

PERSISTENT ORGANIC WASTES

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Summary

Persistent organic wastes are organic compounds that are poorly degraded and thus accumulate in the environment. The most significant contaminants threaten human health and the environment through toxic effects. Acute exposure to high concentrations of these compounds is rare, but chronic exposure to low concentrations may cause reproductive changes, immunotoxicity, neurotoxicity, behavioral problems, and cancer.

Many persistent organic wastes are synthetic hydrophobic compounds and contain functional groups that are not commonly found in nature. The absence of “natural” analogs of these compounds means that degradation pathways may not exist for them. The less like a natural product, the more difficult it will be for microorganisms to develop a pathway for the degradation of the compound, since more steps are required to feed into an existing pathway. Some functional groups also result in chemically stable

molecules that require energy addition to begin the degradation process. This further decreases the likelihood of degradation by both biotic and abiotic means.

The hydrophobicity of these compounds has two significant consequences. It results in a decreased concentration of the contaminant in the water phase, which is the most accessible form for organisms that can degrade the material. This lack of availability lowers the rate of degradation and increases the residence time, since biodegradation is a major cleansing mechanism for organic contaminants in soils. The second consequence of hydrophobicity is that contaminants that are slowly metabolized in the body accumulate in lipid-rich tissues, sometimes reaching toxic levels, even if the concentration in the environment is low.

Remediation of soils contaminated with persistent organic wastes is limited by the tendency of the contaminants to remain associated with the solid phase. Techniques that increase the rate of desorption can improve the rate of removal of the contaminants, but cleanup is generally expensive and slow.

1. Introduction

Persistent organic wastes are organic compounds that largely resist photolytic, chemical or biological degradation. Resistance to degradation results from a combination of the following factors: high molecular weight, hydrophobicity, halogen substitution, and a high degree of branching. Two additional characteristics that make some persistent compounds particularly noteworthy are semi-volatility, a property which allows some chemicals to travel long distances by evaporating into the atmosphere in the warm tropical climatic zones, and precipitating in the colder regions, and toxicity. Some of the chemical properties that make these compounds persistent in the environment also make them more likely to bioaccumulate in the food web, often to many times their concentration in the environment. Bioaccumulation increases the likelihood that these compounds will reach toxic levels in animals and humans.

Industrial Chemicals	Industrial Byproducts	Pesticides
Polychlorinated Biphenyls (PCB) Hexachlorobenzene (HCB) Chlorinated Solvents (carbon tetrachloride, chloroform, trichloroethane (TCA), trichloroethene (TCE), tetrachloroethene (PCE))	Polycyclic Aromatic Hydrocarbons (PAH) Dibenzodioxins Dibenzofurans	DDT Toxaphene Aldrin Dieldrin Lindane Heptachlor Chlordane Mirex Endrin

Table 1. Some persistent organic wastes

With over 70 000 synthetic organic chemicals in general use today, the list of compounds given here with some or all of the above properties is not comprehensive. It includes only those chemicals that have elicited the greatest concern, and some chlorinated solvents that are commonly found contaminants in groundwater. Persistent organic wastes can be roughly divided into industrial chemicals, industrial or combustion byproducts and pesticides. Table 1 lists examples of persistent organic

wastes, and the chemical structures of these are shown in Figure 1. The physical-chemical properties of significant persistent organic pollutants are listed in Table 2.

Some of the listed chemicals, such as PCBs and DDT, have been banned but are still problematic in some locations due to their persistence in the environment. Another group of industrially relevant chemicals, brominated organic flame retardants, has lately begun to receive closer attention despite lower toxicity relative to their chlorinated counterparts. The reason for concern is that the quantity of these chemicals used in some parts of the world (most notably, North America) has increased sharply as they have replaced chlorinated compounds and as the demand for fire retardant materials has increased. The environmental concentrations of these compounds have increased with their use. Some of these compounds are resistant to degradation just as chlorinated compounds are, and as the environmental concentration of this group rises, so does the risk of toxic effects.

