most important toxicological characteristic; it is given for comparison since detailed description of toxic effects is outside the scope of this paper. The

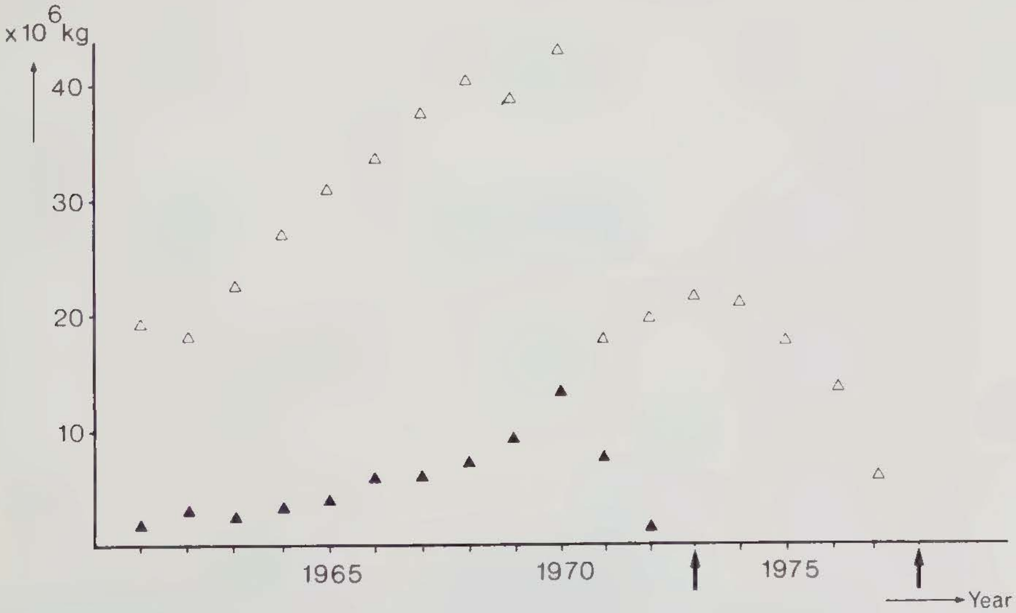


Fig. 5. PCB production figures for USA (Monsanto) (△) and Japan (▲). Arrows indicate termination of production in these countries.

Table 4

General information on some important organochlorine compounds

	First synthesis	First patent	First industrial production	Production			LD_{50} oral, rat (mg/kg)	10^{x} Bioconcentration factor (lipid weight)	Persistence	Use
				Country	Year	Amount ($\times 10^{6}$ kg)				
$PCB^{1,2}$	1867^{3}	1929^{4}	1929	$US^{5,6}$	1960	17.2	2000–12 000	$6–7^{7}$	+ +	Hydraulic fluid, transformer fluid, heat-transfer fluid, plasticizer, etc.
				US	1970	38.5				
				US	1971	18				
				US	1974	18.4				
				US	1979	0				
				OECD	1971	48				
				OECD	1976	30				
				OECD	1977	13				
$Mirex^{8}$	1946^{9}	1954^{10}	1959	—	—	—	230–370	6^{7}	+ +	Insecticide, flame retardant
		1961^{11}		US	1977	0				
Kepone	1950^{12}	1952^{13}	1958	—	—	—	95–140	5.2^{14}	+ ?	Insecticide
				US	1977	0				
HCB	1825	1910^{15}	1945^{16}	—	—	30	10 000	6^{7}	+ +	Fungicide, flame-retardant
Lindane (γBHC)	1825^{17}	1933^{18}	1941	US^{19}	1948	10	50–88	4^{7}	+	Insecticide
				US	1950	40				
				US	1951	58				
				US	1954	35				
				US	1960	20				
				US	1964	0				
DDT^{20}	$1873^{21,22}$	1940^{23}	1942	US^{19}	1945	12.5	113	6^{7}	+ +	Insecticide
				US	1950	40				
				US	1955	60				
				US	1960	80				
				US	1965	70				
				US	1970	30				
				World	1973	60				

PCP	1836[24,25]	1937[26]		US	1967	21	210	4.6[7]	+	Fungicide
				US	1969	23				Wood preservative
2,4D	1941[27,28]	1945[29]	1945	US[30]	1967	41	300- 1000	—	–	Herbicide
				US	1969	21				
2,4,5T	1941[27]	1945	1945	US[30]	1967	15	300–1000	3[32]	—	Herbicide[31]
				US	1969	2.25				
Chlorinated paraffins	1858[33]		1914	World	1973	270	–	–	– ?	Solvent, lubricant, plasticizer, flame-retardant
Toxaphene	1947[34]	1945[35]	1947	US[19]	1966	32	50–70	3.4[7]	+ ?	Insecticide
				US	1970	25				
				US	1972	37				
				US	1975	25				
Cyclodiene group										Insecticides
Aldrin	1944[36]	1948	1959	US[38]	1967	38	67	—	+ +	
Dieldrin		1948	1949	US	1968	20	48	5[39]	+ +	
Chlordane		1946[37]	1945	US	1969	45	457–590	—	+ +	
Heptachlor		1951	1951	US	1970	31	90- 135	—	+ +	
Ethylene dichloride (Dichloroethane)	1794/95[40]	1922[41]	-	OECD[42]	1973	4214	770	2[44]	–	Solvent
				OECD	1974	3492				
				US[43]	1977	5498				
				US	1978	5231				
Vinyl chloride	1835[45]	1915[46]	1936	US[2]	1936	2.5	250 ppm[47] (inhalation)	see ref. 44	–	Polyvinyl chloride production
				US	1971	1100				
				US	1973	1500				
				US	1978	3500				
				World	1973	7730				

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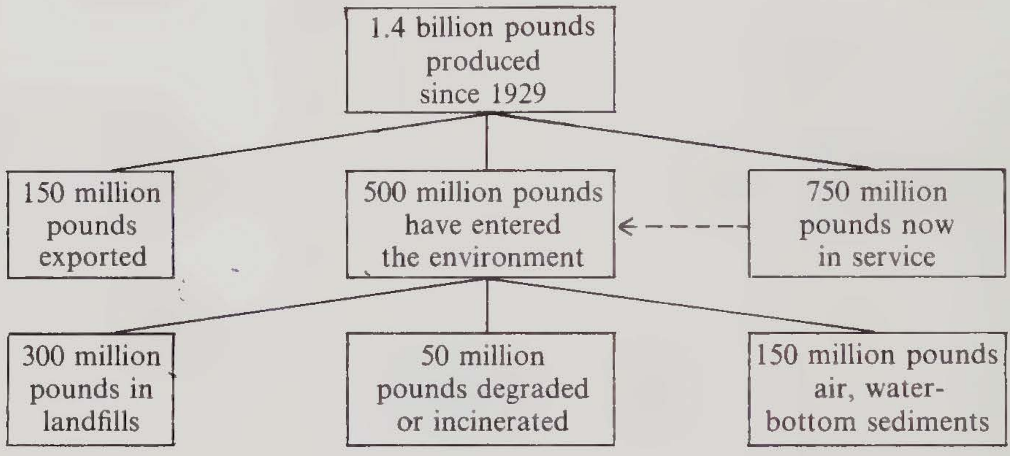
bioconcentration factor and persistence add information on the undesirable environmental properties of most of these compounds.

Three chlorine compounds are listed among the "top fifty chemical products" in the USA (Storck, 1979). One is hydrochloric acid with a yearly production of 2.8×10^6 t, and the other two are organic chlorine compounds ethylene dichloride, at rank 16 (5×10^6 t per year) and vinyl chloride at rank 19 (3.4×10^6 t per year). The total US production of chlorine gas itself was 12×10^6 t in 1978.

PCB history in the USA



Production Data and Release into the Environment

Over 5 million chemical compounds have been described in *Chemical Abstracts* up to 1980. At the present time, some 45 000 substances are traded worldwide, as such, and in a vast variety of mixtures and products. One hundred and fifty chemicals are produced in quantities in excess of 50 000 tons per annum (Schmidt-Bleek, 1980, Schmidt-Bleek and Wagenknecht, 1979) yet very little is known about the undesirable effects of many of them (Table 5).

Table 5
Chemicals (figures for 1980)

Source	Total number
Reported in "Chemical Abstracts"	>5 million
In US-Commerce	66 000
In NIOSH Registry[a]	35 000
Ecotoxicological data	<1000

[a] Registry of Toxic Effects of Chemical Substances, National Institute for Occupational Safety and Health, US Dept. Health, Education and Welfare, Rockville, Md. (Yearly publication.)

The total world production of synthetic organic chemicals is now estimated at 150 million tons per year. According to Storck (1979), the total amount of the top fifty chemical products in the USA was about 250 million tons in 1978, about 80 million tons of this total being organic compounds. Tables 6–8 give information on the production of various industrial commodities (Korte, 1980).

Waste products from chemical manufacture or technological processes involving combustion (burning of coal, gasoline or diesel engines) usually contain large numbers of different organic compounds, most of which have not yet been identified. But even "defined" industrial products are often complex mixtures. Polychlorinated biphenyls consist of at least a hundred chlorobiphenyls (of the 209 possible products). In addition, a number of impurities have been found. Furthermore, conversion products in the environment (photoproducts, metabolites) from the PCB components bring the total number of *known* products associated with PCB in the environment to almost 200 (Table 9).

