LEARNING TOXICOLOGY
THROUGH OPEN EDUCATIONAL

POLYCHLORINATED BIPHENYLS

Ileana MANCIULEA, Lucia DUMITRESCU

Transilvania University of Brașov

i.manciulea@unitbv.ro, lucia.d@unitbv.ro

Erasmus+

This work is licensed under a Creative commons attribution – non commercial 4.0 international license

INTRODUCTION

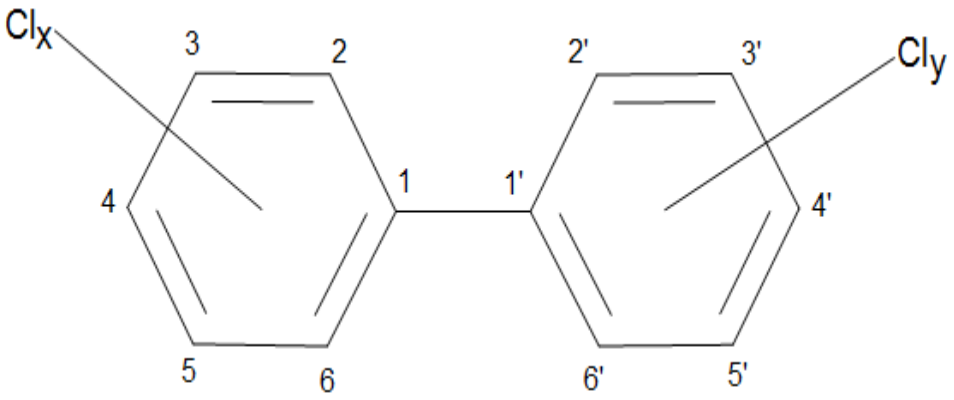
The polychlorinated biphenyls (PCBs) are a group of xenobiotic organic compounds, mixtures of chlorinated aromatic hydrocarbons, They consist of the biphenyl structures with two linked benzene rings, in which some or all of the hydrogen atoms have been substituted by chlorine atoms. There are 209 possible PCBs congeners, based on various combinations of the numbers and positions of the chlorine atoms on the biphenyl molecule. PCBs were manufactured/marketed mainly in the U.S. between 1930 and 1977 under the trade name Aroclor (e.g., Aroclors 1016, 1242, 1248, 1254, 1260, etc.). More than 600 million kg of PCBs were commercially produced in the U.S and the worldwide production of PCBs was approximately twice that quantity. Due to their chemical stability, electrical insulating properties and relative inflammability, PCBs were used in many industrial applications as heat exchange and dielectric fluids in transformers and capacitors; hydraulic and lubricating fluids; diffusion pump oils; flame retardants; plasticizers; extenders for pesticides, and as additives in caulking compounds, coatings, paints, adhesives, inks, carbonless carbon paper and plastic**s. (**EPA, ATSDR, 2004). Due to evidence that PCBs persist and accumulate in the environment and can cause toxic effects, in 1979, EPA issued final regulations banning the manufacture and uses of PCBs. In 1985, the use and marketing of PCBs in the EU Community were restricted, and in 2004, the production, placing on the market and use of PCBs were totally prohibited by Regulation EC) No 850. (Stockholm Comision, 2004**).** Despite the final regulations banning the manufacture/use of PCBs, in 1979, PCBs continue to be present in air, soil, sediments, food and are redistributed from one environmental compartment to another. PCBs also can be released through the continued use and disposal of PCBs containing products (window glazes, fluorescent light ballasts, ceiling tile

This work is licensed under a Creative commons attribution – non commercial 4.0 international license

coatings, paints and floor finishes and potential sources of PCBs in the indoor environment (Lehmann et al., 2015).

CHEMICAL STRUCTURE AND OF PCBs

There are 209 possible PCBs isomers, from three monochlorinated isomers to the fully chlorinated decachlorobiphenyl isomer. The properties and toxicity of PCBs isomers are determined by the number and position of chlorine atoms. The degree of toxicity is also function of the chlorination degree. Generally, the water solubility and vapour pressure decrease with increasing the degree of substitution and the lipid solubility increases with increasing chlorine substitution. Impurities, such as polychlorinated dibenzofurans (PCDFs), naphthalenes (PCNs) and quarter- phenyls (PCQs), also have been identified in commercial PCBs products.



X = 1 to 5, Y = 1 to 5

Figure 1. Chemical structure of PCBs

To estimate the properties and behavior of all 209 PCBs, it can be used as a reference the compound PCB-153, because it is a constituent of the calibration mixture used for identification and quantitative estimation of all 209 PCB congeners. PCB-153 is a hexaisomer (2,2',4,4',5,5'–hexachlorobiphenyl) which is a constituent of polychlorinated biphenyls. There are 42 hexachlorobiphenyls.

