CHEMISTRY OF ORGANIC POLLUTANTS, INCLUDING AGROCHEMICALS

Des W. Connell
Griffith University, Brisbane, Queensland, Australia

Rudolf S.S. Wu, Bruce J. Richardson and **Paul K.S. Lam**
City University of Hong Kong, Hong Kong, China

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Summary

Since the late 1800s the range of synthesized chemicals has increased dramatically to include pesticides, plastics, hydrocarbon fuels, soaps, detergents and other useful substances. The effects in the environment are result of a sequence of processes that depend on the properties of individual chemical. DDT has been the focus of a large amount of early research due to its effects on the endocrine system leading to egg shell thinning and reduced breeding in birds. DDT is a member of chlorohydrocarbons, a family of chemically related insecticides. Chlorohydrocarbons are highly toxic to aquatic organisms, persistent, soluble in fat and have very low solubility in water. They move from water to animals with a large increase in concentration by a process described as bioaccumulation. This group, banned from use in many countries, includes industrial chemicals such as PCBs and combustion products like polycyclic aromatic hydrocarbons, dioxins and furans.

In terms of used quantities herbicides are of major importance but their properties differ significantly from chlorohydrocarbons. Herbicides are relatively water soluble but less soluble in fat and less persistent. Thus they don't bioaccumulate and are less toxic having a much lower impact in the environment. Organophosphates, carbamates, pyrethrins and pyrethroids also have, in general, low solubility in fat, relatively high solubility in water but low persistence and are not bioaccumulative. Members of this group can be highly toxic to biota including mammals and aquatic organisms but overall their environmental effects are usually low.

Soaps and detergents, containing surfactants, have relatively low toxicity, persistence and bioaccumulation. Although discharged to environment in large quantities their effects are generally low. Plastics differ from other contaminants since these substances enter environment as solid wastes with little toxicity but have other adverse environmental effects. The management of these effects relates to their degradation and removal from the system.

1. Introduction

1.1. Historical Perspective

Essentially the environmental chemistry of organic pollutants is a branch of chemistry that has grown in response to the practical requirement of governments for a clear understanding of the behavior and effects of chemicals in the environment. In many situations, control measures can have adverse economic and social effects on human communities and, at the same time, may not have beneficial environmental outcomes. Fully effective measures for the management of chemicals require a detailed understanding of such factors as: the distribution of chemicals in the environment, their persistence and degradation and toxicity to humans and other biota. In addition, control and management requires a sound knowledge of methods for the treatment and reduction of the discharge of organic pollutants to the environment.

The beginning of environmental chemistry was during the latter part of the 19th century when scientists were endeavoring to explain the chemical nature of matter and to synthesize existing and new compounds. One of these early chemists was William Perkin (1838 to 1907) who was an enthusiastic young synthetic chemist working at the Royal College of Chemistry in London in the early 1850s. He had synthesized some highly colored substances based on aniline from coal tar and recognized that these compounds had the potential to dye clothing, an industry which he knew very little about. He contacted the industry and had a generally unfavorable response but, nevertheless, some industry figures believed the dyes had potential.

In 1857, the first synthetic chemical industry was set up by Perkin and the dyes were soon adopted by the industry worldwide. This marks a major change in human development in that compounds with desirable uses could now be produced by synthetic processes designed by the application of scientific knowledge. Since then the synthetic chemical industry has expanded enormously and now produces a host of synthetic organic chemicals including plastics, agricultural pesticides, petroleum products and pharmaceuticals. These substances have been of enormous value to human society and continue to produce ever-increasing benefits. However the environmental and public health effects of these chemicals became a matter of major public concern which continues to the present day.

1.2. Development of the Chemistry of Organic Pollutants

Within a few years, almost from the very beginning of Perkins industrial operation, the industry was being accused of using, and discharging to the environment, chemicals which were harmful to the workers and local residents and damaging the natural systems where the industry was established. This problem started to crystallize in 1864 when a Swiss dye factory had to close as a result of its discharges causing major health problems with the local population. The debate surrounding the industry and its effects on the environment and public health problems expanded and continued. Legislation to control industrial chemical operations was slow in developing since this was a new problem with which governments had little experience. Extensive legislation developed over the years and has had to be continually improved and revised as new chemicals came on the market and a need for improved control of existing chemicals was recognized.

