



Review

An overview on the accumulation, distribution, transformations, toxicity and analytical methods for the monitoring of persistent organic pollutants

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ABSTRACT

Recent years have seen an upsurge of interest in developing low cost and reliable methods for the detection and precise determination of ultra-trace concentrations of persistent organic pollutants (POPs), because of their bioaccumulation, transformation and toxicity. Therefore, a comprehensive review with 108 references referring to the distribution, source, accumulation, transformation, types and toxicity of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) is presented. The review also aims to highlight on the current best practices for the analysis of PCBs and OCPs. Moreover, with the signing of the Stockholm convention on POPs and the development of global monitoring programs, there is an increased need for laboratories in developing countries to determine such class of chemicals. A major focus revealed the need for low cost methods that can be implemented easily in developing countries such as electrochemical techniques.

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1. Historical overview

After the Second World War, scientists began to recognize that, certain chemical pollutants were capable of persistent in the environment for long time, migrating in air, water, soil and sediments and accumulating to levels that could harm wildlife and human health. These chemical pollutants called persistent organic pollutants (POPs) [1]. These pollutants are organic compounds of natural

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or anthropogenic origin that possess a particular combination of physical and chemical properties such that, once released into the environment, they remain intact for exceptionally long periods of time as they resist photolytic, chemical and biological degradation [2,3]. Compounds of this nature are highly resistant to degradation by biological photolytic and/or chemical means [3].

Recently, POPs are a matter of concern because of their toxicity and tendency to accumulate in food chains [4]. The environmental impact of a particular species becomes more important than a total metal concentration. Thus, metal speciation is of great importance in environmental science. However, due to their low concentrations, pre-concentration (enrichment) step is needed prior to their determination. The pollution by POPs and determination and chemical speciation of toxic trace metal ions will be discussed more in detail below.

The carbon–chlorine bond is very stable toward hydrolysis and the greater the number of chlorine substitution and/or functional group, the greater the resistant to biological and photolytic degradation. Because POPs break down very slowly, they will present in the environment for long time to come, even if all new sources were immediately eliminated [5]. POPs in the environment are transported at low concentrations by movement of fresh and marine waters and, as they are semi-volatile, are transported over long distances in the atmosphere. The result is widespread distribution of POPs across the globe, including regions where they have never been used [2]. The POP's level found in the Arctic of Alaska is surprising to many people. This is because some of these pollutants have been banned from the United State and Canada for many years. POPs travel toward colder area like Alaska and then sink due to the colder temperature. The settled contaminants remain in the area for a long period of time because the temperature does not allow them to break down very easily. Because of this, they move from the air and water in to soil and plants, then to animals and humans with ease. The persistence of contaminants in the Arctic from distant sources first came to light in the late 1970 when pesticides were found in polar bear fat tissue, then the reality of atmospheric POPs, their effect on wildlife and human health. A well-known story in the Arctic, researches have begun to look for evidence of airborne POPs in other cold ecosystems, our mountain environments [6,7].

2. Distribution of POPs

In 1945, a booming industry launched a new, effective tool for dealing with insect pests: DDT. It held great promise, including the hope of saving crops and eradicating disease-carrying insects. Twenty years later, DDT and other similar chemicals had indeed benefited agriculture and relieved some of the problems associated with insects in many areas of the world. However, these gains came at a price, as DDT is toxic to many more organisms than those it was intended to kill. In particular, birds of prey had trouble to reproduce, and their population declined in many polluted parts of the world. Since, the commercial manufacture of anthropogenically synthesized organic chemicals began in the 1920s. Production, use and trade of these substances rose sharply after World War II, driven by a desire to produce more and better food and cash crops, protect public health, and facilitate industrial development [8,9].

The first public warnings about possible dangers came in relation to local environmental effects in the early 1960s, and grew stronger in the 1970s [7]. During 1960 and 1970 they were extensively utilized in order to protect crops and to prevent health diseases. Some of these compounds such as hexachlorobenzene (HCB), hexachlorocyclohexane (HCH) and Dichlorodiphenyltrichloroethane (DDT) were among the most widely used pesticides in the world during 1970–1980. Nowadays they are banned or restricted in the majority of the industrialized

countries, but they still used in Africa, South Asia, Central and South America [7–10].

In the late of 1980s, new scientific discoveries resulted in changing perception, highlighting the transboundary nature of the POPs problem. Many of the discoveries were related to the Arctic region. These discoveries were spurred by both qualitative and quantitative improvements in data samples, measurement and analytical techniques. Also, in August 1989, Canada presented a report on hazardous persistent organic chemicals [8].

In the 1990, research found that the largest lake trout in Bow Lake contain high levels of some of these pollutants such as toxaphene. Since, the lake supports only a small population of large lake trout (2.5 kg) and people do not consume high amounts of fish from the lake, human health is not at risk. However, predators such as osprey feed exclusively on fish [12]. Also in Taiwan, the Danshui consider the largest river in the north, it receives liquid effluents and atmospheric fallout resulting from industrial and municipal emissions which include multiple forms of POP pollutants associated with these emissions, including polychlorinated biphenyls (PCBs), are transported down-river in association with particulates and deposited in river sediments, as well as those in nearby coastal areas. The presence of these pollutants causes a large toxicity on fish and other living organisms in the river [13].

The persistence in the compounds allows them to accumulate in animals and pass on more. When the pollutants progress in to animals, they accumulate in the fat cells, organs and muscles. In Adriatic sea which is an arm of the Mediterranean sea separating Italy from the Balkan peninsula, there are concentrations so low of some of these pollutants such as PCB, HCB, HCH and organochlorine pesticides (OCPs) in the fish liver collected from the Adriatic sea during 1993–2003 such as DDT in order to estimate the long-term changes in residue levels and the present status of contamination of this aquatic zone [14].

In China, many high-yield grain fields have become high-intense by POPs – especially pesticide – application areas in China. It was shown by sampling surveys from 1985 to 1991 that pesticide consumption ranged from 4.65 to 15.75 kg/h m² increasing by threefold and 41.8% annually. Pesticide consumption in southeast regions of China including Zhejiang, Shanghai, Fujian, and Guangzhou provinces accounted for 36.7% of the nationwide consumption, while six provinces in the northwest of China, including Qinghai, Ningxia, Gansu, Xinjiang, Heilongjiang, and Inner Mongolia, only accounted for 3.4%. The consumption of pesticides in Zhejiang was about 9.96 kg/h m² and 3.7 times that of the national average (2.71 kg/h m²), and 28 times more than that in Inner Mongolia, which was the lowest user of these chemicals. The distribution pattern of pesticide application in China shown in Fig. 1 was as follows: southeast > central > northwest [15].