This work is licensed under a Creative commons attribution – non commercial 4.0 international license

Although PCB-153 is not toxic it can be modulator of toxic impacts of other PCBs congeners. The most important is that PCB-153 is present practically in all technical mixtures in sufficiently large quantities - from 5 to 17% (on the average to 10%). Therefore PCB -153 also can be an indicator of the PCBs input to the environment and removal from it (Alcock et al., Joint WHO, 2003).

CHEMICAL PROPERTIES OF PCBs

Trade Names for different mixtures (partial list): Aroclor, Pyranol, Pyroclor, Phenochlor, Pyralene, Clophen, Elaol, Kanechlor, Santotherm, Fenchlor, Apirolio, Sovol.

CAS No.: 1336-36-3

Some chemical properties of PCBs are presented in Table 1.

Table 1. Chemical **properties of PCBs**

Congener group	**Molecular weight**	**Vapour pressure Pa**	**Water Solubility (mg/m3)**	**Log KOW**
Monochlorobiphenyl	188.7	0.9-2.5	1.21-5.5	4.3-4.6
Dichlorobiphenyl	223.1	0.008-0.60	0.06-2.0	4.9-5.3
Trichlorobiphenyl	257.5	0.003-0.22	0.015-0.4	5.5-5.9
Tetrachlorobiphenyl	292.0	0.002	0.0043-0.010	5.6-6.5
Pentachlorobiphenyl	326.4	0.0023-0.051	0.004-0.02	6.2-6.5
Hexacholorbiphenyl	360.9	0.0007-0.012	0.0004-0.0007	6.7-7.3
Heptachlorobiphenyl	395.3	0.00025	0.000045-0.00	6.7-7
Octachlorobiphenyl	429.8	0.0006	0.0002-0.0003	7.1
Nonachlorobiphenyl	464.2	-	0.00018-0.0012	7.2-8.16
Decachlorobiphenyl	498.7	0.00003	0.000001-0.00	8.26

Source: adapted after Ritter et al.1996

This work is licensed under a Creative commons attribution – non commercial 4.0 international license

PCBs are insoluble in water and soluble in most organic solvents and have tendency to partition into the atmosphere. PCBs form vapours heavier than the air and therefore their residues have been detected in the Arctic region, water and living organisms. Aqueous solubility ranges from 1.08×10^{-5} to 9.69×10^{-10} mol/litre and generally decreases with the molecular mass. Henry's law constants ranges from 0.3×10^{-4} to 8.97×10^{-4} atm x m^3/mol and increases with the degree of chlorine substitution.Vapour pressure generally decreases with molecular mass and increases with increasing degree of chlorine substitution. Log Kow values range from 4.46 to 8.18 for all congeners. PCBs in the environment may be associated with the organic components of soils, sediments and biological tissues, with dissolved organic carbon in aquatic systems, rather than being solubilized in water. PCBs volatilize from water surfaces in spite of their low vapour pressure, and partly as a result of their hydrophobicity. As consequence the atmospheric transport may be a significant pathway for the distribution of PCBs in the environment (Ritter et al., 1996).

PERSISTENCE OF PCBs

Despite the ban on manufacturing, PCBs continue to be present in environmental media (e.g., air, soil, sediment, food) and are redistributed from one environmental compartment to another . The persistent nature of PCBs and their distribution through the food chain has resulted in continuing human exposure. They also can be released through the continued use and disposal of PCB-containing products. PCB-containing building materials such as window glazes, fluorescent light ballasts (FLBs), ceiling tiles, coatings, caulk, paints and floor finishes are potential sources of PCBs in the indoor environment (EPA, ATSDR, 2012). They adsorb readily to organic materials such as sediments and soils, with adsorption increasing with the chlorine content of the mixture and the organic content of the environmental media. PCBs have low to no mobility in soil and are relatively insoluble in water. Volatilization from moist soil and water surfaces may be attenuated by adsorption to solids. In air, PCBs exist in both

This work is licensed under a Creative commons attribution – non commercial 4.0 international license

vapor and particulate phases, and atmospheric transport mechanisms have dispersed PCBs globally. Vapor-phase PCBs are photolytically degraded with half-lives ranging from 3-490 days. Particulate-phase PCBs are removed from the atmosphere by wet or dry deposition. In general, biodegradation of PCBs is slow, the higher chlorinated congeners being the most resistant to environmental biodegradation (EPA, HSDB, 2011). As a result, PCBs have been detected in a variety of environmental media that may be sources of human exposure. It has been demonstrated that PCBs can be transported by air, wind and atmospheric diffusion for long distances from source areas, including Arctic and Antarctic regions (AMAP, 2014). In the atmosphere, water and soil, PCBs mostly adsorbed to particles and the tendency to adsorb increases with the degree of chlorination. In the atmosphere, the dominant transformation process is the reaction of vapour phase PCBs with hydroxyl radicals. Estimated half-lives for this reaction is from 10 days for monochlorobiphenyl to 1.5 years for heptachlorobiphenyl. In the aquatic environments, PCBs are not significantly degraded by hydrolysis and oxidation.

