STRUCTURAL ORGANIC CHEMISTRY IN ECOTOXICOLOGY

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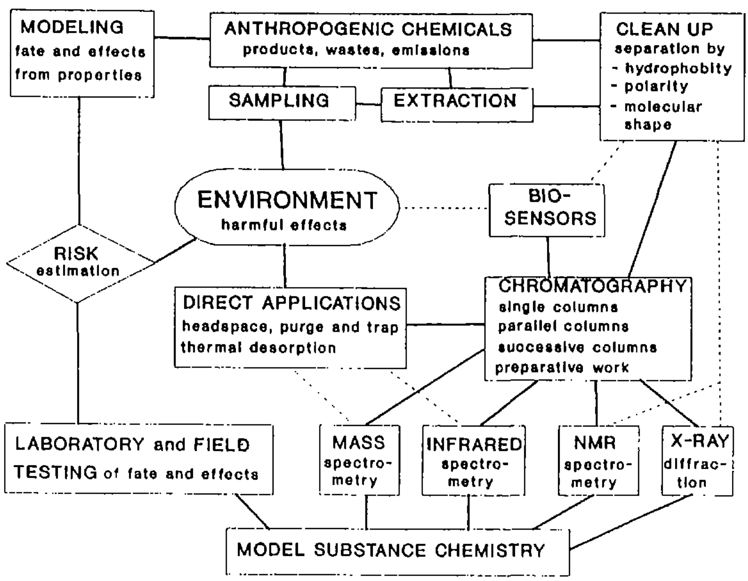
Introduction. Ecotoxicology is the science that studies impact of environmental chemicals on natural systems - organisms, populations and ecosystems - including the mechanisms leading to toxic effects and their recovery. Ecotoxicology aims to find out the risk chemicals for preventive measures before any serious damages occur. A number of physical, chemical and biological tests to predict the exposure-related fate and toxic effects of chemicals in environment are applied together with follow-up studies in nature. Exposure of biota to an organic chemical and its adverse effects depend in great part on its molecular structure. Therefore, structural organic chemistry has a central role in activities and methodology of chemical ecotoxicology as summarized in the following scheme:



Harmful effects. Occurrence of ecotoxic anthropogenic chemicals has been normally observed from damages in exposed populations. Examples are hatching loss by birds[1-3], non-fertility of seals[4], hormonal and metabolic disturbances in fish[5,6]. These effects have been attributed to aromatic halogen compounds, but compounds most responsible of these effects could be the still unknown ones.

Risk estimation. A central task in ecotoxicology is to estimate environmental risk (probability of a specified ecotoxic damage) of new chemicals released. Numerically expressed risk (R) is product of exposure (Ex) of the target species and toxic potential (Ef) of the chemical (dose-response ratio):

$$R = Ex * Ef$$

Exposure assessment is preliminarly done using fate modeling from the known properties of the chemical, and verified by analyses in the environment[7]. A preliminary fate modeling needs only a limited number of properties of the chemical: molecular mass, water solubility (S), vapor pressure (P) in environmental temperature, bioconcentration factor (Bcf), and rates of hydrolysis (k_H), photodegradation (k_P) and biodegradation (k_B) in the compartments (air, water, soil/sediment) of the model environment. Some of these properties, instead of expensive testing, can be roughly estimated from readily available properties, like from octanol-water partition coefficient (-> Bcf) or from boiling point (-> P).