During the early part of the 20th century there was continuous development in the industrial production of organic chemicals for a variety of purposes. In agriculture, prior to World War Two, natural pesticides such as derris dust, pyrithrins and nicotine were commonly used to control pests. These attracted little attention as environmental pollutants probably because they were not used on a comparatively large scale and they were not persistent. Importantly there were no reliable techniques available to chemically analyze environmental samples of water, fish and sediments to evaluate the occurrence of these substances. Improvements in techniques for chemical analysis have had a major effect on the development of environmental chemistry as outlined in Table 1. It is noteworthy that this group of early pesticides includes many substances that are fish poisons, such as derris dust, which are quite capable of damaging the environment.

Prior to 1952	No reliable methods for analysis of organic compounds in environmental samples.
1952	Gas-liquid chromatography invented for the separation of organic chemicals on a small scale.
1957-1958	Detectors (flame ionization and electron capture) invented which could detect trace organic chemicals. These detectors coupled with gas-liquid chromatography resulted in a powerful technique for the analysis of trace chemicals in environmental samples.
1960s	The gas chromatograph coupled to the sensitive detectors and to mass spectrometers provided a powerful tool to detect and identify trace chemicals in environmental samples at very low levels.

Table 1: Development of analytical methods for trace organic chemicals in the environment

In the history of environmental chemicals pesticide DDT occupies a central position. In 1939, Paul Mueller of the Swiss company Geigy patented the use of this substance as a pesticide and received the Nobel Prize in 1948 for his outstanding discovery which was of enormous benefit in controlling insect borne disease and agricultural pests. Many synthetic organic chemicals were prepared during the period prior to and during the Second World War and were brought to commercial production and wide use during the 1940s to 1960s when usage increased substantially. DDT in particular was found to be effective and cheap in the control of many agricultural insect pests and was sprayed widely throughout the United States and other countries. At the same time the capacity to reliably analyze for DDT and other compounds in environmental samples was made available for the first time by the development of gas-liquid chromatography in 1952 with subsequent coupling of this technique to other analytical methods (see Table 1).

Within a few years a wide range of results were available and a pattern of widespread environmental contamination emerged particularly with DDT. The publication in the United States of Rachel Carson’s book Silent Spring during 1962 raised many concerns regarding the biological effects of this substance in the environment and resulted in a major reaction against its continued use. In 1973 DDT was banned in the United States and later in many other countries and subsequently all of the persistent organochlorine group including dieldrin, mirex, aldrin and lindane were banned. However these substances continue to be used and manufactured in a range of countries particularly because of their low cost and effectiveness in controlling malaria and other insect borne disease as well as pests in food crops.

During the investigations of DDT some new groups of environmental pollutants emerged including the polychlorinated biphenyls (PCBs). These substances were widely used in industry and share many of the properties of DDT. Despite severe restrictions on their manufacture and use there are significant quantities of PCBs in old equipment and in the environment. From these starting points the range of pollutants in the environment has expanded. Important contaminants now include petroleum, polycyclic aromatic hydrocarbons (PAHs), dioxins, chlorophenoxy acetic acids (2,4-D and 2,4,5-T), organophosphates, triazines, carbamates, plastics and related compounds and organometallic compounds. The range of pesticides has expanded and in 1997 the estimates of world usage of pesticides was: herbicides (1023 million kilograms, 40 percent of total pesticide usage), insecticides (667 million kilograms, 2 percent), fungicides (245 million kilograms, 9 percent) and other pesticides, e.g. sulfur and petroleum (645 million kilograms, 25 percent).

1.3. Chemistry in Environmental Management

When chemical use results in environmental contamination it is necessary to set standards for acceptable concentrations in water, air, soil and biota. Monitoring of these concentrations in the environment, and resultant biological effects, must be undertaken to ensure that the discharge standards are realistic and provide protection from adverse effects. Also considerable attention is now being focused on regulation of the use of new chemicals and prevention of chemicals that may have adverse effects from entering the marketplace and the environment. A considerable proportion of this work involves the prediction of the behavior and effects of a chemical from its properties. A concept for the prediction of environmental behavior is shown in Figure 1.