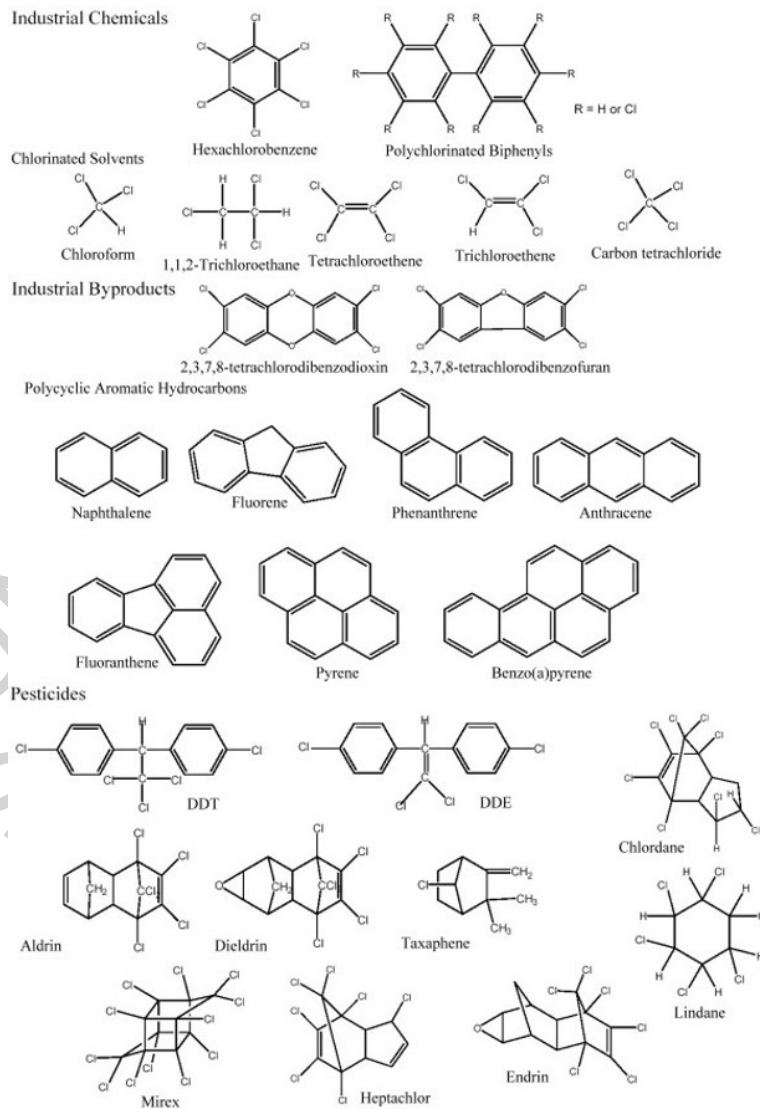


Figure 1. Chemical structures of some persistent organic wastes

Compound	$\log K_{ow}^a$	$\log K_{oc}^b$	Solubility ($\mu\text{g L}^{-1}$)	H^c ($\text{atm m}^3 \text{mol}^{-1}$)	Vapor pressure (atm)
PCBs^d	4.3-8.26	4.7-7.9	0.001-5500	1.7×10^{-5} - 1.5×10^{-3}	3.0×10^{-13} - 2.5×10^{-5}
3,3',4,4'-PCB	6.5	no data	292	1.7×10^{-5}	1.2×10^{-8}
2,2',3,4,5'-PCB	6.5	no data	1300	2.4×10^{-4}	1.2×10^{-8}
2,2',3,3',4,4'-PCB	7.0	no data	217	1.2×10^{-4}	1.8×10^{-9}
Dibenzodioxins^e	4.75-8.2	4.36-7.81	.074-417 000	2.7×10^{-6} - 1.2×10^{-4}	1.8×10^{-12} - 7.5×10^{-7}
2,3,7,8-TCDD	6.8	6.66	20	3.3×10^{-5}	1.2×10^{-9}
Dibenzofurans^f	5.44-8	5.05-7.6	1.16-14 500	5×10^{-6} - 6×10^{-5}	5.3×10^{-12} - 1.4×10^{-7}
2,3,4,7,8-PCDF	6.5	6.1	240	5×10^{-6}	1.7×10^{-10}
PAHs^g	3.37-6.5	3.11-6.49	1.5-34 000	4.9×10^{-7} - 4.9×10^{-4}	7.2×10^{-12} - 1×10^{-4}
Phenanthrene	4.57	4.36	1124	3.6×10^{-5}	1.62×10^{-7}
Pyrene	5.13	4.8-4.92	137	1.1×10^{-5}	6.03×10^{-9}
Benzo(a)pyrene	5.97	4-8.3	1.5	1.2×10^{-6}	7.24×10^{-12}
HCB	3.03-6.42	2.56-4.54	6-40	6.8×10^{-4} - 7.1×10^{-3}	1.4×10^{-8} - 3.1×10^{-8}
Chlorinated solvents^h	1.93-2.88	1.72-2.42	2×10^5 - 2×10^6	0.0005-0.01	0.025-0.26
Tetrachloroethene	2.88	2.42	1.5×10^5	0.0275	0.0253
Trichloroethene	2.42	1.97	1.2×10^6	0.0107	0.0973
Pesticides					
DDT	6.91	5.15-6.26	1.2-5.5	9.5×10^{-6} - 1.29×10^{-5}	1.3×10^{-10}
Aldrin	6.5	2.61-4.69	17-180	4.96×10^{-4}	3.1×10^{-8}
Dieldrin	5.2	4.08-4.55	140-224	1.1×10^{-5} - 5.8×10^{-5}	2.4×10^{-10} - 6.6×10^{-7}
Endrin	5.34	4.03	220-260	5×10^{-7}	9.3×10^{-10}
Heptachlor	4.4-5.5	4.38	180	2.3×10^{-3}	4×10^{-7}
Lindane	4.14	3.03	8000	3.2×10^{-6}	8.5×10^{-8}
Mirex	6.9	6.0	0.065	8.3×10^{-3}	9.9×10^{-9}
Toxaphene	3.23-5.5	3.18	550	6.3×10^{-2}	2.7×10^{-5} - 5.3×10^{-4}
Chlordane	6.00	4.58-5.57	56	4.8×10^{-5}	1.3×10^{-9}

^aOctanol-water partition coefficient

^bOrganic carbon-water partition coefficient (K_{oc}) values may vary significantly depending on the soil. These values are given for comparative purposes.

