Chapter 1

Introductory Chapter: Organochlorine

Aurel Nuro

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.81271

1. Introduction

Organochlorines (OCs) are organic molecules with chlorine in their structure. There are known a large number of organochlorine compounds. A large amount of chlorinated organic compounds are produced for industrial, agricultural, pharmaceutical, household purposes, etc. In many studies, the main focus is on OC which has been evaluated as environmental contaminants with toxic effects on humans. Different types of organochlorine have been produced throughout the world. Some of the most popular classes are organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), dioxins, chlorobenzenes, chlorophenols, chlorinated alkanes, etc. Organochlorine compounds usually have a large molecular mass. They are very stable. Generally, they are molecules of moderate polarity (low solubility in water). This makes OC easily soluble in fats. They were found in almost all environments: air, water, soil, sediments, and biota samples. They can spread out easily in different geographic altitudes and latitudes. Volatile and semi-volatile OCs have the ability to spread far away from the place where they were used. Some studies have reported some organochlorines in the North Pole at the same levels as the areas where they were produced or applied. They have the ability to bioaccumulate easily in biota. Passing through the food chain levels, they increase their concentrations (biomagnifying). Contaminated foods with OCs and exposures to them are their main ways to arrive in the human body. Generally, they display their effects after a relatively long period of exposure. This is the main reason why they are produced and used for a long time before their production and use were banned. The most important health effects that organochlorines can cause are mutagenic, endocrine-disruptor, carcinogenic and central nervous or peripheral disorders. After identification of the consequences for many organochlorines, their production and use in many countries were banned but unfortunately their effects were shown for many other years.

2. Organochlorine pesticides

Organochlorine pesticides were used widely for agricultural purposes after the Second World War. The insecticidal properties of DDT were discovered firstly. After that many other OCPs were synthesized and used. Many tons of DDT, aldrin, heptachlor, lindane, hexachlorobenzene, toxaphene, and many other pesticides with chlorine in their molecules were produced and used all over the world for many years. They affected significantly the growth of agricultural products around 1960, bringing what was called the "Green Revolution." Their use was very effective especially in countries that suffered from many diseases spread by insects such as malaria. In early 1970s, their toxic effects were verified firstly in birds and fishes. After that, OCPs were banned in the USA and Europe. OCPs and their degradation products are found in many ecosystems until now because of their persistence and their bioaccumulation ability. The presence of OCPs was reported in many environmental and food studies. Water irrigation and rainfall landslides make them possible to pass over surface and underground waters. So, they can spread far away from areas where they have been applied. Bioaccumulation processes make their presence possible in all food chain [1, 2].

3. Polychlorinated biphenyls

PCBs were produced from 1930 to 1977. PCB mixtures were prepared from chlorination of biphenyls in the presence of various catalysts. There are 209 different congeners depending on the number of chlorine atoms and their positions in the molecule. Usually they were used as mixtures (aroclor, kanechlor, etc.). These mixtures are classified and used according to the percentage of chlorine. They were widely used as insulating and hydraulic fluids in numerous industrial processes. They were banned in 1980 because of the possible risks to human health and the environment. Higher toxicity presents non- and mono-ortho-substituted congeners because of their planarity. They are called dioxin-like congeners of PCBs, classified as endocrine disruptor and possible carcinogen to humans [3, 4]. Many accidents have occurred around the world due to the use of PCB: Kyushu, Japan (1968); Hudson River, USA (1977); Brescia, Italy (1999); etc. These accidents and laboratory in vivo/in vitro data verified their toxic ability to humans [5–8].

4. Dioxins and furans

Polychlorinated dibenzo-p-dioxin (PCDDs) and polychlorinated dibenzofurans (PCDFs) are highly toxic, the most dangerous being 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Testing study on toxicity of the TCDD is used as a mechanism and reference value for other dioxins [9–11]. PCDD/Fs and PCB dioxin-like were verified in different experiments to have the same mechanism of toxicity via the aryl hydrocarbon receptor (AHR). Dioxins can produced in higher temperature as secondary products, e.g. by increate of urban wastes or many industrial processes. Dioxins have no common use. PCDD/F even in low levels can cause serious problems to humans and other organisms because of their high toxicity [12, 13]. Various studies have clarified the implications of their presence at ultra-trace levels like that in Seveso, Italy (1976), Belgian PCB/dioxin incident (1999), etc [14, 15].