Toxaphene, which is obtained by chlorination of a terpene fraction, is a mixture even more complex than PCB. The analysis of components in this mixture is not yet complete, but in 1974 separation into at least 175 different compounds was possible (Casida *et al.*, 1974).

Table 6
Contribution of different countries to world production of chemicals (%)

Country/continent	% in 1971
Europe	36
North America	43
Japan	10
Rest of the world	11

Table 7
Production of synthetic chemicals and other industrial materials

Commodity	World production in 1971 (in 10^6 t)
Synthetic organic chemicals	60
Inorganic chemicals	250
Iron	400
Non-ferrous metals	22
Oil (petroleum)	2065
—used for organic chemicals	~100

Table 8
Production of 15 Bulk Organic Chemicals in the USA[a]

Compound	Amount produced in 1978 (in 10^6 t)
Ethylene	13
Propylene	7
Benzene	5.5
Urea	5
Ethylene dichloride	5
Toluene	4.5
Ethylbenzene	4
Vinyl chloride	3.4
Styrene	3.3
Formaldehyde 37%	3.1
Methanol	3.1
Xylene	3
Terephthalic acid	2.8
Ethylene oxide	2.3
Ethylene glycol	1.9
Butadiene (1,3)	1.7

[a] Storck (1979)

Table 9
Compounds associated with PCB

Compounds	Number
Components of PCB (chlorobiphenyls)	>100
Impurities	
Chlorodibenzofurans Chloronaphthalenes	>10
Chloroquaterphenyls Chlorobiphenyl ethers	>20
Metabolites	
Hydroxy derivatives	~20
Products containing sulfur	~30

Little is known about the composition of a potentially yet more complex mixture of compounds, the chlorinated terphenyls (Jamieson, 1977). Figure 6 shows the potential number of chlorinated compounds in this series (Tulp, 1979). An analogous calculation for chlorinated quaterphenyls indicates that such products, even if only part of the theoretically possible compounds existed, would defy analysis. The composition of mixtures and impurities in technical products depends on the production process. Different by-products

Table 10
Impurities in technical chlorophenol preparations

Compound	Impurities (ppm)
2,4,6-trichlorophenol	Chlorophenols with different numbers of chlorine atoms (up to several %) Chlorohydroxydiphenyl ethers Chlorobiphenylols Chlorobiphenyl ethers (100–1000) Chlorodibenzofurans (5–20)
Pentachlorophenol	Tetrachlorophenols (up to several %) Chlorodiphenyl ethers Chlorohydroxydiphenyl ethers (to 50 ppm) Chlorodibenzofurans Chlorodibenzodioxins (to 10 ppm)

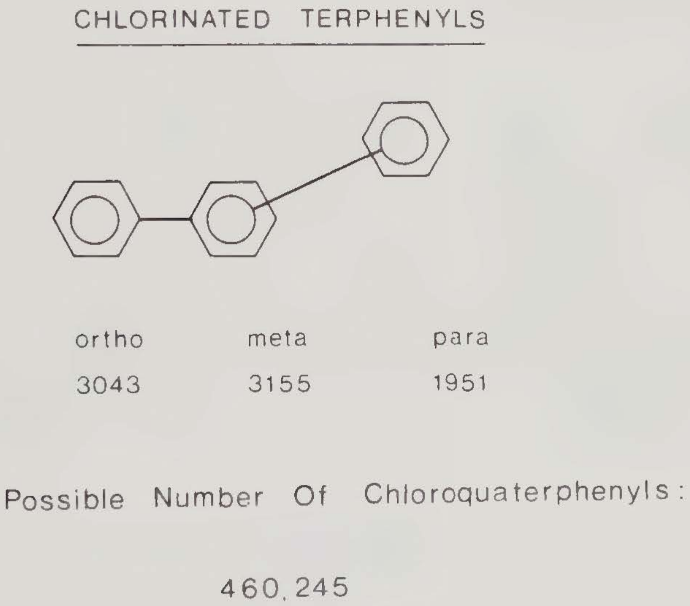
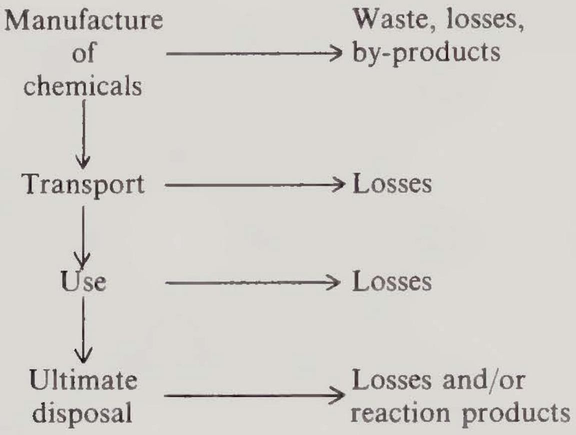


Fig. 6. Total possible number of chloroterphenyl and chloroquaterphenyl compounds.

and different, unreacted intermediates may thus give different types or different levels of impurities. Sometimes even small quantities of contaminants can become very important if, as with chlorodibenzo-*p*-dioxin impurities in chlorophenols and related products, these side-products show unusual toxicological properties. In this well-publicized case, up to 10 ppm of highly toxic compounds were found in technical products (Table 10) (Esposito *et al.*, 1980; Korte, 1980).

The entry of xenobiotic chemicals into the environment depends on the production methods, shipment, use patterns and ultimate disposal of industrial compounds.



The use pattern, in particular, often determines the total amount of compound released into the environment. Pesticides are usually directly and deliberately applied in the environment whereas some industrial chemicals are locked for tens of years in closed systems. Most xenobiotic compounds are intermediate in this respect: solvents are regenerated, yet evaporate; hydraulic systems leak; plasticizers, flame retardants and other additives leach out and surface coatings are exposed to the environment. Exact figures in this area are usually difficult to obtain. In one study the atmospheric emission during chlorination processes as it was known in the USA in 1970 was investigated (Table 11; anonymous, 1977).

Attempts have been made to set up emission inventories (Harris and Arp, 1979). For air pollution, major source types for which emission factors have

Table 11
Atmospheric emission in selected chlorination processes[a]

Product		Total production (approximate) (in 1000 t)	Emission[b] (approximate) (in 1000 t)
Ethylene dichloride	Chlorination	2350	46
Chloroethylene	Dehydrochlorination	1200	8
Vinyl chloride	Hydro- or dehydrochlorination	1500	13
Chlorobenzene	Chlorination	270	3
(Poly)chloromethanes	Chlorination	500	9

[a] US figures for 1970
[b] Includes starting material and HCl

Table 12
Air pollutant emission factors[a]

Major source

1. *External combustion sources*
    - Bituminous coal combustion
    - Fuel oil combustion
    - Wood-waste combustion in boilers
    - Residential fireplaces
2. *Solid-waste disposal*
    - Refuse incineration
    - Open burning
    - Sewage sludge incineration
3. *Internal combustion engine sources*
    - Average emission factors for highway vehicles
    - Heavy-duty, diesel-powered vehicles
    - Off-highway, mobile sources
4. *Evaporation-loss sources*
    - Dry-cleaning
    - Surface-coating
    - Storage of petroleum liquids
    - Transportation and marketing of petroleum liquid
5. *Chemical processes industry*
    - Adipic acid
    - Carbon black
    - Explosives
    - Paint and varnish
    - Phthalic anhydride
    - Printing ink
    - Synthetic rubber
6. *Food and agricultural industry*
    - Coffee roasting
    - Feed and grain mills and elevators
    - Fermentation
    - Starch manufacturing
7. *Metallurgical industry*
    - Primary aluminium production
    - Copper smelters
    - Iron and steel mills
    - Lead smelting
    - Grey-iron foundry
    - Secondary zinc processing
8. *Mineral products industry*
    - Asphalt roofing
    - Portland cement manufacturing
    - Glass manufacturing
    - Phosphate rock processing
9. *Petroleum industry*
    - Crude oil distillation
    - Catalytic cracking
    - Polymerization, alkylation and isomerization
10. *Wood-processing*
    - Chemical wood-pulping
    - Plywood veneer and layout operations
    - Woodworking operations

[a] Only some of the emission factors in each category are given

been adopted are presented in Table 12. A different, compound-oriented approach has been taken with emissions into water. Detailed analysis of compounds or water pollution parameters give information on the discharge of compounds into (and their presence in) surface waters (Shakelford and Keith, 1976; International Joint Commission, 1979). From a quantitative point of view oil is probably the single most important pollutant to enter the environment. Although relatively large amounts of oil are released naturally in local marine situations, a diversity of anthropogenic sources add to the environmental load via different routes (Table 13).

Table 13
Annual fluxes of petroleum[a]

Source	Flux (units of 10^{12} g/yr)
World oil production (1971)	2500
Oil transport by tanker (1971)	1400
Anthropogenic injections to marine environment	
—Loss from offshore oil production	0.08
—Marine transportation	2.13
—Loss from coastal oil refineries	0.2
—Industrial waste	0.3
—Municipal waste	0.3
—Urban run-off	0.3
—River run-off[b]	1.6
Subtotal	4.91
Natural seepage	0.6
Atmospheric rain-out[c]	0.6
Total	6.11
Torrey Canyon accident	0.1
Santa Barbara well blow-out	0.03–0.1
Amoco Cadiz accident	0.22
Total vaporization of petroleum products from continents to atmosphere	90

[a] Most data from Garrels *et al.* (1975)
[b] In part natural
[c] In part man's additions

XENOBIOTIC COMPOUNDS AND POLLUTION

Interest in the pollution potential of xenobiotic compounds has increased in the last years for the following reasons:

(a) Increase in both population density and industrial activity has led to a greater release of xenobiotic compounds into the environment. This includes activities associated with the use of resources, the need for energy and intensified agriculture.

