ORGANIC POLLUTION FROM AGROCHEMICALS

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Keywords: pesticides, fungicides, herbicides, insecticides, organochlorine and organophosphorous pesticides, pyrethroids, carbamates, triazines, agriculture, soil, water, atmosphere, plants, animals, humans, population health.

Contents

Summary

It is well known that various agrochemical products (e.g. fungicides, herbicides, insecticides, nematocides, rodenticides**,** defoliants and desiccants, stimulators and regulators, attractants and repellents) have been playing a very important role in the second half of the twentieth century in increasing the volume of agricultural production needed for the Earth's rapidly growing human population., It has been also unambiguously demonstrated, however, that many of these formulations are damaging to the environment and biota, including plants, animals and humans. Thus, an important task for the twenty-first century is to develop alternative approaches that will increase the efficiency of agriculture but without adverse effects on humans and the environment. Already, a few alternative approaches, like biological methods of plant protection and organic farming, are being efficiently applied.

This chapter presents the review of the situation concerning pesticides in the world, including their production and use, contamination of the environment (soils, water and air) with pesticides and products of their transformation. Ecotoxicological and toxicological effects of pesticides (poisoning plants, damaging animals and affecting humans) are discussed in detail. Alternatives for higher efficiency in agriculture, including biological protection of plants, are also discussed.

1. Introduction

Throughout its history humankind has been suffering from shortage of food. Today the problem is becoming more and more important due to the simultaneous increase in population and decrease in the area of agricultural land. To supply people with adequate quantities of agricultural products, farmers around the world are trying to use the new scientific and technical achievements. Some of the innovations, however, have negative consequences, particularly, for the environment but also for human health.

It has been known from Roman times that the use of some naturally occurring chemicals (e.g. manure, ash, lime, gypsum, vinegar, etc.) can substantially increase the productivity of agriculture. Later, in the sixteenth century it was shown in China, that moderate quantities of some arsenic containing materials afforded protection to crops, vegetables and fruits. The first systematic studies of chemicals for plant protection began in the middle of the nineteenth century after the tragic famines in Ireland and Germany, where millions of people suffered as a result of a severe fungus disease of potato.

Chemicals, which have been used for protection of agricultural products from parasites and diseases, have been named “pesticides”. The first pesticide was copper arsenite, that was discovered in the eighteenth century and was successfully used against the Colorado potato beetle. The modern period of plant protection started in 1939 in Switzerland, when the future Nobel laureate Paul Muller discovered the strong insecticidal properties of dichlorodiphenyltrichloroethane (DDT) (see Figure 1). This was the first efficient organochlorine pesticide. Besides its high insecticidal efficiency in plant protection, DDT saved enormous number of human lives in Italy, Spain, Greece, Yugoslavia and USA when malaria epidemics struck these countries. During and after World War II, DDT also played a significant role as a very important sanitary agent. However, it was shown later in many countries, that highly toxic DDT and its metabolite dichlorodiphenyldichloroethylene (DDE) (see Figure 1) are very persistent in the environment and tend to accumulate in the fat tissues of humans and animals.

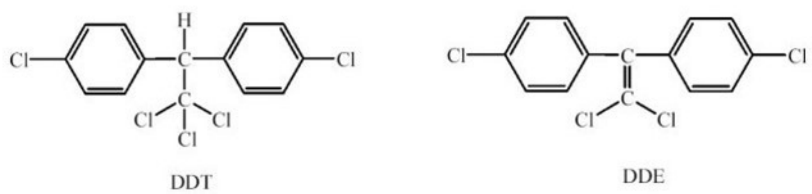

Figure 1. Structures of dichlorodiphenyltrichloroethane (DDT) and dichlorodiphenyldichloroethylene (DDE)

Detailed studies, performed by scientists in various countries, have shown that the Earth's aquatic ecosystems contain about 25% of the whole amount of DDT, produced around the world (since 1950 at a level about 100 000 tons per year). The data obtained show that although the concentrations of DDT and DDE in natural waters are rather low (10^{-7} % in fresh water and 10^{-9} % in sea water) these quantities can be dangerous for the environment because of bioaccumulation of these ecotoxicants in the trophic chains. We have shown this for the Lake Baikal food webs, including phytoplankton, zooplankton, fish, birds and Baikal seal ("nerpa"). A combined team of American and Canadian scientists has observed analogous effect for the Californian sea otter. The quantities of toxicants in such cases may increase by factors of 10^5 to 10^6.