In 1999, during the so-called dioxin scandal in Belgium, Polish Veterinary Inspectorate ordered an analysis of food samples of Polish and international origin. The Inspectorate tried not to make the results of those analyses publicly available. This can be seen from the Inspectorate's response to the request of world protection agency (WPA) for allowing access to them. They said that *in the period in question, no such analyses were made in Poland* as seen in Table 1. These data were published in a scientific publication with a limited circulation [16].

3. Sources of POPs

Volcanic activity and vegetation fires are the two possible natural sources of dioxins and dibenzofurans. Some of these volcanoes are located in central Africa. Some attention will be given to sources or uses particular to southern and South Africa. One of these sources is fire, both natural, accidental and managed burning of vegetation [17–20]. POPs, as are apparent from their definition, are very

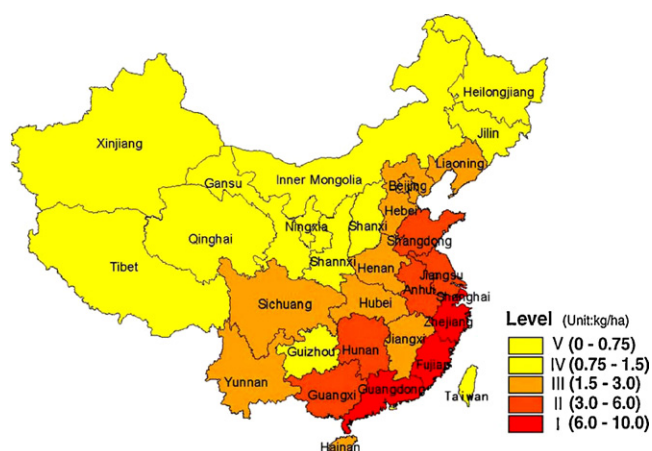


Fig. 1. Distribution of persistent organic pollutants in China in 1996.

stable in all constituents of the environment. They enter the atmosphere from a number of industrial sources such as power stations, heating stations, incinerating plants as well as from household furnaces, transport, use of agricultural sprays, evaporation from water surfaces, soil, or from the landfills. Other sources for POPs compounds such as the unintentional production can be found by incinerations, chemical facilities, diverse combustions, bushfires and putrefaction and wastes containing PCBs. This class of wastes can be found in many areas and stemming from different activities, e.g. the use of obsolete oil, the repairing and maintenance of equipments, demolition of building, evaporation, cement manufacture, animal carcass incinerator, coal combustion, lixiviation of dumps and recycling operations, incineration-municipal, hazardous, medical waste, sewage sludge, industry-chlor-alkali plants, aluminium secondary plants, organ chlorine pesticide plant and cock plant, landfills-hazardous waste/plastic waste, fly ash storage, and organochlorine pesticide storage [21,22].

The sources of access of the substances, oil, fates, liquid fuels, soil, ash and sediment into the water system are wastewaters from plants producing or using POPs, along with runoffs from fields and roads and from the atmospheric deposition. Their largest reservoirs are oceans and seas, where they gather from river sediments, by the atmospheric deposition, by disposing wastes, and by accidents.

Table 1

Analysis of dioxin scandal in fat of food samples (pg-TEQ g^{-1}) of Polish and international origin in 1999 for dioxin scandal with a limited circulation [15–17].

| Product | Concentration, pg-TEQ g^{-1} fat | Reference data, pg-TEQ g^{-1} fat [15–17] |
|---|---|--|
| Fish oil from Baltic fish (imported from Scandinavia) | 12.6–50.0 | – |
| Sea Fish (from Baltic Sea) | 7.0–40.0 | 2.4–214.3 |
| Fish oil from Baltic fish | 11.2–40.0 | – |
| Pork grilled in open fire | 20.0–25.0 | – |
| Fish meal (imported from Scandinavia) | 6.5–20.0 | – |
| Poultry | 0.6–12.8 | 0.7–2.2 |
| Freshwater fish | 1.2–9.4 | 2.4 |
| Beef | 2.4–8.5 | 0.1–16.7 |
| Pork | 0.05–1.3 | 0.31 |
| Hard cheese | 0.2–7.7 | – |
| Eggs (Yolk) | 0.6–7.4 | 1.2–4.6 |
| Butter | 0.6–6.5 | 0.16–4.8 |
| Powdered milk | 0.3–5.0 | – |
| Polish bone meal | 0.25–4.25 | – |
| Milk | 0.1–4.0 | 0.5–3.8 |
| Beef fat | 3.8 | – |
| Yoghurts with fat content >2% | 0.1–1.8 | 0.18 |
| Used vegetable oil (frying chips) | 0.15–0.8 | – |
| Chocolate products | 0.05–0.75 | – |
| Fresh vegetable oil | 0.02–0.1 | 0.01–0.2 |
| Low-fat yoghurts | Less than 0.01 | – |
| Meat of Belgian chicken fed on contaminated feed | – | 700 |

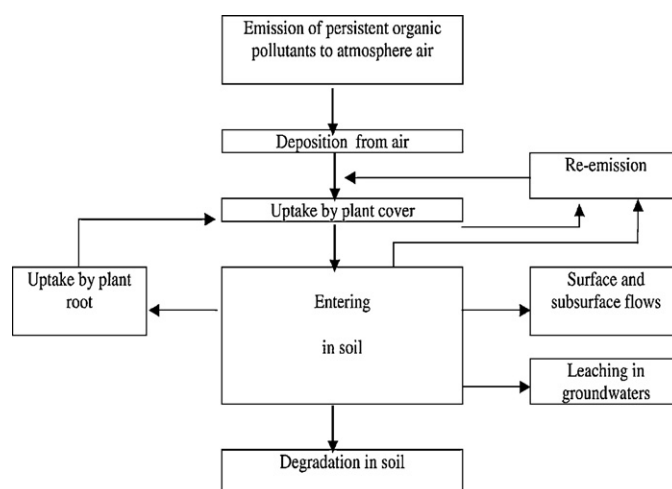


Fig. 2. Conceptual model for the behavior of persistent organic pollutants in the air-plant soil system.

They are stored in sediments on the beds of seas, oceans, and large lakes, where they can be released from after a time and then re-enter the atmosphere as shown in Fig. 2 [23,24].

During the last 10 years, a lot of sources of POPs were stopped due to the economical changes in the country. Moreover a lot of new wastewater treatment plants were built during this period. Another reason of the observed decreasing trends in POPs occurrence in waters and sediments is found in the more principal ecological politics of government and local authorities [22]. In Poland, no wide-ranging investigations of dioxin-related environmental contamination, especially the presence of those compounds in human tissues and milk of breastfeeding mothers, have ever been conducted. Any publicly available data is random or based on unreliable estimates. According to the information provided to the Central Statistical Office by the Institute for Environmental Protection, the dioxin and furan emissions in 1998 are estimated at 290.353 g TEQ. According to the Institute, the main sources of dioxin emissions in Poland are given in Fig. 3 [25].