(b) Analysis of environmental samples and laboratory studies have shown several xenobiotic compounds to be persistent. They do not just "disappear by natural mechanisms". They remain in the environment and thus "dilution is no solution for pollution".

(c) Similar to the subject discussed under (b) it was recognized that certain lipophilic xenobiotic compounds accumulate (concentrate) in biological organisms, some of them reaching very high and dangerous concentrations.

(d) The realization of existing global transport mechanisms, which expand local problems of highly industrial areas into world-wide problems, helped our understanding of why xenobiotic chemicals occur in so-called "pristine" areas such as the arctic regions, in mid ocean or extensive wilderness areas.

(e) Toxicological concepts have changed considerably from the preoccupation with acute toxicity to effects which are more subtle and occur over long periods of time (e.g. carcinogenicity). Also ecotoxicological effects are now being considered.

Intuitively we feel that a xenobiotic, synthetic, unnatural product cannot be "handled" by nature. Such a compound becomes a pollutant if it has undesirable effects (toxicity) which are compounded if the chemical is persistent and bioaccumulates. Here again, the dividing line between xenobiotic and natural compounds is not sharp.

The toxicity of many naturally produced organic chemicals is well known. Examples are tetradotoxin, curare, botulinus toxin, batrachotoxin, amarantine, aflatoxin and saxitoxin. Some toxic natural products even bioaccumulate; the ciguatera toxin, which is produced by algae, can accumulate in fish after several steps in the food chain and can then produce toxic effects in people eating the contaminated fish (Korte, 1980, p. 146). The majority of potentially toxic known chemicals in the environment, however, are xenobiotic compounds. Such chemicals become environmental pollutants when they have an effect (considered undesirable at the time) on the environment or on man via the environment. The effect on the environment can be on organisms in the environment or on non-living entities. In most cases the undesirable effect is a *toxic* effect, i.e. an effect detrimental to life processes.

The relationships leading to the risk of the occurrence of a toxic effect are outlined in the following:

$$\text{RISK} = \text{CHANCE} \times \text{INJURY}$$

$$\text{INJURY} = \text{TOXICITY} \times \text{EXPOSURE}$$

$$\text{EXPOSURE} = \text{CONCENTRATION} \times \text{TIME}$$

RISK is the overall *likelihood of a toxic* (or indeed any other) *effect occurring* for a specific risk group. Two examples can be given where one of the components of the "relationship" keeps the risks relatively low. A serious accident in a nuclear reactor would result in grave injuries. However, the possibility of such an accident occurring is relatively small. The possibility of ingesting residue levels of pesticides in food is very great but, on the other hand, the compounds in question are either relatively non-toxic or present in such small quantities that the overall health risk is minimal.

INJURY, the *occurrence* of a toxic effect, depends on the intrinsic toxicological properties of a chemical compound and the total dose (exposure). The examples given above illustrate this point: the radioactive materials released from a serious reactor accident are highly toxic *and* a certain proportion of the population would be exposed at high concentrations. The lack of injury from ingesting pesticide residue is due to either low toxicity of the pesticide in question or to insignificant exposure to the pesticide resulting from its low concentration.

In the example given above, EXPOSURE to pesticide residue is low (although the contaminants may be eaten daily) because of their low levels in foods. In the case of the reactor accident, exposure will be lower for those who subsequently leave the site (shorter time) and for those at the periphery of the occurrence (lower concentration).

The two parameters in the above-mentioned relationships which are amenable to scientific investigation and which can be approached experimentally are the effect (toxicity) of a xenobiotic compound and the expected concentration (available dose) in environmental compartments.

The toxicity is expected above some "no-effect" level (Fig. 7, horizontal line, concentration = no biological effects). The no-effect level for a chemical

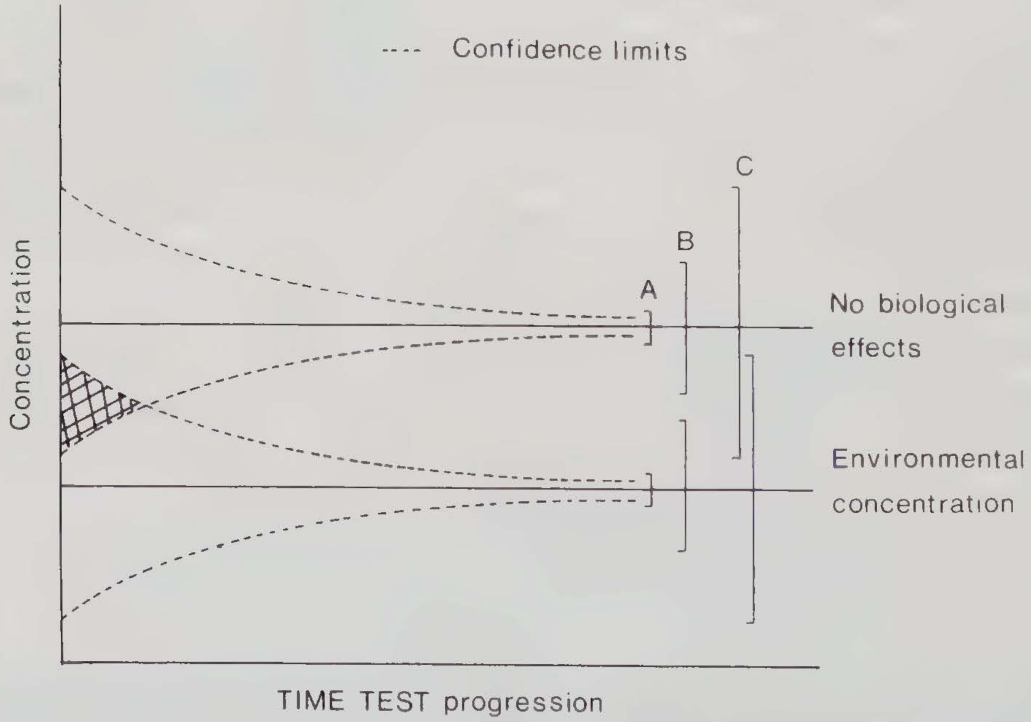
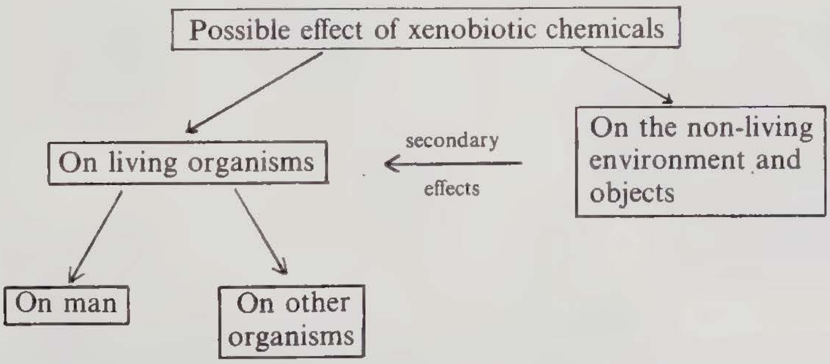


Fig. 7. The relationship between no-biological-effect concentration, environmental concentration and improvement of confidence limits with time-test progression. For details see text (Maki, 1979).

is the highest attainable dose (concentration) in a chronic toxicity study at which no adverse effects are observed in a group of test animals as compared to an untreated control group. The exposure concentration (Fig. 7, horizontal line; concentration = environmental concentration) in an environmental (sub)compartment is the measured concentration of compounds which are already in use and, for new products, the calculated, or extrapolated "expected environmental concentration". This concentration can be estimated from laboratory model studies and/or calculation from a number of measured parameters (see later section). The environmental concentration of a chemical must always be lower than the highest concentration which does not produce harmful effects (no-effect level). The difference between these two concentrations is the so-called "safety factor". Figure 7 outlines the relationship between no-biological-effect concentration, environmental concentration and the improvement of confidence limits for the test results as testing progresses. Generally, the more sophisticated tests which are applied later in the course of a testing programme give more reliable results and this reflects in the shape of the confidence limits drawn on the graph. Depending on the confidence in the experimental results and calculations for toxicity (no-effect level) and the expected environmental concentration, interpretation of results can be considered safe (case A), doubtful (case B) and unacceptable (case C).

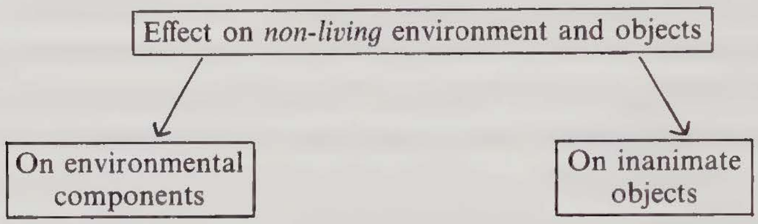
XENOBIOTIC COMPOUNDS: EFFECTS AND TOXICITY

As stated earlier, xenobiotic compounds can be considered pollutants only if they have undesirable effects. Many different effects of chemicals on man and his environment have now been recognized and these are outlined in the schemes below.



