BABEȘ-BOLYAI UNIVERSITY OF CLUJ-NAPOCA

FACULTY OF ENVIRONMENTAL SCIENCES AND ENGINEERING

DOCTORAL THESIS

DOCTORAL SUPERVISOR

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PH.D. CANDIDATE:

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Reconstruction of the history of contamination with persistent organic pollutants of some lakes over the last 100 years

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INTRODUCTION

Sediments are the final deposition step for active contaminants and can provide information regarding the sources and concentrations of contaminants. Starting from the premise that lake sediments are not heavily influenced by external factors (sedimentation, suspension, resedimentation), they could provide a strong basis for the reconstruction of the history of lake pollution.

Persistent organic pollutants and their long lifespan can be used to provide a history of pollution over the last hundred years. For this kind of study, it is necessary to offer accurate chronologies of sedimentation rates, which are important not only for the sediment dating, but also for the determination of sediment accumulation rates.

In order to trace the history of man's effect on environmental matters, we must refer to the period with the greatest impact, namely the last 150 years. With the industrial revolution and the emergence of new industries and human activities, the human effect on the environment had the greatest impact after the middle of the 19th century. Given the industrial expansion in the post-war period in Romania, pollution was not considered a priority for the policies of the governments of that period. Furthermore, there is no monitoring data for the compounds selected in the study, which creates a gap in the understanding and knowledge of the extent of pollution of environmental factors with these substances.

Many substances have trace quantities of natural origin radioactivity, radioactive trace elements being found in all environmental matters and all lifeforms. The application of radiometric methods for the geochronology of sediments has enjoyed serious success, the measuring of trace quantities of radionuclide has been performed for decades. This procedure is performed on sediment cores, taken from different depths, which are later analyzed according to the substances and compounds of interest. With the emergence of a growing interest in the environment and the need for knowledge of the distribution of both natural and artificial radioactive species, these radioactive dating methods became a perfect tool for the interpretation of chronological history of contaminated sediments. These traces are later interpreted for sedimentation rates and establishing a chronological timeline for different sediment depths, being later linked to the contamination profiles (Jeter, 2000).

In Romania, there is little information and studies regarding pollution with persistent organic compounds (Covaci et al., 2006; Ene et al., 2012; Ciucure et al., 2023), and even less studies regarding the history of pollution with persistent organic pollutants (POPs) (Winkels et al., 1998).

Therefore, the novelty of this thesis consists in providing information regarding the reconstruction of historical pollution, being the first determination of this kind in Romania, this study aiming to provide new data on the extent and variation over time of pollution with selected compounds in the last hundred years, using as methodology the dating of aquatic sediments by Gamma spectrometry, and the analysis of three category of POPs (polycyclic aromatic hydrocarbons, organochlorine pesticides, polychlorobiphenyls) by high-performance analytical techniques such as Gas chromatography-Mass spectrometry (GC-MS) and Gas chromatography-Electron Capture Detector (GC-ECD).

Three different types of lakes were chosen, in which the distribution of persistent organic pollutants from lake sediments was interpreted, all this in order to better understand the differences and the level of pollution between the three lakes. First is the deltaic Lake Iacob, situated in the Danube Delta, second one is the glacial Lake Muntinu (Iezerul Muntinului), which is situated at the southern part of Vâlcea county, very close to the famous Transalpina Road, and the third and final lake is the lowland Lake Știucilor, situated near the old industrial city of Gherla.

To investigate the anthropogenic influence on POP concentrations in the sediment layers analyzed, a series of multivariate statistical analyses were required. Diagnostic parameters for both hydrocarbons and pesticides were based on the use of molecular ratios of the investigated compounds. The values used for the ratios were the absolute values measured of the 16 polycyclic aromatic hydrocarbons (PAHs) and 20 selected organochlorine pesticides (OCPs), which were then combined with 7 diagnostic parameters for PAHs and 7 diagnostic parameters for OCPs.

Another section in pollution assignment is the determination of ecological and bioecological risk aspects. There are multiple methods of determining these kinds of risks, but in this work, the chosen methods are the sediment quality guidelines, often known as SQGs after their acronyms. These quality guidelines performed on sediments are a mean of interpreting the effects of contamination with different types of chemicals on the population of organisms living in the sediments, results which are also reported to human populations. In this work, 4 types of SQGs results were used, results used as threshold levels for 14 individual hydrocarbons as well as the total value of hydrocarbons, values for 8 individual OCPs, and total value reported for all 209 polychlorinated biphenyls (PCBs).