Recently, the Ministry of Environment has undertaken great efforts to provide a basis for estimating the real emission of dioxins and furans. In different regions of Poland, in urbanized areas as well

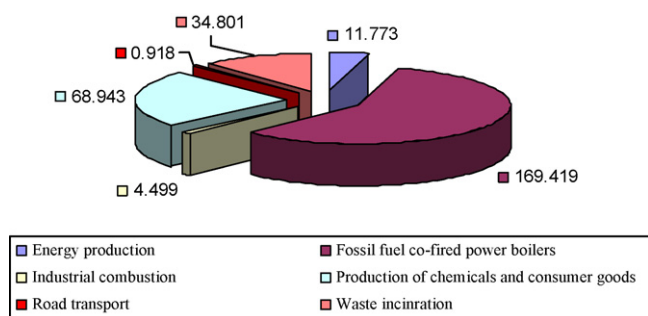


Fig. 3. The main sources of dioxin emissions in Poland.

Table 2

The permissible concentrations (pg-TEQ g⁻¹) of PCBs, DDT and gamma-HCH.

| Substance | The permissible dose, pg-TEQ g ⁻¹ fat |
|-----------|--|
| PCBs | 2.8 |
| DDT | 4.2 |
| Gamma-HCH | 13.3 |

Table 3

Analysis of some selected POPs (mg kg⁻¹) in samples of fatty tissues of patients aged from 10–80 years in one of Warsaw's hospitals.

| Substance | mg kg ⁻¹ of fat | | |
|------------------|----------------------------|---------|-------|
| | Median | Maximum | Mean |
| PCBs | 0.500 | 36.000 | 0.856 |
| HCB | 0.120 | 9.020 | 0.310 |
| Alpha-HCH | 0.160 | | 0.016 |
| Beta-HCH | 0.120 | 5.097 | 0.228 |
| Gamma-HCH | 0.030 | 2.727 | 0.074 |
| <i>p,p'</i> -DDE | 4.382 | 35.850 | 5.745 |
| <i>p,p'</i> -DDT | 0.478 | 9.600 | 0.537 |

as those potentially free from dioxin contamination, 118 geological samples have been taken. The analysis thereof will allow for determining the so-called background dioxin level. The reference source for monitoring of that compounds in milk of breastfeeding mothers has been reported by Ludwicki et al. [25] to assign the content of other persistent organic pollutants. The investigation covered a group of 462 women from Warsaw and other localities [26]. The permissible concentrations (pg-TEQ g⁻¹) of PCBs, DDT and gamma-HCH are summarized in Table 2. The increased level of persistent organic pollutants was found primarily in older women, aged 30 and more, and those who gave birth to more than four children.

In the years 1989–1992, in one of Warsaw's hospitals, samples of fatty tissues have been undertaken from 277 patients aged from 10 to 80 years and were successfully subjected to analysis for a series of PCBs, HCB, alpha-HCH, beta-HCH, gamma-HCH, *p,p'*-DDE and *p,p'*-DDT [25]. The results are summarized in Table 3. Higher concentrations of POPs have been found in tissues of older people [25]. In the case of gamma-HCH, only a higher level was noted in the samples that taken from patients aged below 25 years.

4. Type of persistent organic pollutants

In Stockholm 2001, representatives from 92 countries have agreed to sign the Stockholm Convention on POPs to reduce and/or eliminate the release of 12 original POP substances which are namely the dirty dozen. More contaminants have been discovered; the main concern is over the original 12. These contaminants are the 10 intentionally produced chemicals: aldrin, endrin, chlordane, DDT, dieldrin, heptachlor, mirex, toxaphene, hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs) and the two unintentionally produced substances polychlorinated dibenzo-*p*-dioxins

(PCDDs) and polychlorinated dibenzofurans (PCDFs) [26,27]. Also, polycyclic aromatic hydrocarbons (PAHs) are also classified as persistent organic compounds, and they are formed as unintentionally substances by combustion and burning of organic compounds. Their occurrences are related to anthropogenic processes, and contamination of PAHs in river sediment is especially serious in high-density industrial areas [26]. The chemical structures of the most common persistent pollutants are given in Fig. 4. Moreover, in general POPs can be divided intentionally and unintentionally into two types of POPs as shown in Fig. 5.

4.1. Intentionally POPs

These compounds will be produced as wanted products by different chemical reactions that include chlorine. These types are organic molecules with linked chlorine atoms, high lipophilicity and, usually, high neurotoxicity, and they are called organochlorine compounds (OCs). Examples of OCs are the chlorinated insecticides, such as dichlorodiphenyltrichloroethane (DDT), and polychlorinated biphenyls (PCBs). They have several compounds which can be divided into two types that are industrial chemicals and organochlorine pesticides [28,29].

4.1.1. Organochlorine pesticides (OCPs)

Pesticides are chemicals or biological substances used to kill or control pests. They fall into three major classes: insecticides, fungicides, and herbicides (or weed killers). There are also rodenticides, nematocides, molluscicides, and acaricides. These chemicals are typically man-made synthetic organic compounds, but there are exceptions which occur naturally that are plant derivatives or naturally occurring inorganic minerals. Since, in the seventeenth century the first naturally occurring insecticide, nicotine from extracts of tobacco leaves, was used to control the plum curculio and the lace bug. In the 1940s, many chlorinated hydrocarbon insecticides were developed though they did not come into widespread use until the 1950s. Common examples include aldrin, dieldrin, heptachlor, and endrin. However, in spite of their early promise, these organochlorine insecticides are now much less used because of their environmental pollution impact [30,31].

Pesticides have been widely used throughout the world since middle of the last century. Around 1000 active ingredients have been employed and are currently formulated in thousands of different commercial products. They include a variety of compounds, mainly insecticides, herbicides and fungicides, with very different physico-chemical characteristics, and large differences in polarity, volatility and persistence. Pesticides are employed for many different purposes. About 80% of the pesticides is used in agriculture and moved in the environment by means of volatilization, runoff, infiltration, transport along the food chain, etc. Although the application of OCPs has been forbidden for a considerable period in many countries, the residues continue to induce a significant impact on the environment and its ecosystems [32]. Chemicals used in the control of invertebrates include insecticides, molluscicides for the control of snails and slugs, and nematocides for the control of microscopic roundworms. Vertebrates are controlled by rodenticides which kill rodents, avicides used to repel birds, and pesticides used in fish control. Herbicides are used to kill plants. Plant growth regulators, defoliants, and plant desiccants are used for various purposes in the cultivation of plants. Fungicides are used against fungi, bactericides against bacteria, slimicides against slime-causing organisms in water, and algicides against algae. As of the mid-1990s, U.S. agriculture used about 365 million kg of pesticides per year, whereas about 900 million kg of insecticides were used in non-agricultural applications including forestry, landscaping, gardening, food distribution, and home pest control. Insecticide production has remained about level during