Effects on the *non-living environment* include: damage to structures by acidic air pollutants, effects of fluorocarbons and nitrogen oxides on the ozone layer, effect of carbon dioxide, aerosols and some trace gases on the earth's heat balance (e.g. greenhouse effect) and reduced visibility.

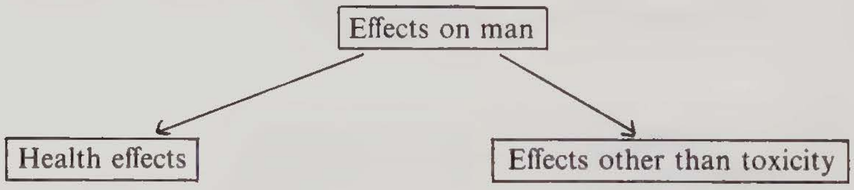
Interestingly, the most important effects in the above-mentioned examples are the secondary biological ones, e.g. the possible increase in skin cancer incidence due to reduction of the filtering capacity of the ozone layer for UV light, or the decrease of ecologically or commercially important species in acidified lakes.



e.g.
—atmosphere
—ozone layer
—greenhouse effect
—reduced visibility

e.g.
—destruction of buildings and structures by acid rain

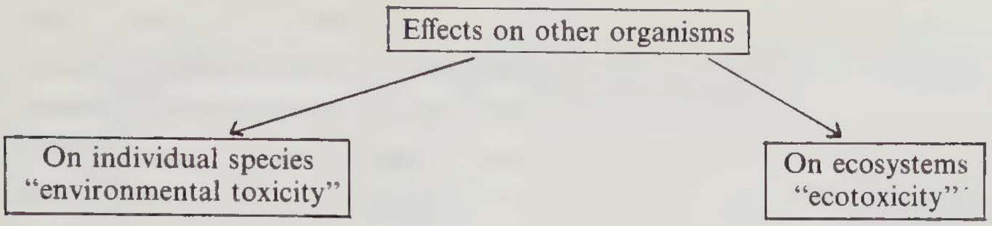
Health effects on man have always been the most-studied undesirable property of chemicals. Special emphasis in recent years has been on the long-term effects (e.g. carcinogenicity, mutagenicity and teratogenicity) from exposure to small concentrations of chemicals. Effects on the nervous system (including behavioural effects) and on reproductive capacity are also being studied. Examples of effects on man which are mainly based on *psychological* or psycho-physiological reactions are e.g. the taste of drinking water, the smell of air, and the general "dirtiness' of the environment.



e.g.
—classical toxicity
—carcinogenicity
—mutagenicity

e.g.
—taste of water
—smell of air
—general "dirtiness" (psychological)

The most significant difference between toxic effects on man on the one hand and organisms in the environment on the other, is that the *individual* is of prime concern in man, but only the preservation of the *population* in the latter case. A further clear distinction, however, has to be made with respect to *effects on organisms in the environment:* those on *population of individual species* and those on *ecosystems.*



e.g. commercially useful species
—crop plants
—fish

e.g. whole ecosystems and their stability
—toxicity to key species
—interference with chemical communication

The concern about individual species is often linked to commercial interest, examples being damage to leaves of crop plants by air pollutants or lethal or sublethal (e.g. growth inhibition) pollutant effects on certain fish species. Toxicity which refers to the effect of chemicals on *individual* species in the environment (e.g. a mammal, bird, fish species, plant, crayfish or earthworm) has recently been called "environmental toxicity" (environmental toxicology) in contrast to "ecotoxicity" which is the overall effect of a chemical on the health and stability of a total ecosystem (Hapke, 1980). Effects of chemicals on whole ecosystems can be tested by using model ecosystems or by measuring a number of significant parameters such as flow of energy, biocenosis structure, metabolism, cycle of nutrients and

Table 14
Differences between mammalian and aquatic toxicology (Dagani, 1980)

Mammalian toxicology	Aquatic toxicology
Objective: to protect humans	Objective: to protect populations of many diverse species
Must almost always rely on animal models since experimentation on humans is unethical	Can experiment directly on species concerned
The dose of a test chemical can usually be measured directly and accurately, and administered by a number of routes	The dose is known only in terms of the chemical's concentration in water and the length of exposure to it. The actual "absorbed dose" is sometimes determined experimentally using bioconcentration and metabolism studies
Extensive "basic" research has been conducted, emphasis has been on understanding mechanisms of toxic action	Hardly any "basic" research has been conducted; emphasis has been on measuring toxic effects, with an eye towards regulatory needs
Test methods are well developed, their usefulness and limits well understood	Test methods are relatively new, their usefulness uncertain

competitive behaviour of species. Effects of chemicals on the overall ecosystem can thus be revealed independently of the mechanism of action—e.g. whether the compound interferes with chemical communication or kills a key species. Intimate knowledge of ecology is necessary for interpretation of results. For further clarification some important differences between human (mammalian) toxicology and aquatic toxicology are shown in Table 14.

The toxicity of a chemical is one of the two important factors responsible for eliciting an effect, the other being the *concentration* (dose) of the compound available to the organism. Almost all effects show a dose–response relationship and thus the overall effect is dependent on the available amount. The available dose for organisms in the environment (and for man, to a large extent) depends on the *fate* of the compound in the environment.

XENOBIOTIC COMPOUNDS: ENVIRONMENTAL FATE

Environmental Chemodynamics[3]

After a chemical compound is released into the environment, an irreversible chain of events is set in motion and the compound is subject to a complex set of distribution and transformation processes. The type of compound, and the environmental exposure concentration which is available for contact with organisms depend to a large extent on what happens to the chemical in the environment before contact with an organism.

A compound may enter the environment in specific amounts and may then be transported or transformed to other structures by biological or (photo)chemical action. The compound or its transformation products, depending on their distribution and fate in air, water, soil or sediment may

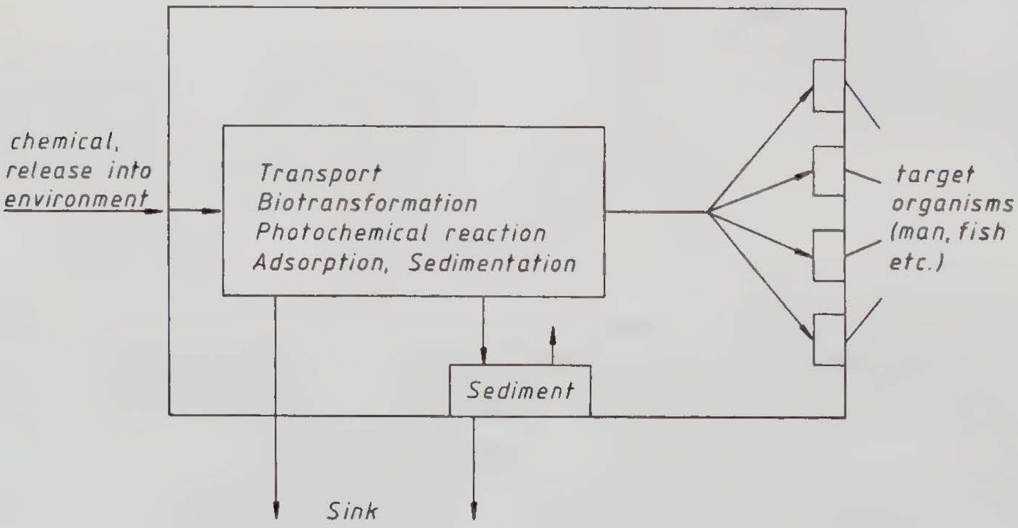


Fig. 8. Concept of environmental chemodynamics (ecokinetics).

become available to different organisms in various environmental subcompartments at different concentrations depending on their "environmental behaviour". Very volatile compounds, for instance, will not be available to fish in high concentrations and the same is true for compounds which are biodegraded rapidly. Compounds which adsorb strongly to sediment or have low solubility in water, again, will not be found in high concentrations in water, but may become available at low concentrations, over prolonged periods of time, from the "reservoir" in the sediment.

The "environmental chemodynamic" or "ecokinetic" approach considers the environment, in analogy with pharmacokinetics, as a complex superorganism (Fig. 8) or process model.

The amount of compound found in any particular environmental subcompartment depends on:

(i) rate and place of release;
(ii) equilibrium distribution processes (dispersion, transport) between phases and their rate;
(iii) loss, degradation (disappearance) mechanisms, called "sinks", and their rate.

(i) The rate of release (pollutant load) and the location of environmental entry are essentially determined by human factors such as economics and law, which are not amenable to scientific experimentation.

(ii) Distribution between environmental compartments depends largely on the physicochemical properties of chemical compounds and occurs across soil/water, water/sediment, water/air, soil/air interphases and across biological membranes of organisms. Natural movements and cycles usually determine the dispersion behaviour of chemicals in the environment. Irreversible adsorption or burial in sediment effectively removes chemical compounds from circulation and contact with the biota and can thus be classified as sink (cf. (iii)).

(iii) Any transformation of a compound effectively removes *this* chemical substance by change of structure. Ideally, the conversion is to carbon dioxide, water and mineral elements or, at least, to some other harmless substances. Sometimes, however, intermediate transformation products (metabolites) are either stable or toxic and thus pollutants in their own right. Examples are DDE and photomirex—produced from the original insecticides by photoreaction—and chlorophenols and chloroanilines which are products of microbial degradation of certain herbicides and fungicides.