BIOACCUMULATION OF PCBs

PCBs are persistent and bioaccumulative. They are highly soluble in biological lipids, accumulate in aquatic and terrestrial animals and humans, and biomagnify in the food chain. The physicochemical properties of PCBs enable their readily absorption in organisms. The high lipid solubility and the low water solubility lead to the retention of PCBs and their metabolites in fatty tissue and in combinations with proteins. The rates of accumulation into organisms vary with the species, concentration,duration of exposure, and the environmental conditions. The high retention of PCBs and their metabolites determine toxic effects in organism in time. The persistence of PCBs, combined with the high partition coefficients of various isomers (log KOW ranging from 4.3 to 8.26) provide the conditions for PCBs to bioaccumulate in organisms. Bioconcentration factors of 120,000 and 270,000 have been reported in fathead

This work is licensed under a Creative commons attribution – non commercial 4.0 international license

minnows. Concentration factors in fish exposed to PCBs diet were lower than those for fish exposed to PCBs in water, suggesting that PCBs are *bioconcentrated* (taken up directly from the water) instead of being *bioaccumulated* (taken up from water and food). The bioconcentration factor (BCF) for Aroclor 1254 in aquatic organisms ranges from 0.24 to 165, in plants from 0.001 to 0.041, and in birds and mammals from 5.15 to 28.5 (EPA, 2011). *The degradation of PCBs in the environment* depends on the degree of chlorination, with persistence increasing with increasing the degree of chlorination. Half-lives for PCBs photodegradation range from10 days for monochlorobiphenyl to 1.5 years for heptachlorobiphenyl. Degradation half-life in soils for hexachlorobiphenyls is 6 years. Degradation half-life values in water for dissolved PCB-153 fraction are 480 for fresh water and 1600 days for coastal sea water and open ocean. In *atmosphere,* degradation half-life of PCB-153 (due to reaction with hydroxyl radical was 13 days in summer, 34 days in spring/autumn, 300 days in winter (EPA, 2012). *Nowadays, after 40 years of the first identification of PCBs in living organisms (human and wildlife tissues), the real cost of the contamination of the ecosystem by PCBs is still unknown and the scientific community is still trying to elucidate the health effects from background exposure worldwide.*

HUMAN EXPOSURE TO PCBs

Humans can be exposed to PCBs via ingestion, inhalation, or dermal contact. Consumption of contaminated foods has historically been considered the major route of exposure among the general population, fatty foods (ifish, meat, dairy products) being the major contributors to dietary exposure

The dietary intake of selected contaminants and dietary exposures to PCBs have declined over the last several decades from 27 ng/kg/day in 1978 to 2 ng/kg/day in 1997. (ATSDR 2000; Lehmann et al. 2015). The main source of PCBs exposure to the general population is consumption of contaminated sport fish, particularly bottom-feeding species from waters contaminated with PCBs,

This work is licensed under a Creative commons attribution – non commercial 4.0 international license

which increases the level of exposure to PCBs. Although PCBs are readily absorbed into the body, they are only slowly metabolized and excreted. Animal studies suggest that absorbed PCBs distributed between the aqueous and lipid compartments of the body, in a biphasic pattern. After first distributing preferentially to the liver and muscle tissue, PCBs are subsequently redistributed to the adipose tissue, skin, and other fat-containing organs.The rate of individual congener metabolism depends on the number and position of chlorine atoms. In rats, the half-lives of PCBs range from 1 to 460 days, depending on the degree of chlorination. In general, less-chlorinated isomers are more readily metabolized than are more highly chlorinated congeners. As a result of preferential metabolism, more highly chlorinated congeners tend to remain in the body longer than do less-chlorinated congeners. Highly chlorinated congeners PCBs are stored in adipose tissues and the slow metabolism of PCBs leads to *bioaccumulation, which can o*cur even at low exposure levels **(**shellfish, present levels of 760 and 1,400 ng/g fat). The main sources of PCBs in the Vietnamese diets (rice and vegetables), and the daily intake of 3.7 µg/person/day is comparable to those of some industrialized countries. Although the manufacture of PCBs was banned in the U.S. in 1979, many buildings constructed before, still contain potential sources of indoor air PCBs contamination. In some indoor settings and for some age groups, inhalation may contribute more to the total PCBs exposure than any other route of exposure. Caulk and other building materials containing PCBs were widely used during 1950s-1970s. Even discontinued in 1970s, many buildings still have fluorescent lighting that contains PCBs and/or PCB residues. (EPA 2012). *Thus, human inhalation exposure to PCBs may be more widespread than previously assumed.*