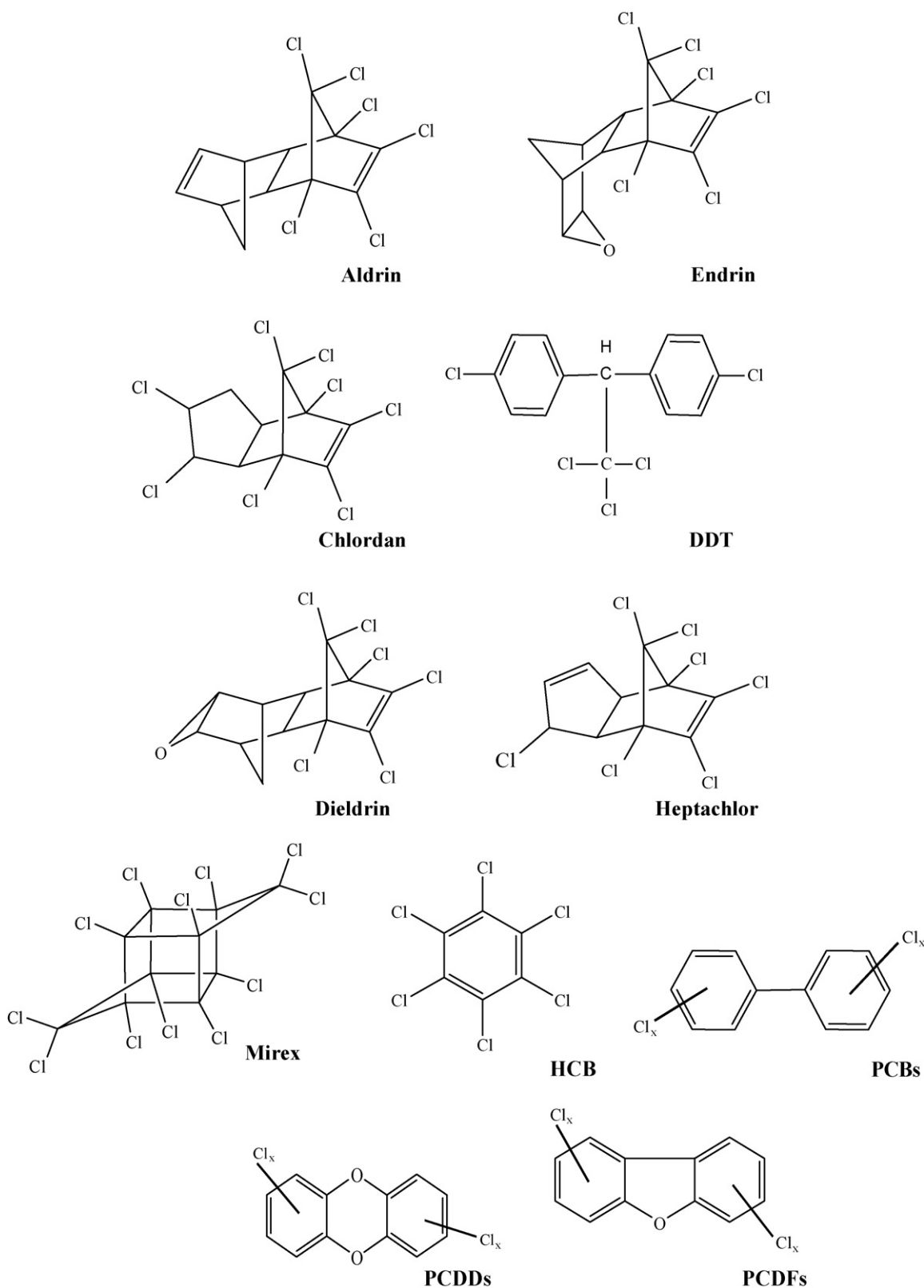


Fig. 4. The chemical structures of the most common persistent pollutants.

the last three or four decades. However, insecticides and fungicides are the most important pesticides with respect to human exposure in food because they are applied shortly before or even after harvesting. Herbicide production has increased as chemicals have increasingly replaced cultivation of land in the control

of weeds and now accounts for the majority of agricultural pesticides. The potential exists for large quantities of pesticides to enter water either directly, in applications such as mosquito control or indirectly, primarily from drainage of agricultural lands [33–35].

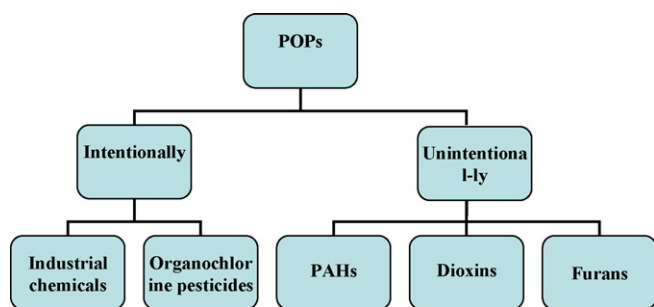


Fig. 5. Classification of POPs.

In the United States in 1993, an approximate percent (75%) of the sold pesticides have been used in agriculture [30]. Government and industry have been used 18%, and home and garden consumption accounts for the remaining 7%. Industrial and commercial users consist of pest control operators, turf and sod producers, floral and scrub nurseries, railroads, highways, utility rights-of-way, and industrial plant site landscape management [31]. The U.S. estimated volume of the conventional pesticides in 1993 is shown in Fig. 6.

Many public health benefits have been gained from the use of synthetic pesticides, but in spite of the obvious advantages, the potential adverse impact on the environment and public health can be substantial. Once in the environment, contemporary pesticides are relatively labile and tend not to persist for long periods of time. However, with the widespread use of pesticides, it is virtually impossible to avoid exposure at some level. Due to the general population's exposure to pesticides, it is important to investigate the concentration levels of pesticides and their metabolites in samples from human origin [29,30].

Before the insidious effects of DDT on humans and wildlife were known, this potent nerve poison was widely used to control mosquitoes, black flies and other vectors that carry diseases such as malaria, typhus and yellow fever. Farmers also used it to control insect damage to their crops. In the 1950s and 1960s, DDT was embraced as a cheap, effective, broad spectrum chemical pesticide. It was used worldwide and applied generously and indiscriminately to communities and crops alike. It did the job, reducing the threat of malaria and the loss of income to the agriculture industry [24]. Residues of PCBs were found in all food samples analyzed. However, their concentrations were many times lower than the permissible limits in place in other countries [24].