Transformations of chemicals in the environment (Fig. 9) occur under the influence of:

—various chemical species (acid, base, nucleophiles, radicals);
—the UV component of solar radiation (photochemical reactions);
—action of enzymes (mainly microbial metabolism).

Conceptually it is convenient to describe transport and transformation as processes which occur separately, though in reality they happen concurrently.

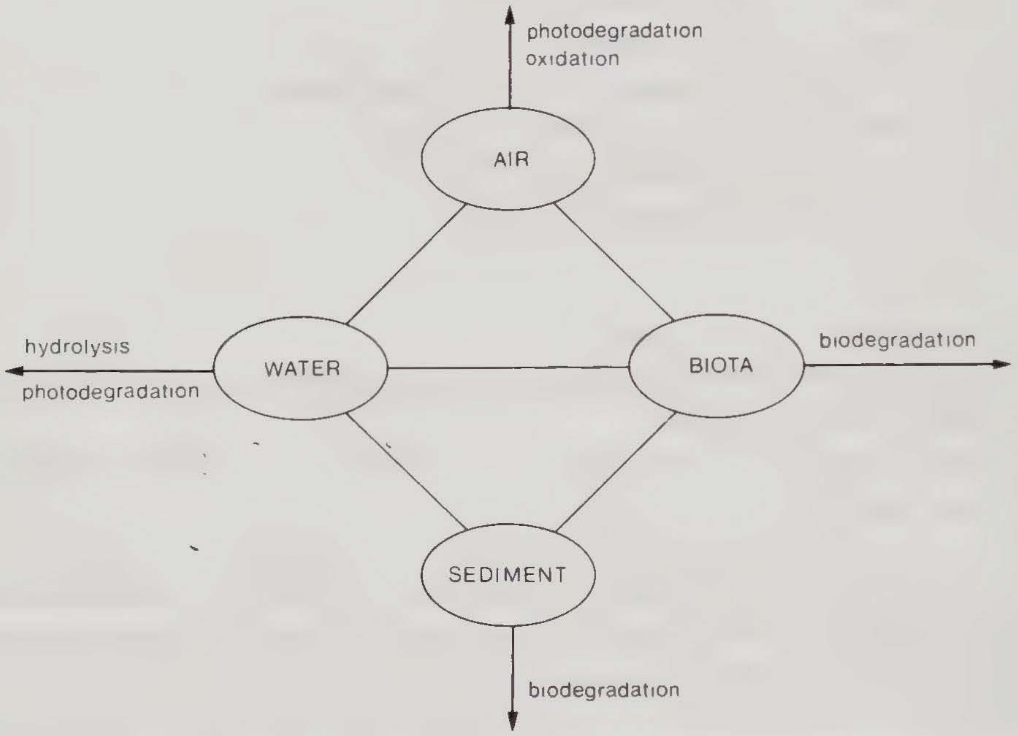


Fig. 9. Schematic representation of main reaction in the environmental compartments.

Kinetics of Reservoirs[4]

The concentration of a chemical substance in an environmental subcompartment depends on the rate of input (loading), the size of the compartment and the rate of removal (sinks).

Environmental
compartment

$$\text{Input} \xrightarrow{k_1} \boxed{\begin{array}{c}\text{Steady state}\\ \text{concentration}\end{array}} \xrightarrow{k_2} \text{Sink}$$

Such a compartment can be considered a reservoir and a number of terms which are used in dealing with the kinetics of a reservoir can then be considered. The flow rate in or out is commonly referred to as the *flux* (ϕ) of the substance. The *residence time* (t_{rs}) is defined as:

$$t_{rs} = \frac{\text{Amount of material in the reservoir at a given time}}{\text{Instantaneous rate of addition (or subtraction) of material}}$$

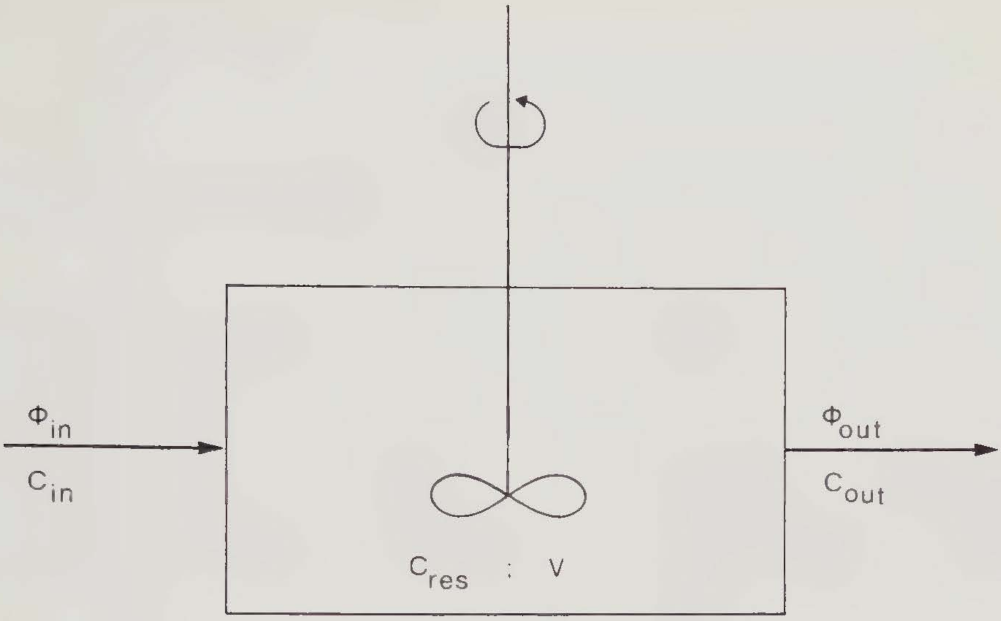


Fig. 10. A reservoir with important parameters. ϕ_{in} = influx; ϕ_{out} = efflux; C_{in} = concentration in influx; C_{out} = concentration in efflux; C_{res} = concentration in the reservoir; V = volume of the reservoir.

Residence times, then, are defined at a chosen moment in time and can be understood either with respect to *addition* or relative to *removal* (subtraction). Thus Fig. 10 shows a well-mixed reservoir with important parameters. Taking clean water ($C_{in} = C_{res} = C_{out}$), the residence time of water can be calculated for example (where $\phi_{in} = \phi_{out} = \phi$) as:

$$t_{rs} = \frac{V \, . \, C_{res}}{\phi_{in} \, . \, C_{in}} = \frac{V}{\phi} \qquad (1)$$

and for examples 2 and 3 (where $\phi_{in} \neq \phi_{out}$) as:

$$t_{rs} = \frac{V}{\phi_{in}} \qquad (2)$$

or

$$t_{rs} = \frac{V}{\phi_{out}} \qquad (3)$$

The time-dependence of the residence time in both cases is given in Fig. 11.

The *half-life* is defined as the time necessary to reduce the concentration to half of the starting value (example 4). Taking a reservoir with polluted water and an influx of clean water ($C_{in} = 0$; $C_{res} = C_{out}$) the half-life can be calculated when the water influx equals the efflux ($\phi_{in} = \phi_{out} = \phi$) as:

$$t_{\frac{1}{2}} = \frac{\ln 2}{\phi / V} \qquad (4)$$

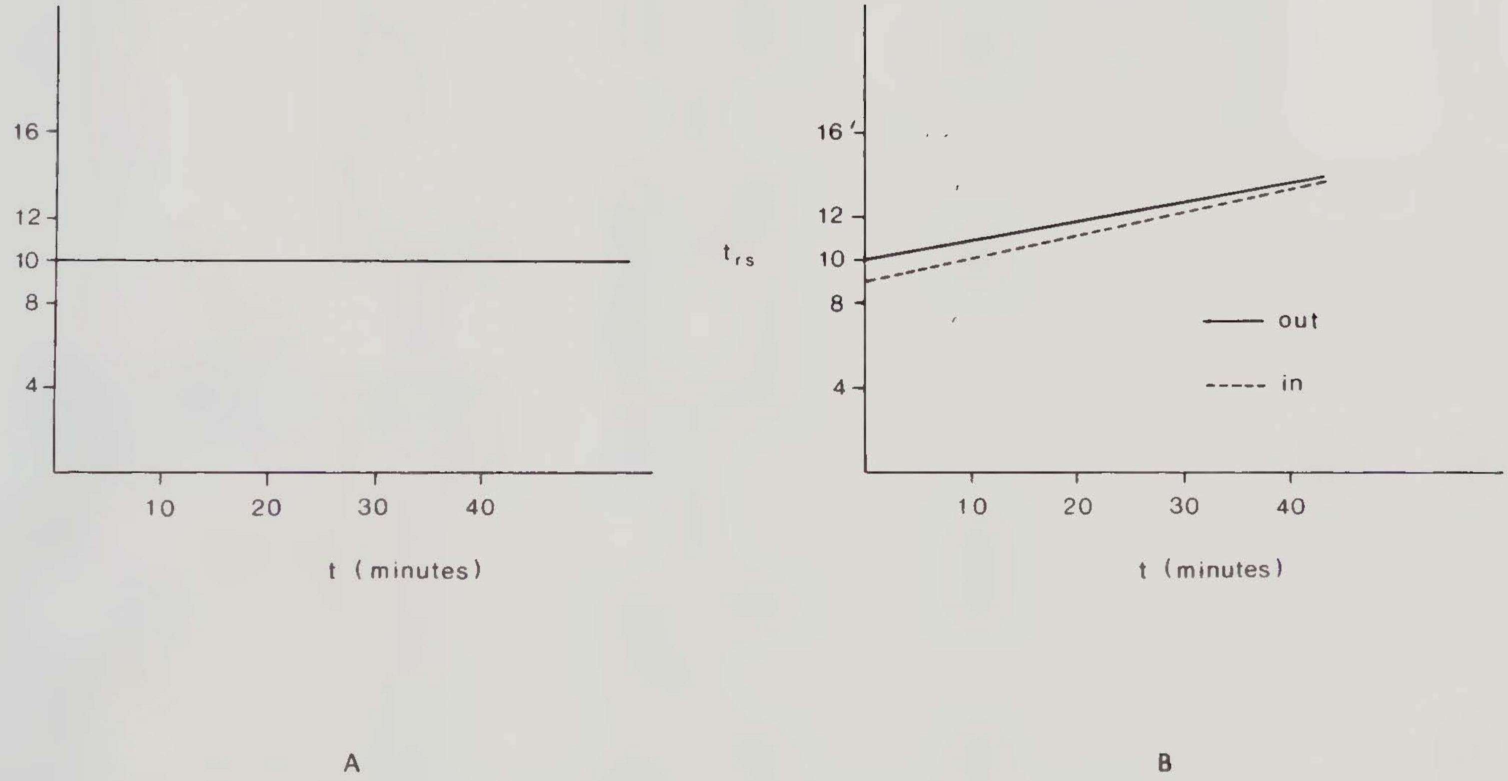


Fig. 11. (A) Time dependence of residence time, for example 1. For $V = 100$ l and $\phi = 10$ l/min. (B) Time-dependence of residence time for examples 2 and 3. For $V = 100$ l ($t = 0$); $\phi_{in} = 11$ l/min and $\phi_{out} = 10$ l/min.

which is derived from:

$$-\frac{dC_{res}}{dT} = \frac{\phi}{V}.C \tag{5}$$

and for $t = 0$, $C = C_0$. the derivation is:

$$C = C_0 . e^{-(\phi/V)t} \tag{6}$$

If $C = \frac{1}{2}C_0$ is then substituted in example 6 the half-life, example 4, is obtained.

Figure 12 gives the relation between half-life, residence time and renewal time ϕ in example 4. The renewal time is sometimes incorrectly identified with the residence time. In example 1 the renewal time could be considered equal to t_{rs}, but normally the renewal time is about six half-lives (see example 3).

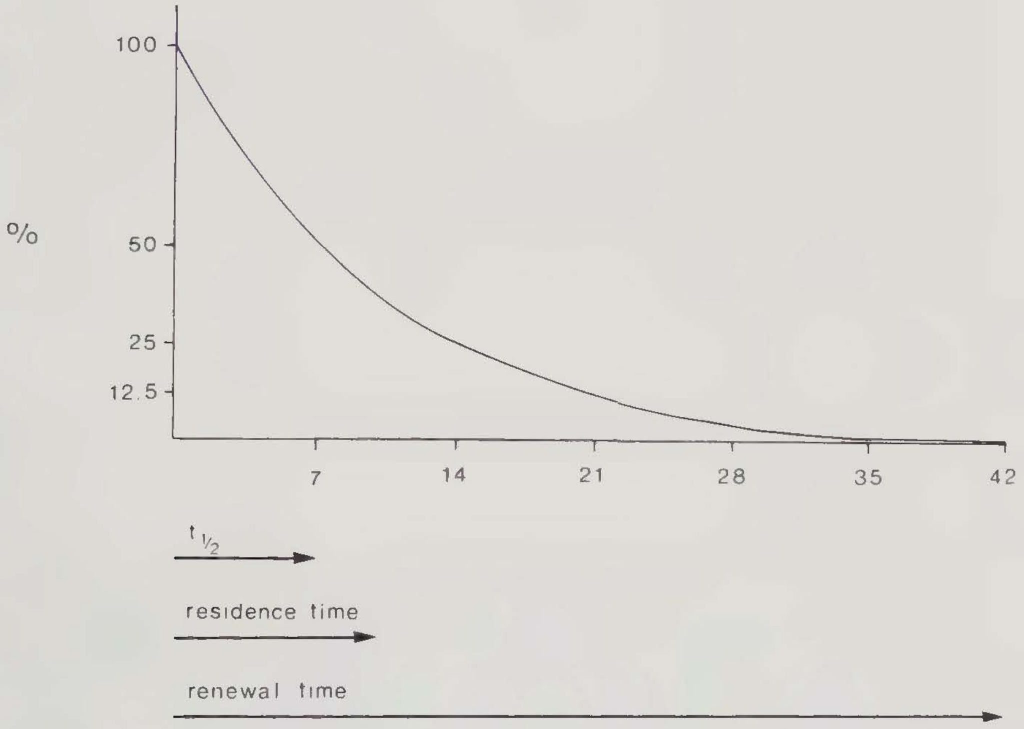


Fig. 12. Relation between half-life, residence time and renewal time in example 4 (V = 100 l and ϕ = 10 l/min). The calculated half-life is 6.9 min and the residence time = 10 min.

The relation between residence time and mixing is critical in real problems. If mixing is slow compared to influx and efflux, new and old water are present in highly variable ratios in different parts of the reservoir (renewal time and residence time are almost equal). If mixing is fast compared to residence time, new and old water are more homogeneous (renewal time is about 4 × residence time).

The *turnover time* is the time required to replace a quantity of substance equal to the amount in the compartment. Thus,

$$\text{Turnover time} = \frac{V \, . \, C_{\text{res}}}{\phi_{\text{in}} C_{\text{in}}} \tag{7}$$

Example 7 resembles example 1; however, the turnover time is independent of ϕ_{out}. In real environmental subcompartments the situation is usually much more complex than single in- and outputs. One has to deal with multiple input fluxes and different mechanisms of output. The latter, for instance, is responsible for the difference in residence time of water (hundreds of years) and phosphate (six years) in Lake Michigan.

A pollutant which has a short residence time in a reservoir (environmental compartment) can, almost *a priori*, be dismissed as a long-term problem. The input residence time of carbon monoxide, which can be calculated from the total reservoir and the input rate of natural and anthropogenic CO, is about three weeks. Since no increase in CO concentration in the atmosphere is measurable (the reservoir does not increase) the residence time calculated for removal (thus the rate of removal) must be three weeks as well. Without effective sink for carbon monoxide the atmospheric content would double in about three weeks. In one year global levels would rise by a factor of 52/3, or about 17-fold. Because the global level has not changed measurably for a number of years, it can be concluded that removal of carbon monoxide must be keeping pace with production.

Environmental Fate Tests and Models[5]

Environmental fate tests and models attempt to predict the fate and behaviour of xenobiotic compounds in the environment before such compounds are actually produced and thus become pollutants. Although artificial sections of the environment (microecosystems, microcosms) are being used to predict environmental fate of chemicals, it is more common to study unit processes governing the behaviour of a chemical, where fate is evaluated by simple assessment or with the aid of computer programs. These processes are separated into a group which occurs relatively rapidly— and thus can be treated as an equilibrium of thermodynamic properties—and a group of slower processes that require kinetic treatment. Baughman and Burns (1980) have recently described some features of such processes and their handling (Table 15). For a description of individual test systems, the literature given above can be consulted.

*E*xposure *A*nalysis *M*odeling *S*ystem (EXAMS) predicts environmental concentrations of chemicals by assuming that the dynamics of a xenobiotic chemical in the environment can be represented as a sum of contributing processes (Lassiter *et al.*, 1979). Thus:

$$\frac{dS}{dt} = V + P_D + P_S + H + A + M \pm Se + D - L$$

where: S = quantity or concentration of compound
V = volatilization
P_D = direct photolysis
P_S = sensitized photolysis
H = hydrolysis
A = breakdown by photo-autotrophs
M = microbial degradation
Se = exchanges with sediments
D = dilution
L = loading of substance into the system