With this concept the characteristics of the molecule govern the physicochemical properties of the compound which in turn influences transformation and distribution in the environment and the biological effects. This suggests that the transformation and distribution in the environment as well as biological effects can be predicted from the characteristics of the molecule and the physicochemical properties of the compound. There has been a considerable level of success with the first two steps of this concept, predicting transformation and distribution in the environment from the characteristics of the molecule and physicochemical properties (see *Ecological Chemistry*). Prediction of biological effects is the most complex of the set of predictions but there has been some success in that area as well.

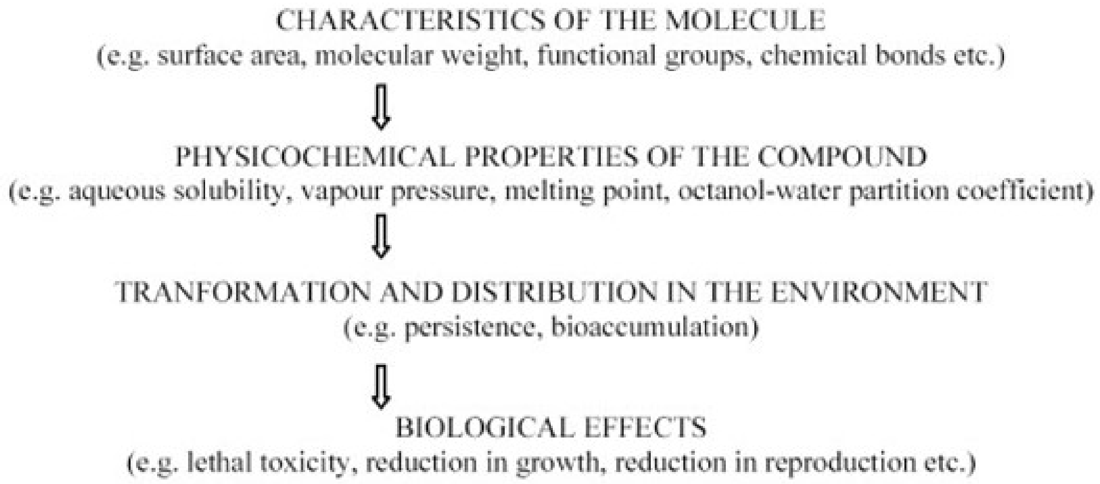

Figure 1: Concept of the relationship of the characteristics of a molecule and compound to its behavior and effects in the environment

2. Types and Properties of Organic Pollutants

2.1. Origin and Occurrence in Discharges

A broad range of organic substances are produced by human society and appear in discharges such as sewage, stormwater and industrial discharges. These discharges can represent major sources of the pollutant substance. For example the concentration of organic pollutants in sewage is low but the volume is large making it a major source of many pollutants. A similar situation applies with stormwater where these substances often originate from discharges from motor vehicles on to road surfaces and are subsequently swept into waterways by storm run-off. Motor vehicles are major sources of petroleum hydrocarbons, polycyclic aromatic hydrocarbons and dioxins which are often discharged to the atmosphere in particulate form. These particulates are deposited close to busy roadways leading to contamination of urban soils and potential human exposure. Urban and industrial wastes are often, either currently or in the past, disposed directly into pits dug into the ground which leads to contamination of the soil and in some cases the adjacent ground water.

Outside urban areas agricultural activities are the major sources of pollutants. The growing of crops often involves the release of pesticides into the environment, which can result in the contamination of waterways and soils, as well as the urban environment. Perhaps the most spectacular example of contamination of the environment is due to the accidental spillage of petroleum. Over the years many disasters of this kind have occurred releasing tens of thousands of tonnes of petroleum into the aquatic environment (see *Oil Pollution and Microbial Regulation*).

2.2. Classes and Properties of Organic Pollutants

The various types of organic pollutant can be placed into three general classes: (i) hydrocarbons, (ii) oxygen, nitrogen and phosphorus compounds or (iii) organometallic compounds. Probably the major category is the hydrocarbons and related compounds, which contains such compounds as DDT, the dioxins and the polycyclic aromatic hydrocarbons (PAHs). These compounds contain the elements of carbon and hydrogen, with some containing chlorine and oxygen as well. There are a limited number of types of chemical bonds present, which are principally C-H, C-C, C-Cl, C=C and C=C (aromatic). All of these bonds are relatively stable and have limited polarity and this property is then conferred onto the related compounds. Some typical structures are shown in Figure 2.