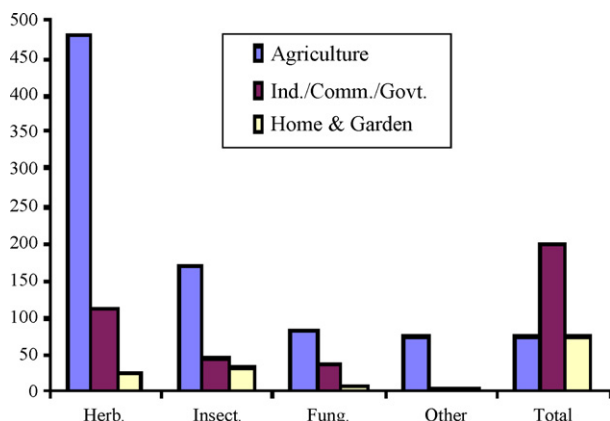


Fig. 6. The U.S. estimated volume for the conventional pesticides in 1993.

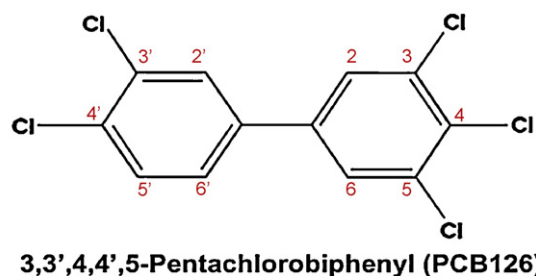
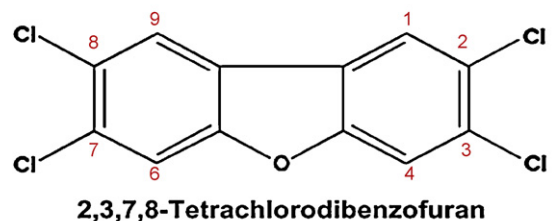
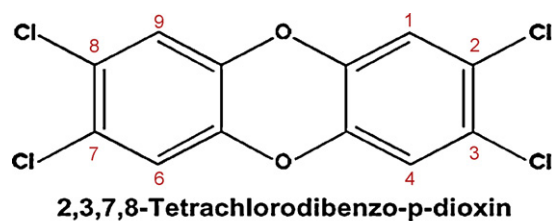


Fig. 7. Basic structures of the chlorinated dibenzo-p-dioxins (dioxins), chlorinated dibenzofurans (furans) and polychlorinated biphenyls (PCBs).

4.1.2. Industrial chemicals

First discovered as environmental pollutants in 1966, polychlorinated biphenyls (PCB compounds) have been found throughout the world in water, sediments, bird tissue, and fish tissue. These compounds constitute an important class of special wastes. PCBs are a class of chemical compounds in which 2–10 chlorine atoms are attached to the biphenyl molecule. Monochlorinated biphenyls (i.e., one chlorine atom attached to the biphenyl molecule) are often included when describing PCBs. The general chemical structure of chlorinated biphenyls is shown in Fig. 7. Theoretically, there are 209 different PCB congeners. Many of them are resistant to degradation, which allows them to persist in the environment for a long time and become widespread via atmospheric and water transport mechanisms [10,36,37].

PCBs are chemicals that were widely used in industrial processes from the 1930s until the late 1970s. Although their production ended in the late 1970s, the majority of the cumulative world production of PCBs are still in the environment. PCBs were used extensively in many industrial applications, including in fire-resistant transformers and insulating condensers. Prior to 1977, they were used as heat exchanger fluids, and in aluminium, copper, iron and steel manufacturing processing [37]. PCBs were also used as plasticizers, in natural and synthetic rubber products, as adhesives, insulating materials, flame retardant, lubricants in the treatment of wood, clothes, paper and asbestos, chemical stabilizers in paints, pigments and as dispersing agents in formulations of aluminium oxide. PCBs are often found both in the effluent and in the sludge of municipal wastewater. Since PCBs were widely used as dielectric fluids from the 1950s, they are present in transformers in several Brazilian cities, despite its prohibition in the 1980s [38,39].

Every year, over 6000 food samples from all over Poland are being analyzed to determine the contents of residues of pesticides,

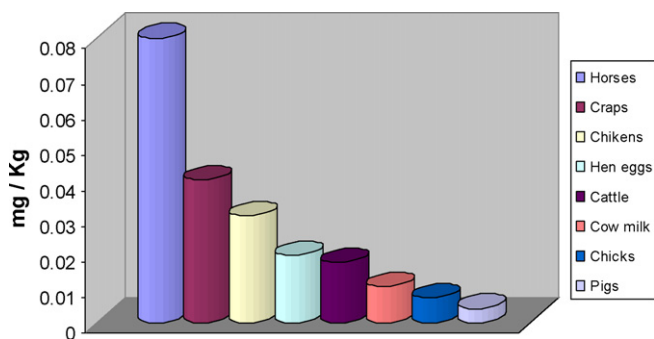


Fig. 8. Distribution of PCBs in food during the years 1995–1999.

polychlorinated biphenyls and other toxic substances in the fatty tissue of various animal species, cow milk and hen eggs. The results are summarized in the diagram given in Fig. 8. This diagram summarizes the results of research in the presence of PCBs in food during the years 1995–1999.

4.2. Unintentionally POPs

They were produced as unwanted by-products of combustion or chemical process that take places in the presence of chlorine compounds. They are divided into three types: polycyclic aromatic hydrocarbons (PAHs), dioxin and furan compounds.

4.2.1. Polycyclic aromatic hydrocarbons (PAHs)

The PAHs consist of two or more fused benzene rings in linear, angular or cluster arrangements, containing only carbon and hydrogen. The central molecular structure is held together by stable carbon–carbon bonds. The United States Environmental Protection Agency (EPA) listed 16 PAHs on a list of priority pollutants since they are considered either possible or probable human carcinogens. Hence, their distribution and the possibility of human exposure to them have been the focus of much attention. The PAHs have been detected in soil, air, and sediments as well as on various consumable products. They can occur naturally in the environment, mainly as a result of synthesis by plants or after forest and prairie fires. However, the greatest amounts of PAHs released into the environment are via anthropogenic processes like fossil fuel combustion and by-products of industrial processing. Agricultural fires as well as cooking may also release PAHs. The distribution of PAHs found in the sediments can give information on precursor sources, that is, if they are pyrogenic or petrogenic [40–42].