The EXAMS model (Fig. 13) makes use of chemical input data (loading

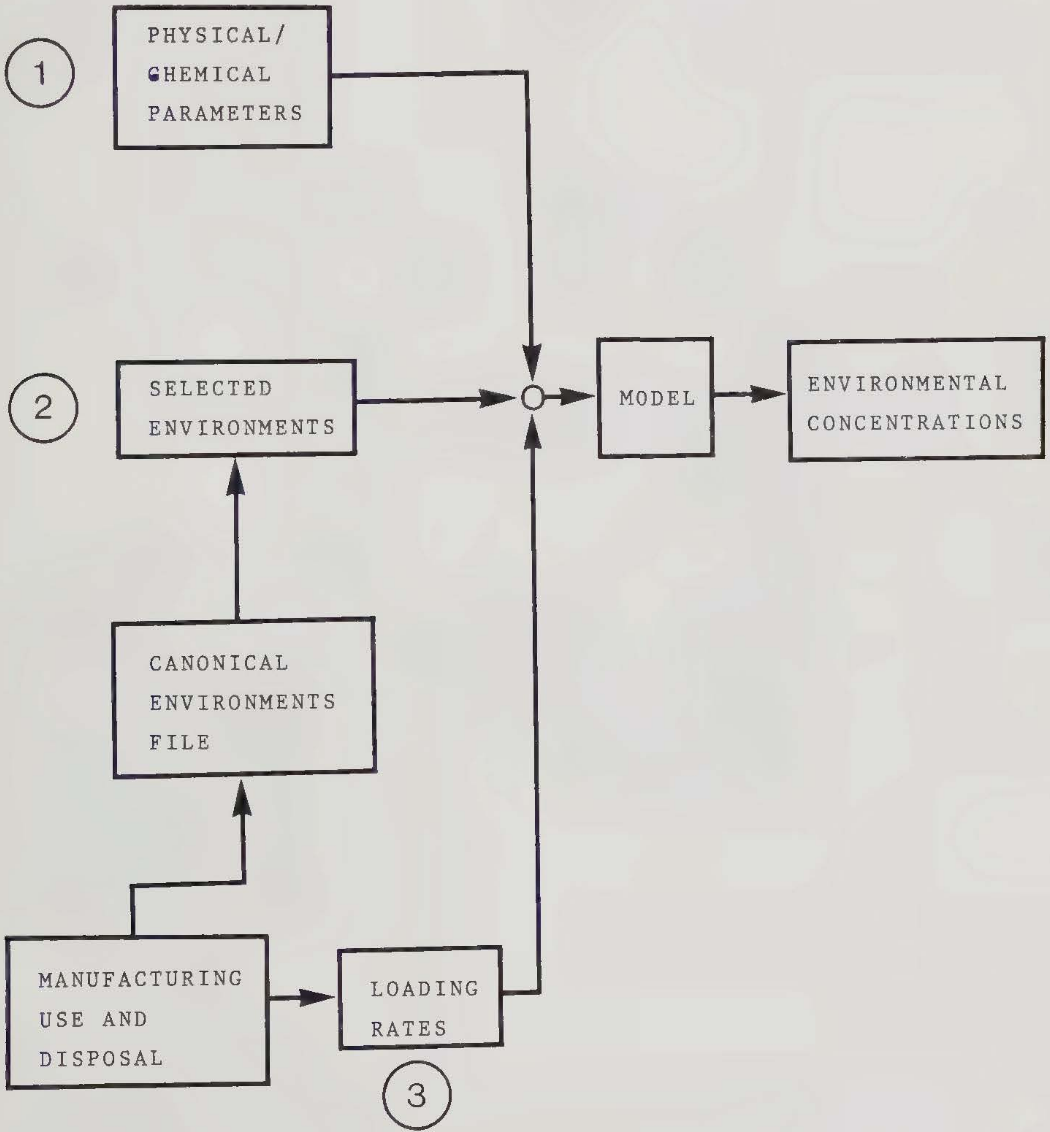


Fig. 13. EXAMS computer model for estimating environmental concentrations. For details see text.

Table 15
Environmental process description[a]

	Status	Problems
Kinetic processes		
Hydrolysis	Vast body of literature for which rate expressions are well studied. Very reliable in aqueous phase. Relationship between structure and rate is often known semi-quantitatively.	Effects of sediments are poorly understood. Relationships for general or specific catalysis by environmental species have not been examined.
Microbial transformation	Rate constants appear to be reasonably constant and independent of site.	Few rate constants in literature. Few data on species other than bacteria. Relationships between structure and rate constants are not known.
Photolysis	Computational procedures are available for direct photolysis. Indirect processes can be measured.	Sensitized reaction is poorly understood. Mixing of water can have large effect on net rate.
Volatilization	The rate constant can be estimated when liquid phase transport is rate-limiting. Readily measured in laboratory.	Can be strongly influenced by mixing and wind velocity.
Oxidation	Large body of data on rate constants of free radical reactions. At least one method has been proposed for measuring rate constants in water based on use of a free radical initiator.	Very few published data on free radical reactions in natural waters except in the case of light-mediated processes. Steady-state levels of free radicals and free radical scavengers in natural waters are poorly known. Influence of particulate matter is not known.

Table 15—continued

	Status	Problems
Equilibrium processes		
Sorption	K_{oc} is largely system-independent for uncharged organic compounds. Sorption is slowest for most strongly bound compounds.	Ion-exchange process is difficult to predict.
Bioconcentration	Bioconcentration potential can be assessed from physical properties such as octanol-water partition coefficient or solubility in the case of hydrophobic organics. Several different methods are available and under development for measurement of bioconcentration especially by fish.	Actual extent of bioconcentration cannot be predicted because the metabolism rate of compounds are not predictable but must be measured.
Ligand exchange	Extensive data available on magnitude of stability constants for a wide variety of compound types and many metals. Measurement procedures are well-established.	Exchange process can be kinetically limited. Influence on other processes such as photochemistry is difficult to predict.
Ionization	Very extensive compilation of data. Process is expected to be very rapid and readily accounted for by existing approaches.	Equilibrium constants can be very difficult to measure for certain compounds.

[a] From Baughman and Burns (1980)

rates; 3), information *where* the chemical may enter the environment with the appropriate environmental factor constant (pH, availability of sunlight or microbial populations; selected environments; 2) and the physical/chemical parameters measured for the compound (1).

XENOBIOTIC COMPOUNDS AND MICROORGANISMS

Microbial Degradation of Organic Matter

Microorganisms play a key role in the biogeochemical cycles that occur in the environment. Many types of different microorganisms participate in the carbon, nitrogen and sulfur cycles and to a lesser extent in cycles of other elements. In this paper, the carbon cycles will mainly be considered. Green plants (photosynthetic organisms) convert solar energy into chemical energy, and carbon dioxide to a complex array of chemical products. The release of carbon for recycling from all these biological molecules depends almost entirely on the action of microbial degradative enzymes. Although carbon dioxide is the main end-product of microbial activity for carbon compounds there are other simple carbon compounds which need consideration such as carbon monoxide and methane. Microorganisms are not the only entities to degrade organic compounds—many other organisms do so to a smaller extent and, particularly for some air-borne compounds, photochemical degradation may become important. An interrelationship with the emphasis on quantitative aspects is shown in Fig. 14. Microbial enzymes as well as some purely chemical mechanisms are also responsible for the organic polymeric products, some of which are lost to the earth's crust in sediments. Most of the microbial activity in the environment occurs in water and soil and to a certain extent in sediments.

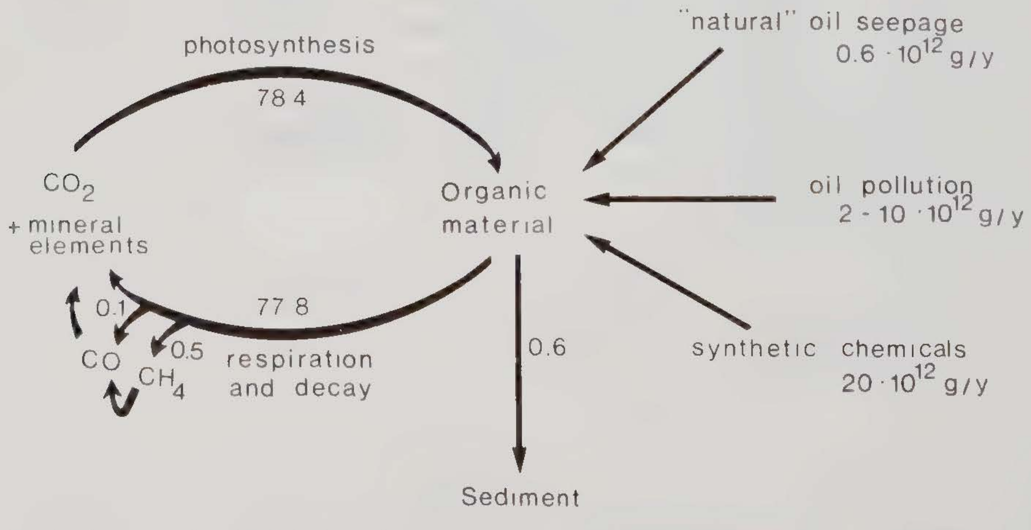


Fig. 14. Carbon cycle (in 10^{15} g/y). Estimated anthropogenic input is shown in 10^{12} g/y.

The overall photosynthetic and mineralization reactions are placed in perspective (Table 16) where the total mass of various spheres is shown in relation to organic carbon on the one hand and living microorganisms on the other. In soil where reasonable estimates of total microbial activity have been made it has been shown that the total organic carbon content in living microorganisms against total organic carbon content (dead) is very small (see Table 16).

Table 16
Mass of environmental compartments (10^{18} g)

Compartment	Weight
Biosphere (total)	15
Living material	0.4
as carbon	0.02
Pedosphere (total)	1600
to 1 m	
Mass	200
Organic carbon	2
Microorganism (as C)	0.005
Ocean (total)	1 348 000
to 100 m	
Mass	36 000
Microorganism (as C)	0.01

Figure 14 also shows that the total environmental load with synthetic chemicals and oil from spills is small compared to the amounts of carbon compounds formed by photosynthesis and degraded by microbial action. One may thus expect most of the anthropogenic production of chemicals which enters the soil and water environments to "fit in" with the degradation part of the carbon cycle.

Biodegradation of most naturally occurring organic compounds is relatively fast. The mean residence time of organic matter in the terrestrial biosphere being 15.7 years and only 26 days in the oceanic environment. There are, however, a number of naturally occurring compounds which are persistent either because of structure or external physical factors. In contrast to the short residence time in surface ocean water, the dissolved organic carbon at about 2000 meter depth in the ocean is about 3400 years old. The mean residence time for a so-called "mobile humus fraction" consisting of humic and fulvic acids is between 250 and 800 years whereas unextractable humus is often older than 2000 years (Zehnder, 1981). The ages of some naturally occurring materials are reported in Table 17.