The last topic regarding modern pollution with POPs is the health risk assessment, which is the evaluation of human health risk from exposure to pollutants such as dioxin-like compounds, which are very toxic and persistent chemicals that tend to bioaccumulate in fatty tissues as a result of their resistance against metabolism and their hydrophobic character. A concept of toxic equivalency factors (TEFs) was developed by the World Health Organization (WHO), which are estimates of toxicity attributed to a few individual compounds such as the dioxin-like class, estimates which are still used today as a guidance for risk evaluation for human health. In this study, PCBs are the only dioxin-like substances, but there are also TEFs developed for a few PAHs, mainly for the 16 U.S. Environmental Protection Agency (EPA) PAH, as certain PAHs have very toxic and carcinogenic features.

This doctoral thesis is structured in two parts, a theoretical part consisting of the study of literature characteristic of the topic of this thesis, and an experimental part, which includes the new experimental results obtained, their interpretation and discussion.

The theoretical part consists of 4 chapters containing general data about persistent organic pollutants and the classes into which they are divided, the fate of these type of compounds in the environment, the risks involved in these compounds both on health and biological and ecological risks, and finally the methodology for reconstructing the pollution history.

The experimental part is also structured in 4 chapters, presenting the instrumental methods used in this research, the results obtained from the study of the three lakes, as well as their interpretation.

The results presented in this study were achieved during doctoral studies and were presented at international scientific events abroad, being published or in the process of being published in WOS-listed journals.

At the end of this thesis the following annexes can be found:

- ✓ List of abbreviations used frequently used in the present doctoral thesis (Annex 1),
- ✓ List of scientific publications and papers presented at scientific events based on the research conducted during the doctoral study (Annex 2).

A GOOD UNDERSTANDING OF THE PAST ALLOWS US TO ESTABLISH FUTURE MEASURES AND DIRECTIONS THAT ALLOW FOR SUSTAINABLE DEVELOPMENT OF SOCIETY AND HIGH HEALTH OF THE ENVIRONMENT AND PEOPLE.

1. Persistent organic pollutants/substances

Persistent organic pollutants (POPs) are carbon-based toxic chemicals, which by the description of the United Nations Environmental Programme UNEP 2025a comprise of materials with certain physico-chemical properties, and once they reach the environment, they tend to remain in their initial form for years, are widely distributed in the environment through natural transport processes, are stored in all living things, and are toxic to all forms of life.

They are mainly lipid-soluble compounds which tend to biomagnify and bioaccumulate in fatty tissues, reaching the food web, therefore posing a risk to the environment and human health for generations to come, resulting in acute and chronic toxic effects (Berntssen et al., 2017; UNEP, 2025a).

As their name suggests, these compounds are persistent in the environment, being able to last for years, even decades, before breaking down. They are ubiquitous in the environment, and due to their persistence and resistance to degradation, they can be carried over very long distances, being detected in environmental matter such as soil, sediments, benthic organisms, water columns, and atmosphere (Mortimer, 2013). They are resistant to most of the degradation phenomena, such as photolytic, biological, and chemical degradation, leading to long half-lives and to a high persistence in the environmental matter (De Rosa et al., 2022).

Due to their persistence and potential toxicity to humans and environment, they were officially banned from use in the 1980s. Although many of the persistent organic pollutants (POPs) were banned and prohibited for use since decades ago, they can still be frequently detected in the human body, certain studies suggesting that the woman’s body not only retains this type of compounds in maternal serum, cord blood, and placenta, but also transmits it to newborns through breast milk. Even at low level of exposure to POPs, they possess a high risk of developing carcinomas, allergies, and hypersensitivity, having disrupting effects on the reproductive, endocrine, and immune system. (Hu et al., 2021; UNEP, 2025a).

POPs include a variety of toxic chemicals, most notably polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDDF), and polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), which have been studied extensively for decades and were among the first classes of compounds which were included in the first list of the 2001 Stockholm Convention on the prevention, release, and reduction of POPs from the environment. The Stockholm Convention list of compounds has been updated along the years with other POPs such as brominated flame retardants such as polybrominated diphenyl ethers (PBDE) added to list in 2009, hexabromocyclododecanes (HBCDD) added in 2013, perfluorinated alkyl such as perfluorooctane sulphonate (PFOS) together with its salts in 2017 and perfluorooctane sulphonyl fluoride (PFOSF) in 2004. Other categories of POPs are beginning to make their toxic presence felt in the environment, among them are brominated and mixed halogenated dioxins, furans, and biphenyls, polychlorinated naphthalene, and polycyclic aromatic hydrocarbons (PAH) (Mortimer, 2013; UNEP, 2025b).