As a result of the low polarity, these compounds are, in general, soluble in fat (i.e. lipophilic), poorly soluble in water and persistent in the environment. Thus, they will be sorbed by sediment and bioaccumulated by organisms (in fatty tissues) and have low concentrations in water and air. The lipophilicity of compounds can be measured in the laboratory as the octanol-water partition coefficient (K_{ow}). The higher the K_{ow} value the higher the lipophilicity. This class includes the most toxic organic compound of abiotic origin, 2,3,7,8-tetrachlorodibenzo(1,4)dioxin, also known as 2,3,7,8-TCDD or TCDD.

The group containing oxygen, nitrogen and phosphorus compounds is very diverse but as a general rule it contains compounds with relatively high solubility in water, low fat solubility and relatively low persistence in the environment. This is due to the presence of bonds with relatively high levels of polarity due to carbon and other atoms being attached to oxygen, nitrogen or phosphorus conferring a high level of polarity onto the related compounds. As a general rule the K_{ow} values are relatively low, much lower than those of the hydrocarbons. In addition, such bonds are relatively easily dissolved by environmental processes and consequently such compounds are less persistent.

The substances in this group only rarely form residues in the environment due to their low persistence, low accumulation in sediments and low bioaccumulation capacity in organisms. The organometallic group is probably the least important from an environmental perspective and includes compounds that are combinations of metal, such as lead and tin, with organic components based on carbon.