Due to understanding of possible dangerous effects of DDT and DDE on human health, the use of this pesticide has been banned in many countries since the 1970s, but in other countries, mainly in Africa, Asia and Latin America, it is still used rather intensively, mostly in the struggle against malaria. Unfortunately, no alternative, less toxic pesticide, has yet discovered, and this is why it is difficult to ban the use of DDT all over the world. This example shows that the situation with pesticides is rather complex. Thus, in the main part of this article, we will consider other cases, considering both the needs of agriculture as well as the negative consequences of pesticide use.

2. Use of Pesticides

When choosing pesticides for practical purposes, one has to give preference to formulations which decompose rapidly to non-toxic products. At the same time the remedies have to be highly selective and must not disturb the ecological equilibrium of the region. The first generation pesticides did not meet these demands and, consequently, second generation pesticides were developed in the middle of the last century. However, once it was shown, in the second half of twentieth century, that these new formulations did not meet the new ecological demands, a third generation of pesticides was proposed. We will consider in this chapter first the classification of pesticides (both chemical and technological) and later their production and application.

2.1. Classification

It is reasonable to start the classification of pesticides from the chemical point of view, because the chemical composition and structure predominantly determine their biological activity. The Quantitative Structure–Activity Relationships (QSAR) approach is widely used nowadays for analysis of the new tendencies in this field (see *Ecological Chemistry*). The chemical classification of the most important types of pesticides is given below in alphabetic order.

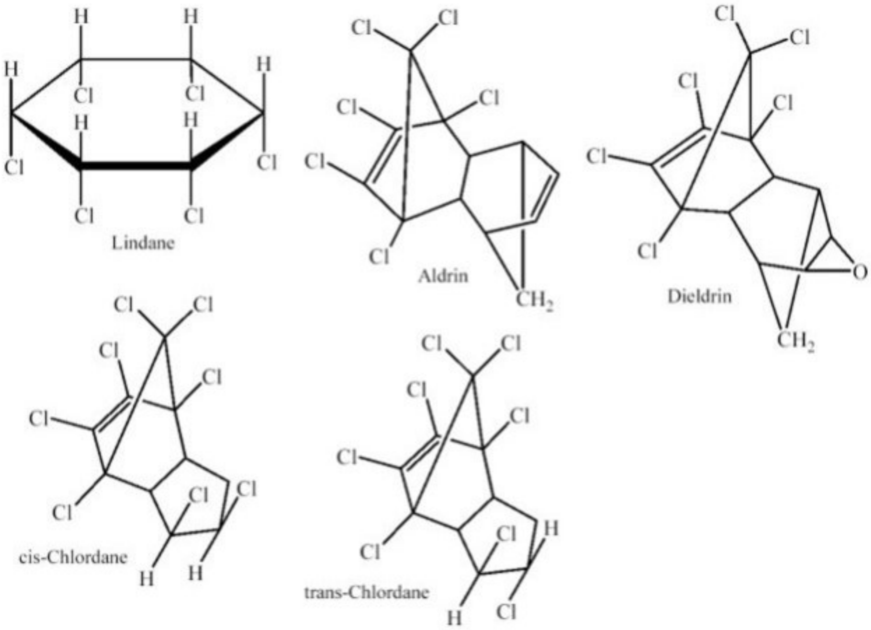

Figure 2. Structures of lindane, aldrin, cis-chlordane, trans-chlordane and dieldrin