1.1. Organochlorine pesticides (OCPs)

Organochlorine pesticides (OCPs) are a class of persistent organic pollutants, often referred to as chlorinated aromatic hydrocarbons (Albanese & Guarino, 2022). This class consists of a vast group of compounds, each of them having diverse structures and features. Organic compounds which contain five or more chlorinated atoms are known as organochlorines (Singh et al., 2022). They are very resistant to biological, microbiological, and chemical degradation, their half-life varying from months to decades (Darko & Acquaah, 2007). Other names attributed to pesticides are insecticides, fungicides, bactericides, herbicides, and rodenticides, with most of the pesticides having the capacity to destroy many of the pests and weeds, but there are some classes which were specifically created for a certain pathogen (Jayaraj et al., 2016).

They have been used for decades in worldwide agriculture, where they were applied in large amounts, still being present in environmental elements such as atmosphere, water, soil, sediments, marine life, and food. OCPs are very persistent chemicals, and tend to bioaccumulate in food chains, thus being considered a health threat to living beings, aspect which resulted in the banning of their production as well as their usage at the beginning of the 1980s (De Rosa et al., 2022).

This class of compounds were used extensively for decades mainly as insecticides, and fungicides in agriculture by interfering with the nervous systems, but they have also been used in public health (Sparling, 2006). OCPs have shown very good results which is why it revolutionized agriculture in the mid-20th century, being preferred in favor of other classes of pesticides from those times.

They are semi-volatile compounds, being therefore carried over long distances as suspended particles and due to their hydrophobic nature, they tend to fix most often on solid materials, being found in a wide range of environmental matter such as soil, sediments, waters, fish, and food. As a result of their application on surface soils, they reach the aquatic environment via runoff or atmospheric deposition, but given their hydrophobic nature, they are removed from the surface water and fix on the bottom sediment, but they can reach the water column due to phenomena such as water turbulence or other activities that disturb the sediments. The sediment particles that have large organic content or porosity have a high adsorption capacity leading to the conclusion that sediment is a major depository source for a large number of applied pesticides and that marine environment is one of the main sites for the accumulation of OCPs and PCBs (Kuranchie-Mensah et al., 2012; De Rosa et al., 2022).

Due to their persistence in the environment and lipophilicity, they have the tendency to bioaccumulate and biomagnify through the food chain, being detected in all classes of living organisms (Albanese & Guarino, 2022). Therefore, they were banned from use since the 1970s in the USA, and worldwide since the 1980s (Purdue et al., 2007). Regardless of their banning, some of them are still used to combat disease such as DDT for malaria in areas such as Africa, India, and South America (IARC 113, 2018), and lindane (*γ*-HCH) for the treatment of lice and scabies (Schaefer et al., 2015).

In 2001, the Stockholm Convention officially classified a certain number of OCPs, as persistent organic pollutants (POPs), 9 of them being listed in their dirty dozen list including compounds such as aldrin, chlordane, DDT, dieldrin, endrin, hexachlorobenzene, heptachlor, *α*-endosulfan, *β*-endosulfan, mirex, and HCH with its isomers *α*-, *β*-, and *γ*- (Albanese & Guarino, 2022).

Many pesticide products that have been marketed over the years were and still are sold as isomeric mixtures, even though their toxicological aspects can differ between isomers. Therefore, there was and still is a tendency in using single-isomer products (Sutherland et al., 2004).

A review on OCPs by Jayaraj (2016) states that around 40% out of all the used pesticides belong to the organochlorine class, and due to their low cost, pesticides such as DDTs, HCHs, aldrin, and dieldrin are considered among the most used from the old pesticides (Jayaraj et al., 2016).

From the structural point of view, OCPs are divided into five groups (Blus, 2002):

I. Dichlorodiphenyltrichloroethane (DDT) with its degradation compounds dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD);
II. Hexachlorocyclohexane (HCH) with its isomers *α*-, *β*-, *δ*-, *γ*-, the first 3 isomers being all byproducts of the latter *γ*-HCH, also known as lindane;
III. Cyclodienes, most notably, aldrin, dieldrin, endrin, endosulfan, heptachlor, and chlordane;
IV. Toxaphene with other related chemicals;
V. Mirex and chlordecone.