4.2.2. Dioxins and dibenzofurans

Chlorinated dibenzo-*p*-dioxins (dioxins) have been of concern for decades because of their toxic properties, as described below. A structurally similar series of compounds, the chlorinated dibenzofurans (furans), have similar chemical properties and toxic effects, and are generally determined as a group with the dioxins. In recent years there has been a growing trend to include a specific subgroup of the polychlorinated biphenyls (PCBs): the so-called dioxin-like PCBs (DLPCBs). This has been added to methods along with the dioxins and furans. Fig. 8 shows the structures of 2,3,7,8-TCDD, 2,3,7,8-TCDF and PCB-126. It is commonly recognized that man-made sources and activities are far greater contributors to the environmental burden of polychlorinated dioxins (PCDDs) and dibenzo furans (PCDFs) than natural processes, especially since the 1930s, from which time there had been a steady increase in environmental levels coinciding with the large-scale production and use of chlorinated chemicals [42,43]. Man-made sources of PCDDs and PCDFs can be divided into three main categories: chemical processes, combustion processes and secondary

sources [44]. Municipal waste incinerator, coal combustion, chemical waste incineration plant, clinical waste incinerator, landfill gas combustion, crematoria, animal carcass incinerator and cement manufacture are the main sources of PCDDs and PCDFs in Hong Kong [45]. The dioxins and furans, congeners with chlorine substitution at the 2, 3, 7 and 8 positions are considered toxic. Of the 75 possible dioxin and 135 possible furan structures, only 17 have 2,3,7,8-substitution. The carbon numbering system is marked next to each carbon to indicate substitution positions. Dioxin and furan congeners substituted in the 2, 3, 7 or 8 position are toxic, while PCBs substituted in the 3,3',4,4',5 or 5' position and no or only one 2- or 2'-substitution are considered to be dioxin-like (Table 4). This class of compounds was found able to exhibit dioxin toxicity (see Table 4).

5. Properties of POPs

The behavior and fate of chemicals in the environment are determined by their chemical and physical properties and by the nature of the environment. The chemical and physical properties are determined by the structure of the molecule and the nature of the atoms present in the molecule. The properties of their physico-chemical characteristics that permit these compounds to occur either in vapour phase or adsorbed on atmospheric particles, thereby facilitating their long-range transport through the atmosphere. Some of these properties are: very low solubility, high lipid solubility since, these two properties leading to their bioaccumulation in tissues, high toxic compound, and semi-volatile enabling them to move long distance in the atmosphere before deposition [47,48].

POPs can be present as vapours in the atmosphere or are bound to the surface of solid (dust) particles (particles of soil, of water sediments, of ashes). They are transferred to the ground surface from the atmosphere either by the deposition of the flying ashes (dry deposition) or by rain that absorbs substances present in the gas phase and pulls solid particles (wet deposition). The solubility of most POPs in water is minimal. They are, however, easily captured on solid particles (dust, ash, soil, and sediments). They are also fairly soluble in organic fluids (oils, fats, and liquid fuels). This implies that the more solid particles and polluting organic liquids present in the water, the higher the probability of their higher POPs content [49].

In the atmosphere, POPs undergo a slow decomposition due to of the solar radiation (photolysis) in the presence of water humidity and of other organic and inorganic substances. Their persistence in the atmosphere depends on thermal and reaction conditions of the given place. This durability in the tropical atmosphere is a maximum several days for a number of POPs; however, this can stretch up to several years for the occurrence of the same compound in the polar atmosphere [50].

Their stability in the atmosphere results into their long-distance transport of thousands of kilometers. This allows their transport from locations, where a number of them, namely pesticides, are still in use in significant amounts (Africa, South America) to the proximity of the North Pole. This was confirmed by a number of measurements of their presence in the snow and in the ice around the North Pole, as well as in the North Sea organisms. As these substances have never been used in these polar areas, their presence there is a clear proof of their long-distance transport [7,47].

POPs are anthropogenic compounds that are possessing characteristics toxic, persistent, bioaccumulate (build up in fatty tissues in individual organisms). Also, POPs are prone to long-range transboundary atmospheric transport and deposition, are likely to cause significant adverse human health or environmental effects near to and distant from their sources and concentrate further, or biomagnify up food chain. POPs can be divided into three categories: pesticides such as: aldrin, endrin, merix and chlordane, industrial

Table 4
Maximum WHO toxic equivalent factors (TEFs) for humans/mammals, fish and birds [46].

| Congener | Humans/mammals | Fish | Birds |
|---|----------------|-----------|---------|
| 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) | 1 | 1 | 1 |
| 1,2,3,7,8-Pentachlorodibenzo-p-dioxin (PeCDD) | 1 | 1 | 1 |
| 1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin (HxCDD) | 0.1 | 0.5 | 0.05 |
| 1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (HxCDD) | 0.1 | 0.1 | 0.01 |
| 1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin (HxCDD) | 0.1 | 0.1 | 0.1 |
| 1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (HpCDD) | 0.01 | 0.001 | <0.001 |
| 1,2,3,4,5,6,7,8-Octachlorodibenzo-p-dioxin (OCDD) | 0.0001 | <0.0001 | 0.001 |
| 2,3,7,8-Tetrachlorodibenzofuran (TCDF) | 0.1 | 0.05 | 1 |
| 1,2,3,7,8-Pentachlorodibenzofuran (PeCDF) | 0.05 | 0.05 | 0.1 |
| 2,3,4,7,8-Pentachlorodibenzofuran (PeCDF) | 0.5 | 0.5 | 1 |
| 1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF) | 0.1 | 0.1 | 0.1 |
| 1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF) | 0.1 | 0.1 | 0.1 |
| 1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF) | 0.1 | 0.1 | 0.1 |
| 2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF) | 0.1 | 0.1 | 0.1 |
| 1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF) | 0.01 | 0.01 | 0.01 |
| 1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF) | 0.01 | 0.01 | 0.01 |
| 1,2,3,4,5,6,7,8-Octachlorodibenzofuran (OCDF) | 0.0001 | <0.0001 | 0.001 |
| 3,4,4',5'-Tetrachlorobiphenyl (PCB 81) | 0.0001 | 0.0005 | 0.1 |
| 3,3',4,4'-Tetrachlorobiphenyl (PCB 77) | 0.0001 | 0.0001 | 0.05 |
| 2',3,4,4',5-Pentachlorobiphenyl (PCB 123) | 0.0001 | 0.000005 | 0.00001 |
| 2,3',4,4',5-Pentachlorobiphenyl (PCB 118) | 0.0001 | <0.000005 | 0.00001 |
| 2,3,4,4',5-Pentachlorobiphenyl (PCB 114) | 0.0005 | <0.000005 | 0.0001 |
| 2,3,3',4,4'-Pentachlorobiphenyl (PCB 105) | 0.0001 | <0.000005 | 0.0001 |
| 3,3',4,4',5-Pentachlorobiphenyl (PCB 126) | 0.1 | 0.005 | 0.1 |
| 2,3',4,4',5,5'-Hexachlorobiphenyl (PCB 167) | 0.00001 | <0.000005 | 0.00001 |
| 2,3,3',4,4',5-Hexachlorobiphenyl (PCB 156) | 0.0005 | <0.000005 | 0.0001 |
| 2,3,3',4,4',5'-Hexachlorobiphenyl (PCB 157) | 0.0005 | <0.000005 | 0.0001 |
| 3,3',4,4',5,5'-Hexachlorobiphenyl (PCB 169) | 0.01 | 0.00005 | 0.001 |
| 2,3,3',4,4',5,5'-Heptachlorobiphenyl (PCB 189) | 0.0001 | <0.000005 | 0.00001 |
| | 0.0001 | <0.000005 | 0.00001 |