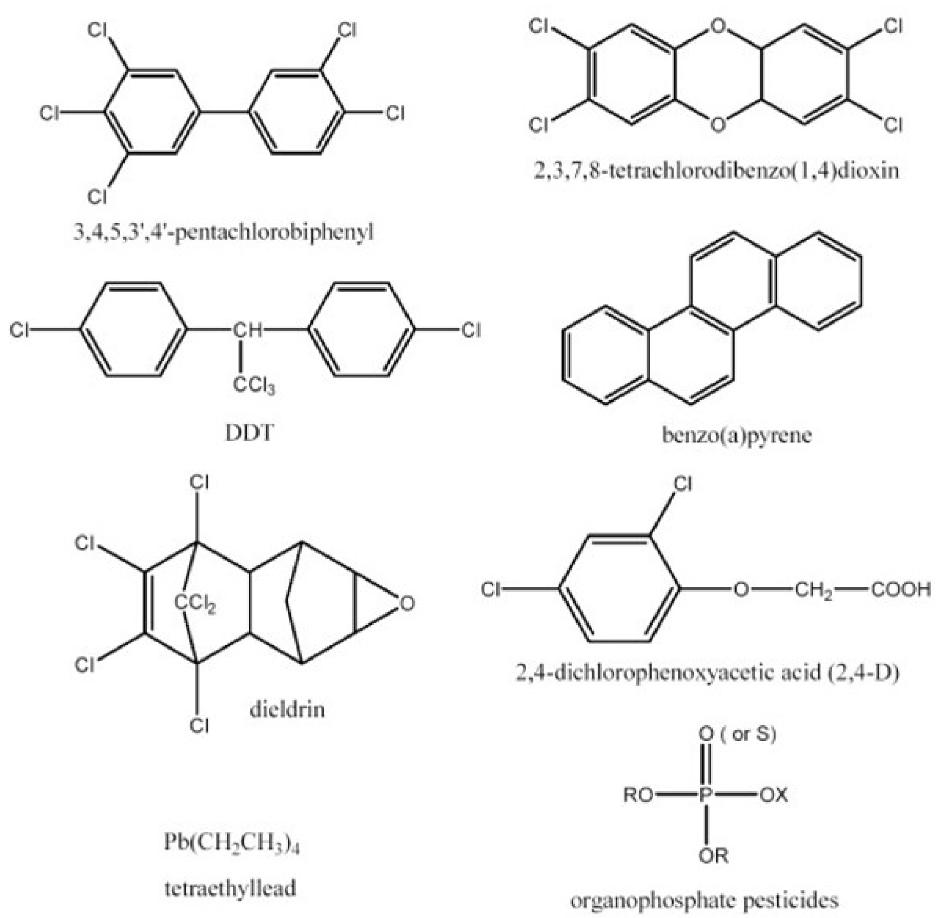

Figure 2: Chemical structures of some well known organic pollutants

2.3. Persistent Organic Pollutants and Endocrine Disruptors

There are a group of chemicals which have posed particular environmental problems due to their fat solubility, bioaccumulation potential and environmental persistence as well as usage patterns. These are referred to as Persistent Organic Pollutants (POPs) and these substances are often distributed over long distances up to a global scale. POPs are commonly members of the hydrocarbon and related compounds group (see Figure 2) and include such compounds as DDT, PCBs and the dioxins (see *Persistent Organic Wastes, Pathways of Organic Chemical Contamination in Ecosystems*). The POPs have been associated with adverse biological effects often related to disruption of the endocrine system in organisms. The endocrine system is a complex array of glands and other organs that control hormone levels within organisms. When POPs are taken up by an organism, even in very low concentrations, they can disrupt the endocrine system causing hormonal changes that can result in reproductive problems. In addition these compounds are often carcinogens. There are several examples of the adverse effects of POPs on reproductive success in the natural environment. Perhaps the best known is the effects of DDE on the reproductive success of birds. In recent times the number of endocrine disrupters has increased dramatically and now includes most organic pollutants as well as the range of other substances. In addition there have been reports of adverse effects, usually associated with reproduction, in relationship to humans as well.

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Biographical Sketches

Des Connell is Emeritus Professor of Ecotoxicology and Environmental Chemistry as well as being the Head of School at the School of Public Health in Griffith University. Prior to joining Griffith University he was Director of the Western Port Bay Environmental Study and later the Gippsland Lakes Environmental Study with the Ministry for Conservation in Melbourne, Australia. He has been Dean of the Faculty of Environmental Sciences at Griffith University and Director of the Government Chemical Laboratory in the Queensland Government. Professor Connell has published a range of papers on Bioaccumulation, Water Quality Evaluation, Environmental Modeling and Risk Assessment. He was awarded the Royal Australian Chemical Institute Medal for contributions to Environmental Chemistry in 1992 and a Doctor of Science in Ecotoxicology by Griffith University in 1993.

Rudolph Wu is Director of the Centre for Coastal Pollution and Conservation within the City University of Hong Kong where he has been Head of the Department of Biology and Chemistry. He has a wide range of publications in international journals in the fields of marine ecology, marine pollution, ecotoxicology and mariculture. He serves on the advisory and editorial boards of several research journals and has been the Chief Guest Editor of three special issues of the "Marine Pollution Bulletin". Professor Wu has served on a number of working and expert groups of the United Nations and the International Maritime Organisation and he contributed to the second review of the "Health of the Oceans" commissioned by the United Nations. Currently he is a member of the Coastal Ocean Observation Panel of the Intergovernmental Oceanographic Commission and also a member of the Multidisciplinary Expert Group of the United Nation's Regional Programme of the East Asian Seas.

Bruce Richardson is a staff member in the Department of Biology and Chemistry at the City University of Hong Kong. He completed his Ph.D. at La Trobe University in Melbourne, Australia. He has worked for the Marine Science Laboratories of the Victorian Department of Conservation, Forests and Lands as a marine scientist. From there he took up a position at Deakin University, Geelong, Australia for several years. Professor Richardson's research interests include the design of monitoring programs for aquatic environments, use of living organisms as monitors of environmental contamination and monitoring trace organic contamination in aquatic environments.

Paul Lam is a graduate of the University of Hong Kong and he completed his Ph.D. degree at University of Sheffield in England and after postdoctoral studies at Kings College in London he returned to Hong Kong. He is the author of a wide range of research papers and chapters in books. Professor Lam's main research interests lie in the environmental measurement and analysis, ecotoxicology and environmental toxicology. Some of the specific research topics he has worked on include biomarker studies in toxicant-exposed animals, fate and effects of persistent organic pollutants in aquatic environments and risk assessment of algal toxins.