The list with the parent compounds and the degradation compounds are presented in table 1 and table 2.

Table 1. OCPs and certain physico-chemical characteristics (from: Sparling et al., 2016)

Name	Class of OCPs	MF[a]	MW	Water Solubility (mg/L)*	Field Half-life	Year of ban	K_{OW}	K_{OC}	mp (°C)[a]	WHO classification[b]
p,p'-DDT	DDTs	$C_{14}H_9Cl_5$	355	0.001	15 years	1972	6	5.63	108.5	Moderately hazardous
p,p'-DDE		$C_{14}H_8Cl_4$	318	0.06	15 years	1972	5.6–6.9	5.94	89	Slightly hazardous
p,p'-DDD		$C_{14}H_{10}Cl_4$	320	0.05	15 years	1972	5.0–6.2	5.36	110	Unlikely acute hazard
Methoxychlor		$C_{16}H_{15}Cl_3O_2$	345	0.1	128 days	2003	4.8–5.1	3.13	87	Unlikely acute hazard
γ-HCH	HCHs	$C_6H_6Cl_6$	291	7	100-1424 days	Still tolerated	3.7	135.5	113	Moderately hazardous
HCB		C_6Cl_6	285	0.04	1000 days	1966	3.9–6.4	4.75	228	Unlikely acute hazard
Aldrin	Cyclodienes	$C_{12}H_8Cl_6$	365	0.03	365 days	1974	6.5	4.24	104	Highly hazardous
Dieldrin		$C_{12}H_8Cl_6O$	381	0.186	1000 days	1987	3.6–6.2	4.08	175	Highly hazardous
Endrin		$C_{12}H_8Cl_6O$	381	0.24	4300 days	1987	3.2–5.3	4.00	200	Highly hazardous
Endosulfan		$C_9H_6Cl_6O_3S$	407	0.5	4-200 days	Phased out since 2010	3.1	4.09	106	Highly hazardous
Chlordane		$C_{10}H_6Cl_8$	410	0.06	283-1387 days	1988	6	4.78	106	Moderately hazardous
Heptachlor		$C_{10}H_5Cl_7$	373	0.06	250 days	Still tolerated	4.4–5.5	4.38	96	Highly – Moderately hazardous

MF – molecular formula; MW – molecular weight; K_{OW} – octanol-water coefficient; K_{OC} – soil-water partitioning coefficient; mp (°C) – melting point

a – PubChem, 2025a;

b – Jayaraj et al., 2016;

* – the higher the water solubility, the higher the chances of finding a certain compound dissolved in water at toxic concentrations. A certain compound with low water solubility is less likely to be present in water columns of lakes, ponds, and rivers (Sparling et al., 2016).

Table 2. Characteristics of metabolites and degrading compounds of certain OCP parent compounds

Name	Class of OCPs	MF[a]	MW[a]	Water Solubility (mg/L)	K_{OW}	K_{OC}	mp (°C)
o,p'-DDT	DDTs	$C_{14}H_9Cl_5$	355	0.085[b]	6.79[b]	5.35[b]	74[b]
o,p'-DDE		$C_{14}H_8Cl_4$	318	0.14[b]	6.00[b]	5.19[b]	-
o,p'-DDD		$C_{14}H_{10}Cl_4$	320	0.1[b]	5.87[b]	5.19[b]	78[b]
α-HCH	HCHs	$C_6H_6Cl_6$	291	2[e]	3.8[d]	3.57[f]	158[c]
β-HCH		$C_6H_6Cl_6$	291	0.2[e]	3.78[d]	3.57[f]	310[c]
δ-HCH		$C_6H_6Cl_6$	291	31[e]	4.14[d]	3.8[f]	138[c]
endrin-aldehyde	Cyclodienes	$C_{12}H_8Cl_6O$	381	-	4.8[a]	-	235[a]
α-endosulfan		$C_9H_6Cl_6O_3S$	407	-		3.6[d]	230[a]
β-endosulfan		$C_9H_6Cl_6O_3S$	407	-		4.3[d]	210[a]
endosulfan-sulphate		$C_9H_6Cl_6O_4S$	423	0.22[a]	3.66[a]	-	358[a]
heptachlor-epoxide		$C_{10}H_5Cl_7O$	389	insoluble	-	-	16[c]
tecnazene	C-nitro compounds	$C_6HCl_4NO_2$	260	2.09[a]	4.38[a]	-	99[a]
quintozene		$C_6Cl_5NO_2$	295	0.44[a]	4.22[a]	-	146[a]