Table 17
Some ages of natural organic materials

Material	Source	Age (in years) from radiodating (^{14}C), geological formation, or pollen analysis
Humus	UK fossil	1500–2900
Humus, organic fraction lake bottom	Fossil soil, USSR	3000–25 000
Peat	USA, USSR	100–35 000
Human hair	Egyptian cemetery	5500
Bat guano	Nevada	11 000
Cellulose, pectin, bound amino acids	Fossil wood, anthracite coal	250 million
Chitin, amino acids	Cambrian fossil	550 million
β-carotene	Sediment	11 000
Succinic acid	Amber	Millions

Microbial Degradation of Xenobiotic Compounds

Although the number of compounds of biological origin in nature is large, only relatively few chemical structures of the many possible are synthesized by enzymatic processes. If microorganisms had evolved enzyme systems only for degrading cellular constituents, man-made products which had structures unlike those synthesized in nature would accumulate in the environment.

However, as Gibson (1980) points out, microorganisms throughout geological time have also been exposed to an array of chemicals produced by diagenesis.

> Many of these compounds bear little structural relationship to the biological products from which they were originally derived. For example, soils and young sediments contain thousands of substituted polycyclic aromatic hydrocarbons. These molecules, formed by the thermal alteration of cellular material, have been in contact with living organisms throughout evolutionary periods of time. Consequently one would predict the existence of microorganisms that will degrade them, and organisms that metabolize aromatic hydrocarbons ranging in size from benzene to benzo(a)pyrene have been described. (Gibson, 1980)

A significant number of man-made chemicals will be biodegradable if the enzymes have been acquired by microorganisms during the course of evolution. This depends on two factors:

(1) The ability of microbial enzymes to accept substrate compounds with structures similar to, but not identical with chemicals found in nature.
(2) The ability of novel substrates to induce or derepress the synthesis of the necessary degradative enzyme in the microorganisms.

Biodegradation is less likely in a molecule having structural features never encountered in natural products.

In addition to the structure of a molecule two other factors are also responsible for the degradation or lack of degradation in a given environmental situation. These three parameters, thus, are:

(i) *The structure of the compound*
Presence or absence of certain moieties and substituents; steric factors, molecular size or other structural features.

(ii) *Available microorganisms*
Types and number, available or inducible enzymes.

(iii) *The environment*
Presence or absence of oxygen and nutrients, light, pH, temperature.

The chemical structure influences the biodegradability of a compound in two ways. First, the molecule may contain groups or substituents which cannot react with available or inducible enzymes (i.e. these chemical bonds cannot be broken). Secondly, the structure may determine the compound to be in a physical state (adsorbed, gas-phase) where microbial degradation does not easily occur. This seems to be a problem with many of the so-called lipophilic compounds, which have very low solubilities in water. Since the ratio of bacteria to non-living suspended matter is very low (e.g. in eutrophic lakes 10^{-5} and in oligotrophic lakes 10^{-7} to 10^{-6}; Smith *et al.*, 1977) such compounds are essentially adsorbed to dead particulate matter and

Table 18
Influence of structure on degradability

Type of compounds or substituents	More degradable	Less degradable
Hydrocarbons	Higher alkanes (~12)	Lower alkanes
	Alkanes	High molecular weight alkanes
	Straight-chain paraffinic	Branched-chain paraffinic
	Paraffinic	Aromatic
	Mono- and bicyclic aromatic	Polycyclic aromatic
Aromatic substituents	—OH	—F
	—COOH	—Cl
	$—NH_2$	$—NO_2$
	$—OCH_3$	$—CF_3$
		$—SO_3H$
Aliphatic chlorine	—Cl more than six carbon atoms from terminal C	—Cl six or less carbon atoms from terminal C

unavailable for microbial action, particularly if they are deposited in microenvironments which do not harbour microorganisms. Although a number of biodegradability relationships for xenobiotic compounds have been established within narrowly defined structural groups, few correlations of structure to biodegradation can be made which are valid for a variety of chemical compound types. Some relationships between structure and biodegradability which seem generally established are outlined in Table 18.

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NOTES

1. In 1972, for example, 160 000 t of sodium glutamate was prepared (Korte, 1980: 40).
2. Chemical compounds are defined as simple or complex organic or inorganic molecules which can be potentially in solution and participate in reactions. Thus clay surfaces and organic matter in sediments are considered chemicals whereas bedrock is not.
3. For literature see Hutzinger, 1980.
4. For literature see Garrels *et al.* (1975).
5. For literature see Baughman and Burns (1980); Hutzinger (1980); Schmidt-Bleek (1980).

APPENDIX

The author of this chapter defines his terms as follows. Whilst their usage is similar throughout the book, the definitions are included here by way of clarification for this chapter in particular. The definitions are from a variety of sources, some the author's own, and extensive use was made of the OECD Report and Gilbert and Watson (1977).

Abiotic Degradation. See *Degradation*.

Analogue-metabolism. The process by which a normally non-biodegradable substance is biodegraded in the presence of an analogous chemical, because the latter can induce the necessary enzymes.

Anthropogenic Compound. Chemical compound which is produced by man or released by human activity.

Biodegradability. The ability of an organic substance to undergo biodegration, hence "inherently biodegradable" and "readily biodegradable". See *Biodegradation*.

Biodegradation. Molecular degradation of a substance, resulting from the complex action of living organism.

- *"Complete mineralization"*. A theoretical concept involving complete breakdown of an organic compound into inorganic compounds. However, over the time-scale of a biodegradability test, ultimate biodegradation rather than complete mineralization will be observed because a proportion of the compounds will be utilized for the synthesis of new cell material. In practice, these natural products will themselves eventually undergo biodegradation and the terms "ultimate biodegradation" and "complete mineralization" are often used interchangeably.
- *Functional biodegration*. Biodegradation of a substance to an extent sufficient to remove some characteristic property of the molecule (e.g. toxicity or MBAS content).
- *Inherent biodegradation* ("inherently biodegradable"). A classification of chemicals for which there is unequivocal evidence of biodegradation (primary or ultimate) in any test of biodegradability even under favourable conditions.
- *Primary biodegradation*. The process in which the chemical structure of the parent compound is altered to such an extent that it no longer responds to the specific analytical technique used.
- *Ready biodegradation* ("readily biodegradable"). An arbitrary classification of chemicals which have passed certain specific screening tests for ultimate degradability. These tests are so stringent that such compounds will rapidly and completely biodegrade in a wide variety of natural aerobic environments.
- *Ultimate biodegradation*. The breakdown of an organic compound to carbon dioxide, water, the oxides or mineral salts of any other elements present and products associated with the normal metabolic processes or microorganisms.

Biomass. The total weight of living organisms in a defined area or volume of habitat.

Biotic Degradation. See *Biodegradation*.

BOD (*Biochemical Oxygen Demand*). The amount of oxygen consumed by mircoorganisms when metabolizing on substrate.

Chemical Compound in the Environment. Simple or complex organic or inorganic molecules which can be potentially in solution and participate in reactions. Thus clay surfaces and organic matter in sediments are considered chemicals whereas bedrock is not.

COD (*Chemical Oxygen Demand*). The amount of oxygen consumed during oxidation of a substrate with hot acid dichromate or other strong oxidants. It provides a measure of the oxidizable matter in a given solution.

Co-metabolism. See *Analogue-metabolism*.

Degradation. The reduction of the complexity of a chemical substance to form simpler molecules by physical, chemical and/or biological processes.

Diagenesis. Recombination or rearrangement resulting in a new product. The reconstructive process by which changes are produced in sedimentary rocks during or immediately after their deposition and which is caused by such forces as the weight of overlying strata or hot water.

Ecokinetics. The study of transport and transformation processes of chemicals in the environment.

Entry into the Environment. The first appearance of a structural entity in any freely accessible environmental compartment outside living organisms.

Exposure. The presence in the environment, i.e. the availability at a site or location where effects might be observed. The concept includes elements of both concentration and time.

Flux. The flow-rate in or out of a reservoir.

Half-life. The time necessary to reduce the concentration of a chemical to half the starting value.

Man-made Compound. See *Anthropogenic Compound*.

Mineralization. See *Biodegradation*.

Persistence. The ability of a substance to remain in the environment in a chemically unchanged state.

Recalcitrant. See *Persistence*.

Residence Time. The ratio between the amount in a reservoir at a given time and the rate of addition (or subtraction) of material.

Sediment. The unconsolidated material deposited at the bottom of natural water and which consists of the phases mineral, water, gas.

Sink. Is understood as the process leading to a (fictive) elimination of the chemical substance from the environment.

Synthetic Compound. See *Anthropogenic Compound*.

Xenobiotic Compound (Xenobiotics; Xenobiotica). Compounds which are foreign (alien) to the biosphere.

"*Definition centred on the biosphere*". Chemical substances which are not produced by any natural enzymatic process; or compounds which biological organisms in the biosphere have not been exposed to in evolutionary history.

"*Definition centred on the structure*". Chemical substances having structural features, which are not commonly found in natural products (unnatural structural features): a methyl analogue of a natural product would be xenobiotic under the first but not under the second definition. A trifluoromethyl-substituted derivative would satisfy the definition "xenobiotic" in both cases; naturally occurring compounds which are released into the environment by the action of man and which occur in an environmental compartment in concentrations significantly higher than without man's interference reach "*Xenobiotic Levels*".

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