5. Chlorobenzenes, chlorophenols, and other derivatives

Derivatives with chlorine of benzene, phenol, aniline, nitrobenzene, benzoic acid, phenyl acetic acid, and many other similar compounds are usually produced as raw materials for many syntheses in the pharmaceutical industry, plastic production, pesticide production, and many other synthetic compounds. Some of them were used as pesticides, for example, tecnazene (tetrachloronitrobenzene), Kvintozen (pentachloraniline), etc. Chlorinated derivatives can be impure in many synthetic products. They can be obtained by degradation processes of large chlorinated molecules. They were reported as part of the metabolism of large chlorine molecules in different organisms. Most of them are harmful to the environment and living organisms. Their toxicity is different depending on the number and position of chlorine in the molecules.

6. Legislation on organochlorine compounds

Many studies have shown that chlorine compounds have harmful health effects not only for exposed persons but also for the entire population, it was necessary to regulate the equivalence of international legislation on limitations on the production and use of toxic substances. So several agreements were reached, but the most important is the Stockholm Convention (2001) on Persistent Organic Pollutants (POPs). This convention, adopted by most countries, aimed at the elimination or reduction and use of many OCs including OCPs, PCBs, and dioxins. It provided several phases and guidelines for the immediate prohibition of use, production, and reduction of those substances called POPs. Although in most countries this convention became effective soon, OC presence was reported in certain areas as a result of waste disposal, equipment accidents, or their use under false trademark. Their high persistence is an important factor. Control of the OC should be continuous in environmental and food samples due to their wide spread.

7. Organochlorine distribution, stability, and degradation

Although they have been banned many years ago, levels of OC were reported frequently in different studies. They are widespread in both applied environments and in areas far away from their application sites. This is due to high stability, high bioaccumulation capacity, biomagnification, and the ability to spread out of the application site. Generally, these compounds are difficult to degrade. In the soil or sediment environment, the speed of degradation is much smaller. Different degradation mechanisms are known, such as photochemical degradation, thermal degradation, biological degradation, and chemical degradation [7]. Their degradation products are derivatives which in most cases also contain chlorine and exhibit certain toxicity. The study of degradation mechanisms will affect the speeding up of their elimination processes under practical conditions.

8. Analytical techniques on determination of organochlorines

The levels of chlorine compounds in both environmental and food samples were found in very low (trace or ultra-trace) levels from ppm to ppt. For their qualitative and quantitative determination, it is necessary to use different techniques of extraction such as Soxhlet, ultrasonic extraction, SPE, ASE, etc. The samples of clean-up procedures generally were realized in SPE columns with adsorbents that have different polarities. Analytical determinations of organochlorines were recommended to be achieved by gas chromatography techniques especially coupled with mass spectrometry (GC/MS). GC/MS/MS and LC/MS/MS are recommended in many methods for OC analysis in environmental and food samples [16, 17]. In many standard methods (EN, ASTM, etc.), techniques of simultaneous determination of organochlorine compounds for the same type or different types due to their similarity are described.

9. Preface on organochlorine chapters

This compact book has some data on organochlorine compounds and their degradation products. Clarification of degradation processes for OC is important for polluted ecosystems. Reviews on legislations for organochlorine compounds especially on persistent and toxic OC were shown also in this book. Analytical procedures (extraction techniques, clean-up procedures, equipment, etc.) and experimental data for OC analysis are mentioned briefly on book chapters.

Chapter I, "Service Sector-Based Dioxin and Furan Emissions and Management Techniques," describes PCDD/F as one of the important classes of organochlorine contaminants. This chapter presents the importance of study dioxins because they cause people's health problems. Through various studies that authors have used, this review is focused mainly on emission sources and monitoring of these contaminants in some countries in order to conclude to the situation in Ethiopia. PCDD/Fs are part of the POPs because of their persistence and toxicity. Also, in this chapter, are given data on other chlorinated compounds, classified as POPs, such as organochlorine pesticides, PCB, PBB, etc. The connection between PCDD/F and other POPs could have been clearly demonstrated.

Chapter II, "Mechanistic Considerations on the Hydrodechlorination Process of Polychloroarenes," is a review of different hydrodechlorination mechanisms for organochlorine pollutants such as PCDD/F and PCB. These pollutants are persistent for many years because of their structure. Their presence could be for many years not only in environment but also in food chain because of bioaccumulation processes. Authors have considered different studies of hydrodechlorination mechanisms based on different redox mechanisms. These mechanisms of hydrodechlorination are important processes because degradation products usually are organic compounds with lower toxicity. Understanding these reaction mechanisms can lead to their efficient use in practice. The use of these reactions in incinerator filters and contaminated areas can bring a reduction of PCDD/PCDF and PCB pollution.