TOXICITY OF PCBs

Being highly lipophilic, PCBs is bioaccumulated in fatty tissues of animals, birds and aquatic live beings. The toxicology of PCBs is affected by the number and

This work is licensed under a Creative commons attribution – non commercial 4.0 international license

position of the chlorine atoms (Alcock et al., Joint WHO 2003). The substitution in the ortho position hinders the rotation of the aromatic rings. PCBs without ortho substitution are generally referred to *as coplanar* and all others as *noncoplanar*. *Coplanar PCBs*, like dioxins and furans, may present dioxin-like effect and can act as tumor promoters. However the manufacture of PCBs has been banned since 1977, there is evidence suggesting that PCBs inhalation may pose a hazard to human health (ATSDR), 2004). The highest human exposures to these compounds occur via the consumption of contaminated fish and in certain occupational settings, via contact with equipments or materials made before 1977. Recent studies indicate that maternal consumption of PCB-contaminated fish can cause disturbances in reproductive parameters and neurobehavioral and developmental deficits in newborns and older children. Blood levels of PCBs generally increase with the age, because these chemicals are persistent. Hepatotoxic, endocrine, dermal, ocular, immunological, neurological adverse reproductive and developmental effects have been observed in humans following occupational exposures to PCBs. PCBs accumulate in body lipids and can be transferred to infants via breast milk. The lactational exposure occurs at higher levels and over a shorter time period compared to maternal exposure, which occurs over the long-term prior to/ during pregnancy and lactation (ATSDR. EPA, 2015). On the basis of sufficient evidence of carcinogenicity in humans and experimental animals, the International Agency for Research on Cancer (IARC) classified PCBs as carcinogenic to humans (Group 1). However, the decline in levels of PCBs in the environment and foods, over the past three decades, suggests that young people today are exposed to lower levels of PCBs than were previous generations. (EPA, 2016) and environmental levels of PCBs declinined, there are concerns that some past PCBs emissions trapped in polar ice may be released to the environment, in coming years, with increasing ice melts. (AMAP, 2014). Furthermore, environments where heavy PCBs contamination previously occurred continue to be remediated, may dislodge or expose additional PCBs. The Stockholm Convention on POPs (2016) requires Parties to eliminate the use of PCBs in

This work is licensed under a Creative commons attribution – non commercial 4.0 international license

equipments by 2025, and to ensure the environmentally waste management of liquids containing PCBs and equipment contaminated with PCB by 2028.

REFERENCES

1. Alcock et al., Joint WHO 2003 / convention task force on the health aspects of air pollution.Hhealth risks of persistent organic pollutants from LRTAP, 2003.
2. AMAP, 2014. Arctic Monitoring and Assessment Programme (AMAP). Trends in Stockholm convention persistent organic pollutants (POPs) in Arctic air, human media and biota.
3. Community Implementation Plan for the Stockholm Convention on POPss 2007.
4. EPA, ATSDR. 2004. Agency for Toxic Substances and and Disease Registry.
5. EPA. (2015). Scoping and Problem Formulation for the Toxicological Review of PCBs): Effects Other Than Cancer. (2015).
6. EPA. ATSDR. 2012. Thomas Kent, Xue, Jianping, Williams Ronald, Jones Paul, Whitaker Donald. PCB) in School Buildings.Sources, Environmental Levels, Exposures. (2012).
7. EPA. ATSDR. 2016. Agency for toxic substances and disease registry - case studies in environmental medicine. PCBs toxicity. 2016.
8. EPA. HSDB. 2011. Biomonitorin PCBs. Hazardous Substances Data Bank (HSDB).
9. Lehmann, M., Geniece, Christensen, Krista, Maddaloni, Mark, Phillips, J., Linda Evaluating Health Risks from Inhaled PCBs: Research Needs for Addressing Uncertainty. Environmental Health Perspectives vol. 123, 2, (2015).
10. Ritter L.,Solomon K. ForgetJ.(POPS).International Programme Chemical Safety (IPCS), 1996.
11. Stockholm Comision, 2004. Regulation EC) No 850.
12. The Stockholm Convention on POPs 2016.

This work is licensed under a Creative commons attribution – non commercial 4.0 international license

This work is licensed under a Creative commons attribution – non commercial 4.0 international license

https://toxoer.com

Project coordinator: Ana I. Morales
Headquarters office in Salamanca.
Dept. Building, Campus Miguel de Unamuno, 37007.
Contact Phone: +34 663 056 665

This work is licensed under a Creative commons attribution – non commercial 4.0 international license