chemicals such as: PCB, PCP and HCB, and unintentionally produced by-product like polycyclic aromatic hydrocarbons (PAHs), dioxins and furans compounds. Long-range transport via the atmosphere is the most likely source of these persistent organic pollutants in the Arctic. However, efforts to quantify the amount of POPs transported in this way and to determine source regions are quite limited. POPs have been associated with a number of environmental risks. These risks include oestrogenic effects, disruption of endocrine function with observed impairments of immune system function, generation of functional and physiological effects on reproduction capabilities and reduced survival and growth of offspring [26,51].

6. Dosage and toxicity of POPs

POPs so including are significant concern due to their potential toxicity and prevalence in arrangement of environmental media, even at remote geographical location. The ecotoxicological effects of POPs in the environment have caused much concern in recent years, and this has led to the control or complete ban on the use of these chemicals in many countries. Among the wide range of organic substances contaminating the aquatic environment a major concern has so far focused on PCBs and (OCPs). High persistence and biological degradation resistance of these toxic organic pollutants make them continue to be yet largely present in the marine environment. POPs are found not only in living organism as animals and plants, but also in humans [26,52].

Public concern about contamination by POPs increased recently because several of these compounds are identified as hormone disrupters which can alter normal function of endocrine and reproductive systems in humans and wildlife. There are many risks and effects of having these chemicals in our environment and none of them are a benefit to the earth. After these pollutants are put into the environment, they are able to stay in the system for decades causing problems such as cancer, birth defects, learning disabilities, immunological, behavioral, neurological and reproductive discrepancies in human and other animal species [52].

POPs contaminate food, water and accumulate in the food chain such as eagles, polar bears, killer whales and human being. There is evidence that many people worldwide may now carry enough POPs in their body fat where POPs accumulate to cause serious health effects, including illness and death. Laboratory investigations and environmental impact studies in the wild have implicated POPs in endocrine disruption, reproductive and immune dysfunction, neurobehavioral and disorder and cancer [53,49].

More recently some POPs have also been implicated in reduced immunity in infants and children, and the concomitant increase in infection, also with developmental abnormalities, neurobehavioral impairment and cancer and tumor induction or promotion. Some POPs are also being considered as potentially important risk factor in the etiology of human breast cancer by some authors [54]. Human exposure to POPs is carried through the food chain. Because the animals are subsisting in water contaminated with these pollutants, they are affected as well when the humans consume these animals, they have also consumed the pollutant which then is accumulated in the body [49].

Because children are still developing, they are much more susceptible to the effects of pollutants. Their developing cells are sensitive to contaminants and are more likely to be affected by exposure of POPs. The brain is apparently in the greatest concern because some studies have shown that children exposed to POPs during infancy had remarkably lower scores on assessments determining intelligence and ability to shut out distractions [19,55].

At a young POPs can have serious consequences side effects such any of the following: birth defects, certain cancer and tumors at multiple sites, immune system disorders, reproductive problems, reduced ability toward off diseases, stunted growth and permanent impairment of brain function, POPs are a suspected carcinogen, diseases such as endometriosis (a painful, chronic gynecological disorder in which uterine tissues are affected), increased incidence of diabetes and others and Neurobehavioral impairment including learning disorders, reduced performance on standard tests and changes in temperament [55]. Commonly used analytical methods

Table 5
Analytical methods for determination POPs in different matrices.

| Methods | Analyte | Environmental matrix | References |
|------------------|--|--|---|
| GC/ECD | PCBs; OCPs; HCH; HCB; PAHs; DDT | Sediments, soil, liver and fat of birds, water, fungal, human hair, plants, adipose tissue | [56,4,58,61,62,66,69,73,78,81,52,85,5] |
| GC/MS | PCBs; OCPs; PBDEs; HCH; HCB; PAHs; OPPs; DDT | Dolphins, river water and sediment, livers and fat of birds, human adipose tissue, ice | [57,63,9,72,75,77,60,21,81–83,88–90,11] |
| HRGC/ECD | HCH; HCB; PCBs | Livers of cod fish, eggs | [4,58] |
| HRGC/LRMS | Pesticides, PCBs, PAHs | Water, plant | [64,91] |
| HRGC/MSD | PCBs; OCPs | Water, liver and muscle of tuna | [65] |
| HPLC-DAD | Pesticides | Ground water | [66] |
| RH-GC-FPD | OPPs | Fruit and vegetables | [67] |
| HRGC/HRMS | PCDD/Fs; OCPs; PCBs; HCB; HCH | Flue gas, livers, eggs of birds, river water, sediment, atmosphere, gastropods | [6,68,80,92–94] |
| GC/NPD | Pesticides | Bananas | [70] |
| GC-MS-MS | Pesticides | Rain water | [71] |
| GC-ECNI-MS | Toxaphene | Bird eggs | [74] |
| LC-MS-MS | Pesticides | Grain sample | [75] |
| SPE-HPLC | PCBs | Endogenous hormones | [76] |
| RP-LC-FLD | PAHs | Marin biota | [79] |
| HPLC/FLD | PAHs | Food sample, soil, air | [21] |
| PLVI-CC/ECNI-qMS | OCPs; HCB; HCH | Fish tissue | [84] |
| GC/FID | HCB | Soil | [87] |

for POPs monitoring and surveillance are summarized in Table 5. Numerous methods have been published over the past 30 years related to specific analytical techniques for the determination of PCBs and OCPs in food and environmental matrices.