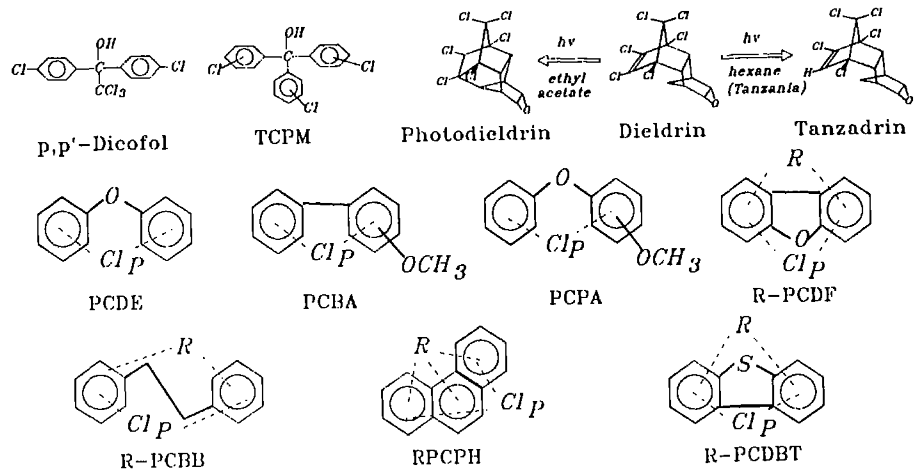
Degradation rates must be measured in environment or in laboratory conditions close enough. For the series of similar compounds, however, evaluation of the rate constants can also be done by semiempirical calculations from accumulated data. For example, substituent increments can be used to estimate photodegradation rate constants for wide variety of volatile compounds[8]. Similar methods could be useful in estimation of other degradation rates and vapor pressures.

Effects are assessed from structural properties (e.g. TCDD-relation) or by laboratory tests and verified by environmental observations.

Screening analyses. For screening of the structure of bioaccumulated organic ecotoxicant, the samples of the affected population could be studied according to expected structure of the toxicant. The organic extract can be shaken with conc. sulfuric acid if high persistency is expected. Further clean-up fractionation can be done according to different polarities and planarities of the remaining molecules. Gas chromatography (GC) with specific detectors including biosensors and MS gives the first clue of the structure, which is then verified by model substances with structure proof and identification by chromatography, MS, IR, NMR and X-ray diffraction.

Examples of structure analyses. 1) The environmental occurrence of PCBs was found by GC/MS as early as 1965[9]. 2) A persistent organochloro compound (OCC) occurred at near µg/g levels without any change during 1972-1982 in blubber of harbor seals in the north-western USA. Its MS had similar fragmentation pattern to p,p'-Dicofol, although molecular ions were different. Partial structure of tris(chlorophenyl)methanol (TCPM) was deduced to this potential toxicant and verified by synthesis[10].

3) Main persistent OCC compound in Tanzanian environment, named tanzadrin, was first thought to be photodieldrin, an isomer of insecticide dieldrin which had been heavily used there. However, GC/MS, model substance synthesis and NMR spectrometry proved that it was 9-dechlorodieldrin[11].



4) Clean up for (eco)toxic PCDDs and PCDFs actually collects many other physically similar persistent trace compounds to the same analytical fraction. These sometimes appear as artifacts in GC/MS determination of PCDDs and PCDFs. For example, polychlorodiphenyl ether (PCDE) molecular ions readily lose two chlorine atoms showing mass spectra identical with those of (P-2)CDFs at lower m/e range[12]. So PCDEs are HRMS artifacts of (P-2)CDFs.

Chlorinated methoxybiphenyls (biphenylanisoles, PCBAs) give the same molecular ion clusters as PCDDs at low resolution: they are LRMS artifacts of PCDDs[13]. Molecular ions of ortho-chloro and ortho-methoxy-substituted (P+1)CBAs and (P+1)CPAs lose methyl chloride giving molecular ions and HR mass spectra of PCDFs and PCDDs, respectively. Consequently, PCDEs, PCBAs and PCPAs, which occur in waste combustion ashes, wildlife and fish liver oil, interfere MS identification and determination of toxic PCDDs and PCDFs[14-16].

Despite that more sofisticated clean-up methods or uses of special MS techniques can separate these artifacts from PCDDs and PCDFs, they self are perhaps serious dioxin-type of ecotoxicants. For PCDEs, dioxin-type of bioactivity has been shown[17]. Several groups of persistent aromatic chlorocompounds from pulp chlorobleaching have been found in the dioxin fraction of analyses. These might be of major ecotoxic importance. Examples of their structure types already veirified by model substance chemistry are R-PCDFs[17], R-PCBBs[18], P-PCPHs[18] and R-PCDBTs[19]:

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