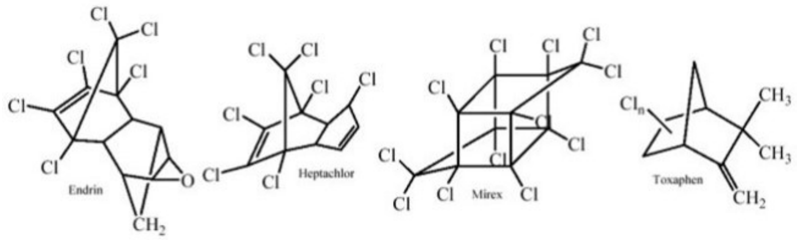

Figure 3. Structures of endrin, heptachlor, mirex and toxaphen

Organochlorine compounds are synthetic pesticides, which contain one or more chlorine atoms on an aliphatic carbon chain, or both in the aliphatic skeleton and at the double bond, or on aromatic carbon rings. Besides DDT, an example of a first generation pesticides is lindane (see Figure 2) while some of the second generation formulations are aldrin, chlordane, dieldrin, endrin, heptachlor, mirex and toxaphene (see Figures 2 and 3). Due to their high toxicity and extreme risk to environment and human health (see *Persistent Organic Wastes*, *Chemistry of Organic Pollutants, including Agrochemicals*), these pesticides were included on the list of chemicals, production and use of which had to be eliminated according to the Stockholm Convention signed by many countries on May 23, 2001, and now open for ratification.

Other widely distributed organochlorine pesticides are derivatives of phenoxyacetic acids, i.e. 2,4-dichlorophenoxyacetic acids (2,4-D) and 2,4,5-trichlorophenoxyacetic acids (2,4,5-T) (see Figure 4).

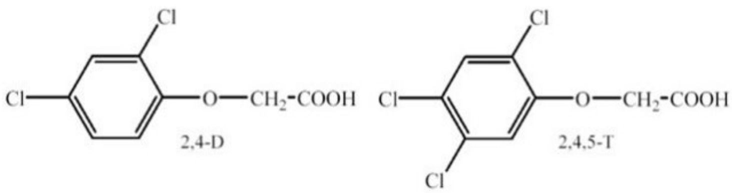

Figure 4. Structures of 2,4-dichlorophenoxyacetic acids (2,4-D) and 2,4,5-trichlorophenoxyacetic acids (2,4,5-T)

Organophosphorous compounds are synthetic pesticides, which contain one or two phosphorous atoms with either additional oxygen, sulfur or nitrogen atoms. Examples are chlorophos (trichlorophone), carbophos (malathion), thiophos (parathion) and metaphos (parathion-methyl) (see Figure 5).

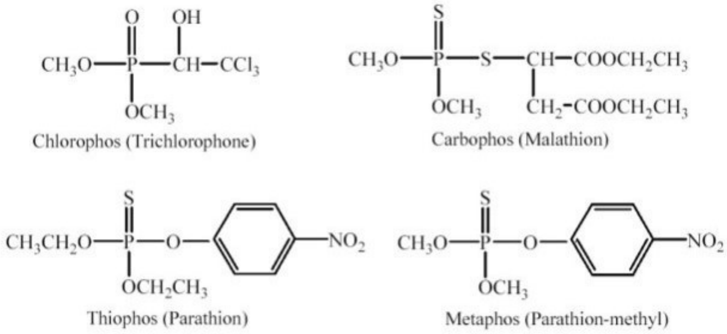

Figure 5. Structures of chlorophos (trichlorophone), carbophos (malathion), thiophos (parathion) and metaphos (parathion-methyl)

Pyrethroids are synthetic pesticides, which are related to the naturally occurring pyrethrines, that have insecticidal properties. The widely distributed formulations are permethrin (ambush) and cypermethrin (cymbush) (see Figure 6).