MF – molecular formula; MW – molecular weight; K_{OW} – octanol-water coefficient; K_{OC} – soil-water partitioning coefficient; mp (°C) – melting point; "-" not specified;

a – PubChem, 2025a;
b – ATSDR, 2022a;
c – IARC 20, 1979;
d – Sutherland et al., 2004;
e – NTS, 2025;
f – ATSDR, 2005;

1.1.2. Sources of OCPs

OCPs can reach the environment after the applications of pesticides, wastes polluted with organochlorine compounds that have been discarded into certain landfills, discharges of industrial wastes from certain units that synthesize organochlorine chemicals. Being volatile compounds, they can also be transported over long distances, afterwards being deposited on solid materials (**Figure 2**) such as soils and sediments (Jayaraj et al., 2016).

Human exposure to OCPs is achieved by inhalation of OCPs particles from air, dermal absorption, water, and food intake, which is the main source of OCPs to human, especially food of animal origin, some studies indicating a dietary intake between 5-30 ng/kg body weight for adults and children (Berntssen et al., 2017; EFSA, 2006a; Singh et al., 2022; Pănescu et al., 2024a). Another important source of exposure to OCPs is long-term dermal absorption from contaminated cosmetic products (Darbre, 2006; Singh et al., 2022).

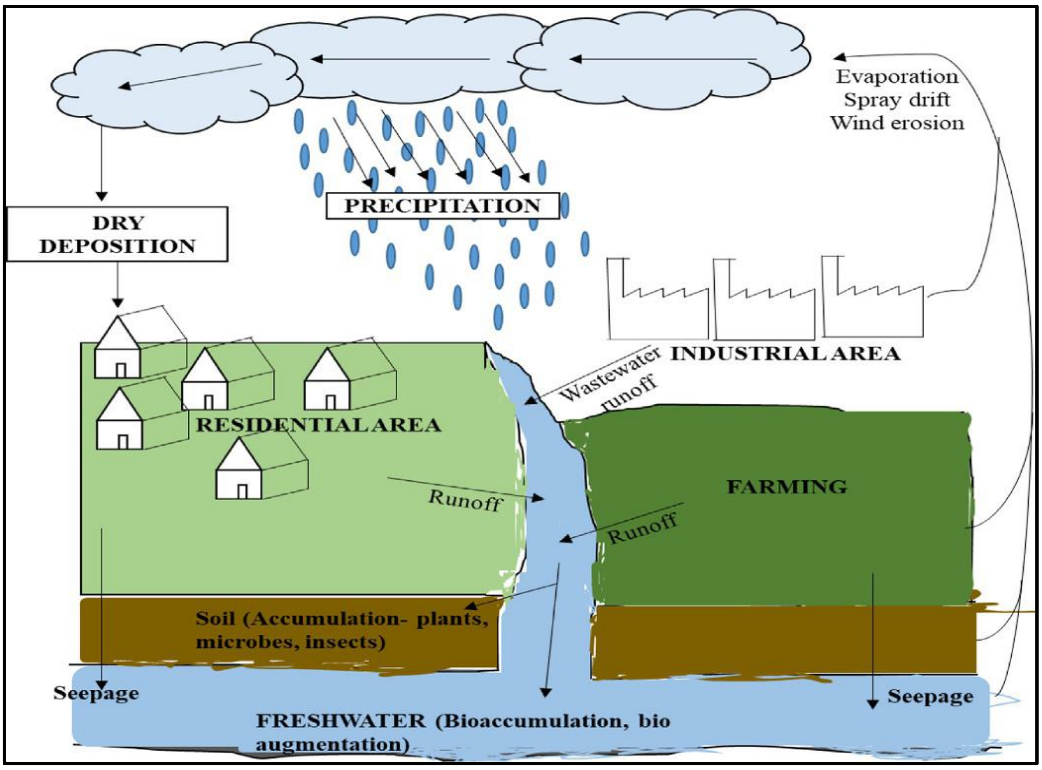

Figure 2. Pesticides environmental cycle (source: Singh et al., 2022)

1.2. Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are a class of synthetic aromatic chemical compounds, in which all or some hydrogen atoms that are attached to a biphenyl ring are substituted by chlorine atoms. These pollutants are divided into 209 congeners, and are considered highly persistent in environmental matters. PCBs carry other synonyms such as, chlorinated biphenyls, chlorinated diphenyls, chlorobiphenyls, or polychlorobiphenyls (IARC 107, 2016).