7. Extraction and analytical techniques

Classical extraction techniques like liquid/liquid extraction and Soxhlet extraction are described in detail in the methods listed in Table 6. A number of alternative extraction techniques are summarized in Table 3. Supercritical fluid extraction (SFE) uses a gas above the critical point (the combination of temperature and pressure where the gas has liquid-like properties enabling enhanced extraction capability) to extract analytes from the matrix. The main advantage with SFE is that the extracting gas can be evaporated and so solvent disposal is not required. SFE behaves significantly differently to classical solvent extraction and recoveries can be reduced or enhanced. Pressurized liquid extraction (PLE), also known as accelerated solvent extraction (ASE) evolved from SFE. Solvents were added to SFE extractions as modifiers in order to mimic classical liquid extractions. SFE without extraction gas and only solvent modifier best matched classical extraction recoveries. This led to the development of PLE. Microwave-assisted extraction (MAE or MASE) uses closed vessels to increase pressure and extraction efficiency. Polar solvents like acetone or water are required to supply heat for extraction. San et al. [95] reported the analysis of wet

samples by MAE, indicating that significant time was saved by the reduced sample drying requirements. Solid-phase extraction can significantly reduce analysis times and solvent usage for the extraction of water and wastewater samples, even with significant particulate loadings [95]. Particles collected on C18 extraction disks can be extracted quantitatively without Soxhlet or PLE extraction. Water samples have also been analyzed using semi-permeable membrane devices (SPMDs). SPMD sampling is a form of passive sampling that can be used for water, air or sediments [86,96].

Recently, Namiesnik et al. [97] have reviewed passive sampling techniques in environmental samples. Passive sampling is based on the free flow of analytes from the sampling medium to the collecting medium. This technique eliminates the requirement for power, and is a composite sampling procedure that can reduce analysis cost because of reduced sampling events and analyte loss during shipping and storage as the analyte is on a trapping medium. Swipe tests of biofilms on surfaces can also be used to monitor ambient conditions, especially after fires or from fugitive emissions.

8. Removal and/or minimization of POPs

Environmentally relevant polar persistent organic pollutants (pharmaceuticals and diagnostic agents) have been chosen according to human consumption and occurrence in the aquatic environment (sewage plant effluents, rivers and groundwater) to investigate their behavior during photo catalytic oxidation. From

Table 6
Extraction techniques of POPs in various matrices at different regions.

| Sample matrix | Extraction technique. | Region/country | Analyte | References |
|---|---|---|---|------------------------------|
| Sediment | SE, LSE, LLE, SFE, MASE | Argentina, Singapore, China, Germany, Italy, Canada | PCBs, OCPs, PAHs, HCB, HCH, DDT, PBDEs, PCDD/Fs | [56,60,63,77,82,90,93,97,98] |
| Soil | SE, SPE, PLE, LLE, sonication | Singapore, Australia, Europe, Brazil, China | PAHs, OCPs, HCB, PCBs | [60,78,21,87,89,99,100] |
| Fruit and vegetable | GPC, SE, SPE, PLE, passive sampling | Europe, Sweden, China | OPPs, OCPs, DDT, PCBs, PAHs | [67,70,72,73,21,89,91] |
| Water (marine, fresh, ground rain and wastewater) | Sonication process, SPMD, LLE, filter DOC | Europe, Zambia, Indonesia, Italy, Spain, Turkey | HCH, HCB, PCBs, PAHs, OCPs | [59,64–66,69,71,79,80,85,88] |
| Fish (liver, tissue, egg and muscle) | SE, LLE | Pakistan, Japan, Philippines, Brazil, China | HCB, HCH, PCBs, OCPs | [4,58,65,84,5] |
| Dolphin | GPC | India | PBDEs, PCBs, OCPs | [57] |
| Bird (tissue, egg, liver and fat) | LLE, SE | Greece, USA, Japan | OCPs, PCBs, toxaphene | [62,74,6] |
| Air | Swipe/biofilms, passive sample | Italy | PCDD/F, HCB | [80,101–103] |
| Ice and snow core | LLE | Italy | OCPs, PCBs | [9] |
| Human (hormone, hair, tissue and adipose tissue) | LLE, SPE, SE, LSE, hot SE | China, USA, Romania, Belgium | PCBs, HCH, OCPs, HCB, DDT | [63,76,81,52] |

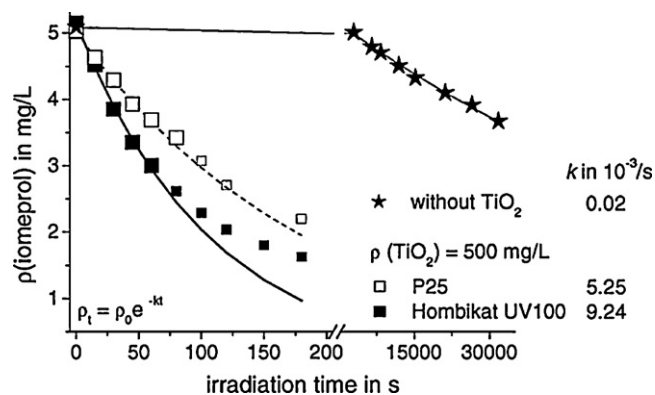


Fig. 9. Changes of iomeprol concentrations (2 mg L^{-1} , pH 6.5) during irradiation with and without suspended TiO_2 (Hombikat UV100 or P25 (TiO_2) = 0.5 mg L^{-1}).

the data compilation in the literature, the active metabolite clofibrac acid of some lipid lowering agents, the antiepileptic drug carbamazepine and the X-ray contrast media imperils were selected. The degradation of the persistent pollutant was monitored by HPLC/DAD/FLD. The study has been focused also on the identification and quantification of possible degradation products by HPLC/DAD/FLD and HPLC/MS/MS. The degradation process has also been monitored the determination of sum parameters and inorganic ions. Various aromatic and aliphatic degradation products have been identified and quantified [104,105]. Since, the photochemical degradation (irradiation without TiO_2) of the persistent organic pollutants was studied [106]. It turned out to be negligible compared to their photocatalytic degradation. For example the photocatalytic degradation rate constant (k) of iomeprol with Hombikat UV100 was about 500 times higher than the photochemical degradation rate constant of iomeprol (Fig. 9). For the determination of the first order rate constant (k) only the concentration values with $t/t_0 = 0.5$ (large symbols) were used. The fitting was done by the least squares method [106]. Moreover, the stabilized nanoparticles of FeS have showed excellent degradation (over 94%) of lindane pesticide in its hexane extract to 1,2,4-trichlorobenzene or TCB, a key intermediate of lindane degradation pathway. The non-stabilized FeS could degrade merely 25% lindane in the same period clearly indicated that these nanoparticles catalyzed a rapid reductive dehalogenation reaction [107,108].

9. Conclusion

The determination of POPs in various matrices is characterized by instrumental complexity and highly cost. The electrochemical techniques in particular stripping analysis have no contribution on the analysis of such class of chemicals. Thus, the use of voltammetric techniques for the analysis of such class of compounds will provide an efficient and excellent alternative approach for the determination of POPs in different matrices because of its low cost, sensitively and selectivity for trace and ultra-trace concentration of the POPs in complicated matrices. However, further work is still continuing for the possible application of the on-line voltammetric stripping analysis of the pesticides in serum, routine and various environmental samples.

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