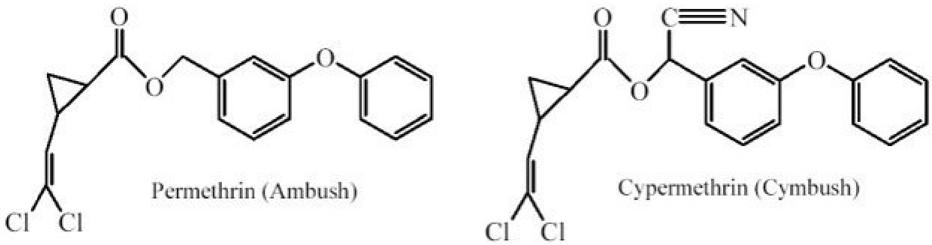

Figure 6. Structures of permethrin (ambush) and cypermethrin (cymbush)

Other important pesticide classes are carbamates and triazines which are based on organonitrogen compounds (see Figure 7).

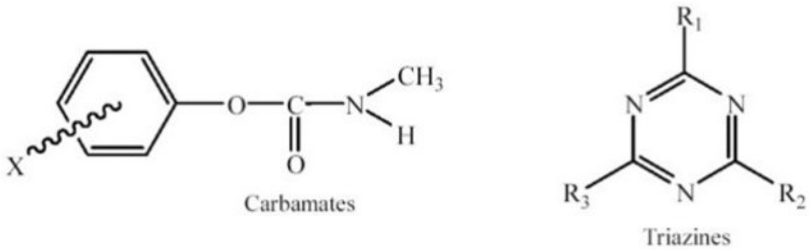

Figure 7. Structures of carbamates and triazines

It is also possible to classify pesticides from the technological point of view, when one has to decide what is the group most at risk from the particular agricultural product. Having this in mind, the following technological classification is possible for the most important classes of pesticides:

- **Fungicides –** chemicals killing various types of fungi, which destroy agricultural products.
- **Herbicides** – chemicals that eliminate weeds, but also disturb normal growth of crops, vegetables and fruits.
- **Insecticides** – chemicals killing various insects, which destroy agricultural products.

There are also specific types of chemicals for destroying nematodes (**nematocides**) and rodents (**rodenticides**). Defoliants and desiccants, causing leaves to drop off prematurely, are also pesticides. Finally, chemicals that regulate lives of various plants (growth – **stimulators and regulators**) or animal behavior (**attractants and repellents**) can also be classified as pesticides.

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Biographical Sketch

Valery S. Petrosyan obtained his Ph.D. degree in chemistry in 1967 at M.V. Lomonosov University in Moscow under the sponsorship of Professor O.A. Reutov. The title of his thesis was “NMR spectra and structures of organomercury compounds”. He continued working as a research chemist at the Department of Organic Chemistry and spent one year as a Research Associate at California Institute of Technology with Professor J.D. Roberts.

Since 1974 he has been Associate Professor of organic chemistry at M.V. Lomonosov University in Moscow. In 1979 he received his D.Sc. and the title of thesis was “Solvent effects in chemistry of organic derivatives of non-transition metals”. Since 1981 he has been Professor at the same Faculty and from 1988, Head of the Physical Organic Chemistry Laboratory. In 1987 he was a founder of the Open Ecological University in Moscow and he has acted as the Rector since then.

His main research interests are in organic, organometallic and environmental chemistry. The particular fields of investigations are structures and interaction mechanisms of organic and organometallic compounds, behavior of organic and organometallic toxicants in the environment, mechanisms of their toxicity to biota and humans, and detoxification of priority toxicants in the environment by humic substances.

He is a member of several international scientific councils and committees. In 2002 he received the SETAC-Europe Award in Environmental Education and in 2003 the Medal of the Italian Chemical Society “For Distinguished Achievements in Environmental Chemistry”.