They were discovered in 1825, synthesized by Michael Faraday, presented as “benzene hexachloride”, obtained by the reaction of benzene with chlorine in the presence of sunlight. They have been successfully marketed for commercial use in 1929, being entirely of anthropic origin, produced as industrial chemicals, being marketed as complex mixtures, never as single compounds, with multiple isomers at different degrees of chlorination and used in various industries such as dielectric fluids for capacitors and transformers, lubricating and cutting oils, heat transfer fluids, and as additives in pesticides, paints, carbonless copy (“NCR”) paper, adhesives, and plastics, being produced in over a million tons from 1929 to the mid of 1970s (Erikson, 2001; Loganathan & Lam, 2011).

Depending on the origin and country it was produced, PCBs were commercialized under different names, Aroclor in the United States, Chlophen in Germany, Kanechlor in Japan, Phenoclor and Pyralene in Italy, (Megson, 2019; Erikson, 2001), Fenclor in France (Erikson, 2001), Sovtol and TCB in USSR-Rusia (AMAP, 2000), and Delor in Czechoslovakia (Erikson, 2001).

Due to the fact that PCBs have shown resistance to high temperatures (UNEP, 1999), oxidation, acids and bases (Bozlaker et al., 2008), the majority of these PCB products were used mainly for industrial activities like dielectric fluids in electronic capacitors and transformers (Jiang et al., 1997; Harrad et al., 1994; AMAP, 2000), production of carbonless copy paper, additives in plastic, surface coatings in paints, lubricants and hydraulic oils (Markowitz, 2018; Hong et al., 2005; AMAP, 2000; UNEP, 1999; Kalmaz & Kalmaz, 1979).

After several considerations from environmental representatives from different countries, it has been decided that PCB congeners represent a hazard for the environment due to their toxic behavior, persistency, and bioaccumulation, so their production was stopped in the late 1970s, early 1980s (Reddy et al., 2019), but they were still being produced in some regions until the beginning of the 1990s (AMAP, 2000). The first big official regulations regarding PCBs were in 1998 at the Aarhus protocol, in which the goal was to reduce and to eliminate them from the environment, but the most important decision was taken in 2001 at the Stockholm convention, in which they were included in the first list of hazardous chemicals, the so called “dirty dozens”, where they appear in both annex A (elimination) and annex C (Unintentional production) (UNEP, 2025c).

They are commonly identified using the numbering system in numerical order, from PCB 1 to the last, which is PCB 209. This system was first used back in 1980, where Ballschmiter and Zell have developed a scheme for numbering each individual PCB congener in ascending order depending on the number of chlorine atoms substitutions from each sequence (Ballschmiter & Zell, 1980) (**Table 5**). For example, the synonym for PCB 158 is *2,3,3’,4,4’,6-Hexachlorobiphenyl*. This system is still used as reference in present days and its use is even confirmed by the International Union of Pure and Applied Chemists (IUPAC).

In this class of compounds, between 2 and 10 chlorine atoms are attached to a biphenyl molecule. Depending on the location and the number of chlorine atoms present in a PCB molecule, data can be found about their toxicity, physicochemical characteristics, and their origins, but their behavior in the environment is also determined by the number of chlorine atoms from the biphenyl ring (Wolska et al., 2012).

“*Each homolog group has a particular number of isomers: mono-chlorobiphenyl- 3, di- 12, tri- 24, tetra- 42, penta- 46, hexa- 42, hepta- 24, octa- 12, nona- 3, and decachlorobiphenyl 1*” (Megson, 2019).

PCBs can be grouped according to the number of chlorine atoms, resulting in 10 homologue groups (**Table 6**), from nonachlorobiphenyls to decachlorobiphenyls, the majority of PCBs (more than 60%) being tetra- to hexachlorobiphenyls (IARC Monographs 107, 2016).