^cHenry's Law constant

^dAll PCB, dibenzodioxin and dibenzofuran compounds are included in the ranges given.

^ePAH that were included in the range are naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, dibenz(a,h)anthracene, and coronene.

^fChlorinated solvents that were included in the range are carbon tetrachloride, chloroform, trichloroethane, trichloroethene and tetrachloroethene.

Table 2. Physical-chemical properties of some persistent organic wastes

2. Sources

The sources of persistent organic wastes to the environment depend on their uses, properties and disposal, but some generalizations can be made. Since many of these chemicals are produced and used industrially, they can reach the environment in a number of ways. They may come from:

- Air emissions and atmospheric transport
- Leaking storage tanks (underground or above-ground)
- Improper disposal or landfill leachate
- Wastewater
- Spills or accidental release
- Intentional application of the product to the environment (e.g. pesticides)

Industrial byproducts may be contaminants of synthetic reactions, in which case they reach the environment with the industrial product, or they may be formed and escape as air emissions during processing or as a result of combustion of materials. This is often the case, for example, with PAHs, dibenzodioxins and dibenzofurans.

3. Effects

Many of the compounds listed in Table 1 are of particular concern because of their toxicity. Acute poisoning is relatively rare, and typically restricted to occupational, accidental or intentional exposures. While the causes of chronic effects are more difficult to ascribe to a specific cause, long-term exposure to low levels of pollutants have been correlated to a host of problems including reproductive changes, immune or nervous system toxicity, behavioral problems, and cancer (see *Ecotoxicity, Genotoxicity, and Cytotoxicity of Pesticides and their Degradation Products*).

Most of the compounds listed in Table 1 are not synthesized and released in massive quantities, so their concentrations in environmental media are usually fairly low. The fat-loving or lipophilic nature of persistent organic wastes, however, causes bioconcentration in fatty tissues to levels far above those in the air or water. Compounding this problem is biomagnification in the food web. As larger animals consume smaller organisms, the persistent compound load from the smaller organism partitions into the fatty tissue of its predator. For excretion, the compounds must first be metabolized to produce more hydrophilic products. Many persistent organic pollutants are only metabolized slowly, if at all, resulting in the gradual buildup of toxicants with every meal. This process of biomagnification occurs at each step along the food chain,

resulting in higher and higher concentrations. At the level of the higher predators, the tissue concentration can reach levels at which severe effects are observed. This was the manner in which DDT, while present at low concentrations in the environment, accumulated to concentrations in eagles and other fish-eating birds that seriously impaired their ability to reproduce.

The lack of availability of some of these compounds in the environment has led some people to suggest rewriting cleanup criteria to include only that material that is bioavailable. The rationale is that material that is not available for degradation is not available to exert toxic effects. In general, this correlation has proved true, although not all animals have been tested to see if their behavior affects the availability of pollutants. While altering the cleanup requirements would increase the likelihood of successful remediation, conditions (pH, temperature, salt concentration or redox conditions) could change, altering the availability of the pool of contaminant. Soils and sediments with residual contaminants could therefore represent long term risks to the environment.

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Biographical Sketches

Jean D. MacRae is an Assistant Professor in the Department of Civil and Environmental Engineering at the University of Maine, USA. She has an undergraduate degree in Life Sciences from Queen's University in Kingston, Ontario, a Master of Science degree in Microbiology from the University of British Columbia and a Ph.D. degree in Environmental Engineering, also from the University of British Columbia. Prior to joining the faculty at the University of Maine, she worked at Environment Canada and Health Canada for the Canadian government. Her current research projects include studies on the roles of microorganisms in arsenic transformations in groundwater and the fate of polybrominated flame retardants in sewage treatment systems and the environment. She has studied bioavailability and biodegradation of PAHs in sediment and is broadly interested in biologically-mediated degradation and transformation processes as they relate to prevention and remediation of pollution.

Therese desJardins Anderson is a Ph.D. candidate in Ecology and Environmental Science at the University of Maine, USA. Her undergraduate degree is in Microbiology and Biochemistry with a minor in Chemistry and her Master of Science is in Biochemistry. She has previously worked in both private and public sector laboratories as an Organic Analyst, Supervisor and Laboratory Manager. She has worked on methods development and the analysis of environmental samples for a variety of organic pollutants, including PCBs, pesticides, dioxin and PAHs for over fifteen years. She is currently investigating the accumulation of brominated organics in the environment.