Chapter III, "Application of Heterogeneous Catalysts in Dechlorination of Chlorophenols," is a review on heterogeneous catalysts for dechlorination of chlorophenols. These compounds are widely distributed especially in waste and surface waters because of household products, urban wastes and other chlorinated compounds such as pesticides. Heterogeneous catalyst can replace the homogeneous catalyst to solve the catalyst recycling problem, especially for the precious metal catalysts. The heterogeneous catalyst costs are more reduced than homogeneous catalyst. Dechlorination of chlorophenols using heterogeneous catalyst could be useful for dechlorination of other chlorinated compounds.

Author details

Aurel Nuro

Address all correspondence to: aurel.nuro@fshn.edu.al

Faculty of Natural Sciences, University of Tirana, Tirana, Albania

References

[1] Stoytcheva M. Pesticides-formulations, effects, fate. In: Nuro A, Marku E, editors. Chapter 9: Organochlorine Pesticides Residues for Some Aquatic Systems in Albania. Rijeka, Croatia: InTech; 2011. ISBN: 978-953-307-532-7

[2] Jokanović M. Impact of pesticides. In: Nuro A, Marku E, editors. Section 2: Pesticides in the Environment-An Overview of Organochlorinated Pesticide Residues in Albania. Case Study: Porto Romano, Adriatic Sea. USA: Academy Publish.org; 2012. pp. 225-239. ISBN: 978-0-9835850-9-1

[3] Erickson MD. Introduction: PCB properties, uses, oçurrence, and regulatory history. In: Robertson LW, Hansen LG, editors. PCBs: Recent Advances in Environmental Toxicology and Health Effects. Lexington, Kentucky: The University Press of Kentucky; 2001. pp. 131-152

[4] Zuçato E, Calvarese S, Mariani G, Mangiapan S, Grasso P, Guzzi A, et al. Level, sources and toxicity of polychlorinated biphenyls in the Italian diet. Chemosphere. 1999;**38**(12):2753-2765

[5] Safe S. Polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and related compounds: Environmental and mechanistic consideration which support the development of toxic equivalency factors (TEFs). Critical Reviews in Toxicology. 1990;**21**(1):51-88

[6] ATSDR. Toxicological Profile for Polychlorinated Biphenyls (PCBs). US Department of Health and Human Services. Atlanta, Georgia: Public health Service, Agency for Toxic Substances and Disease Registry; 2000

[7] Abramowicz DA. Aerobic and anaerobic biodegradation of PCBs: A review. Biotechnology. 1990;**10**(3):241-251

[8] Ahlborg UG, Brouwer A, Fingerhut MA, et al. Impact of polychlorinated dibenzo-p-dioxins, dibenzofurans, and biphenyls on human and environmental health, with special emphasis on application of the toxic equivalency factor concept. European Journal of Pharmacology. 1992;**228**(4):179-199

[9] Van den Berg M, Birnbaum LS, Bosveld ATC, Brunstrom B, Cook P, Feely M, et al. Toxic equivalency factors (TEFs) for PCBs, PCDDs and PCDFs for humans and wildlife. Environmental Health Perspectives. 1998;**106**:775-792

[10] Papadopoulos A, Vassiliadou I, Costopoulou D, Papanicolaou C, Leondiadis L. Levels of dioxins and dioxin-like PCBs in food samples on the Greek market. Chemosphere. 2004;**57**:413-419

[11] Focant J-F, Pirard C, De Pauw E. Levels of PCDDs, PCDFs and PCBs in Belgian and international fast food samples. Chemosphere. 2004;**54**:137-142

[12] U.S. Environmental Protection Agency Health Assessment Document for 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and Related Compounds. Prepared by the Office of Health and Environmental Assessment, Office of Research and Development, Washington, DC. External Review Draft. Vol. 3; 1994b. Report No. EPA/600/BP-92/001c

[13] Hirai a Y, Sakai S-i, Watanabe N, Takatsuki H. Congener-specific intake fractions for PCDDs/DFs and Co-PCBs: Modeling and validation. Chemosphere. 2004;**54**:1383-1400

[14] Schepens PJ, Covaci A, Jorens PG, Hens L, Scharpe S, van Larebeke N. Surprising findings following a Belgian food contamination with polychlorobiphenyls and dioxins. Environmental Health Perspectives. 2001;**109**:101-103

[15] Takekuma M, Saito K, Ogawa M, Matumoto R, Kobayashi S. Levels of PCDDs, PCDFs and Co-PCBs in human milk in Saitama, Japan, and epidemiological research. Chemosphere. 2004;**54**:127-135

[16] Petrick G, Schulz DE, Duinker JC. Clean-up of environmental samles for analysis of organochlorine compounds by gas chromatography with electron-capture detection. Journal of Chromatography. 1988;**435**:241-248

[17] Rene van der Hoff G, van Zoonen P. Trace analysis of pesticides by gas chromatogaphy. Journal of Chromatogaphy A. 1999;**843**:301-322