From all the 209 PCBs congeners it is difficult to determine all of them, so in order to have a proper determination, certain PCBs mixtures are used as standard for quantification of matching congeners from environmental samples or other products. One important PCB indicator is the 12 dioxin-like PCBs (77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189), which is suggested by the World Health Organization (WHO), and it is recommended to be used for the evaluation of human health risk (Megson et al., 2019). All these dioxin-like PCBs have been assigned toxicity equivalency factors (TEFs) by the WHO, revised by Van den Berg et al., 2006, as they are considered to possess higher toxicity in comparison to the rest of the PCB compounds (IARC Monograph 107, 2016).

Table 5. PCBs[a] number determined by Ballschmitter & Zell, 1980 and position of chlorine atoms for each phenyl ring of the PCBs determined by IUPAC (from: IARC Monograph 107, 2016)

Position[b]	**2**	**3**	**4**	**2,3**	**2,4**	**2,5**	**2,6**	**3,4**	**3,5**	**2,3,4**	**2,3,5**	**2,3,6**	**2,4,5**	**2,4,6**	**3,4,5**	**2,3,4,5**	**2,3,4,6**	**2,3,5,6**	**2,3,4,5,6**
none	1	2	3	5	7	9	10	12	14	21	23	24	29	30	38	61	62	65	116
2’	4	6	8	16	17	18	19	33	34	41	43	45	48	50	76	86	88	93	142
3’		11	13	20	25	26	27	35	36	55	57	59	67	69	78	106	108	112	160
4’			15	22	28	31	32	37	39	60	63	64	74	75	**81***	**114***	115	117	166
2’,3’				40	42	44	46	56	58	82	83	84	97	98	122	129	131	134	173
2’,4’					47	49	51	66	68	85	90	91	99	100	**123***	137	139	147	181
2’,5’						52	53	70	72	87	92	95	101	103	124	141	144	151	185
2’,6’							54	71	73	89	94	96	102	104	125	143	145	152	186
3’,4’								**77***	79	**105***	109	110	**118***	119	**126***	**156***	158	163	190
3’,5’									80	107	111	113	120	121	127	159	161	165	192
2’,3’,4’										128	130	132	138	140	**157***	170	171	177	195
2’,3’,5’											133	135	146	148	162	172	175	178	198
2’,3’,6’												136	149	150	164	174	176	179	200
2’,4’,5’													153	154	**167***	180	183	187	203
2’,4’,6’														155	168	182	184	188	204
3’,4’,5’															**169***	**189***	191	193	205
2’,3’,4’,5’																194	196	199	206
2’,3’,4’,6’																	197	201	207
2’,3’,5’,6’																		202	208

a – Scheme developed by Ballschmitter and Zell, 1980, for numbering each individual PCBs congener in ascending order in relation with the number of chlorine atoms substitutions from each sequence

b – Position of chlorine atom on each ring

* – Dioxin-like PCBs indicated with another color

Table 6. PCBs homologue groups with certain physical and chemical properties (from: IARC Monograph 107, 2016)

Homologue group	CAS No.[a]	Molecular Formula	No of isomers	BZ no[b]	Relative molecular mass	Chlorine (% w/w)	Melting point (°C)[c]	Boiling point (°C)[d]
Monochlorobiphenyl	27323-18-8	$C_{12}H_9Cl$	3	1–3	188.66	18.79	25–77.9	285
Dichlorobiphenyl	25512-42-9	$C_{12}H_8Cl_2$	12	4–15	223.10	31.77	24.4–149	312
Trichlorobiphenyl	25323-68-6	$C_{12}H_7Cl_3$	24	16–39	257.55	41.30	28–87	337
Tetrachlorobiphenyl	26914-33-0	$C_{12}H_6Cl_4$	42	40–81	291.99	48.65	47–180	360
Pentachlorobiphenyl	25429-29-2	$C_{12}H_5Cl_5$	46	82–127	326.44	54.30	76.5–124	381
Hexachlorobiphenyl	26601-64-9	$C_{12}H_4Cl_6$	42	128–169	360.88	58.93	77–200	400
Heptachlorobiphenyl	28655-71-2	$C_{12}H_3Cl_7$	24	170–193	395.33	62.77	83–149	417
Octachlorobiphenyl	55722-26-4	$C_{12}H_2Cl_8$	12	194–205	429.77	65.98	159–162	432
Nonachlorobiphenyl	53742-07-7	$C_{12}HCl_9$	3	206–208	464.22	68.73	182.8–206	445
Decachlorobiphenyl	2051-24-3	$C_{12}Cl_{10}$	1	209	498.66	71.10	305.9	456

a – CAS (Chemical Abstract Service)
b – PCBs number determined by Ballschmitter & Zell, 1980
c – Values approximated depending on the range across the isomers
d – average values for all isomers of the certain group

1.2.1. Sources of PCBs

Other by-products of PCBs continue to be released in the environment unintentionally through chemical activities like waste incineration, fuel combustion and even from vaporization from sources that contained PCBs products (Pandelova et al., 2006; Dyke et al., 2003; Bozlaker et al., 2008). Even in present days, the major sources of PCBs belong to the intense use of the old commercial products that contained PCB and their volatilization, but they can also be released through combustion, industrial thermal processes or unintentionally as by-products from various industries (Mao et al., 2021). However, the main sources of PCBs are emissions from the production of electricity, production of steel, incineration of various wastes, emissions which will later volatilize and deposit on solid materials such as soils and sediments (Montano et al., 2022). Since they are resistant to degradation, and do not degrade rapidly in the environment, they tend to bioaccumulate (Erikson, 2001).

Thus, these chemicals have been found in environmental matter like air (Dreyer & Minkos 2023; Mastin et al., 2022), soil (Remelli et al., 2022; Qin et al., 2022), and water (Güzel et al., 2022; Huang et al., 2020), with significant amounts even in vital food products like fish (Mikolajczyk et al., 2020), meat (Barone et al., 2019), fruits (Grassi et al., 2010) and vegetables (Shen et al., 2016).

Fruits and vegetables tend to have lower concentrations of organic pollutants like PCDDs, PCDFs and PCBs in comparison to fish and other products of animal origins (Zuccato et al., 1999). In the present and more recent days, lesser-known PCBs by-products have been detected in environmental sources from different locations. They have also been found in newer and more modern pigments and dyes, this being a strong argument that these types of PCBs do not have their origins from legacy commercial PCBs products from the early days, thus, attesting a new era of non-legacy PCBs presence in environmental matter (Grossman, 2013).

After being considered highly toxic and since their ban in the late 1970s, they are found across almost all environmental matters, where they continue to be considered harmful for humans and animals. Thus, they have become an important source that requires permanent monitorization.

1.3. Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a class of compounds of organic origin which are found ubiquitously in all environmental sections and are considered a hazard for both human and environmental health due to their high toxicity and carcinogenicity. Their origin is for the most part coming from anthropogenic activities, but it can derive from natural processes as well. Many of them are classified as persistent organic pollutants and are chemically inert.

This class of compounds has been intensively studied for several decades in order to understand their effects and fate on the environment. Stogiannidis & Laane, 2015 cite a list of 660 parent PAH compounds developed in 1997 by Sander and Wise, which consists of a list of aromatic compounds containing fused rings connected to each other, ranging from one aromatic ring (benzene) up to nine-ringed PAHs.

They are not odorless, as they can have a very faint smell. PAHs usually occur as a multicomponent mixture, not as single compounds, and as pure state chemicals they are usually found as white, colorless, faint yellow or green solids (ATSDR, 2014). These pure PAHs are usually known to be colorless, white, pale yellow, or pale-green solids (Ravindra et al., 2008b). PAHs are classified as semi volatile organic compounds, with hydrophobic and lipophilic characteristics, and due to their hydrophobic nature, they tend to adsorb rather fast to particulate organic matter in sediments or soot (Stogiannidis & Laane, 2015).

PAHs are widely distributed in the environment, reaching all environmental sections such as atmosphere, water, sediments and biota and their fate and distribution in the environment is closely related to their physico-chemical properties (Lourenço et al., 2023).

They are present in the atmosphere in two phases, one being as gas, and the other as particulate phase. The way they are distributed depends on factors such as the size of the suspended particles, their vapor pressure, the ambient temperature, and the solubility of the compound (Baek et al., 1991).

The majority of PAHs are soluble in non-polar organic solvents and are not soluble in water. These compounds of organic origin are comprised of two or more fused aromatic rings. They are also referred to as polynuclear aromatic hydrocarbons (PNAs), fused ring aromatics or condensed ring aromatics. The PAHs that are widely found in the environment can contain more aromatic rings, usually from two to seven rings, but the presence of compounds with more rings was also reported. PAHs do not differ from other hydrocarbons, they having hydrogen and carbon in their composition, but there are some compounds in which one of the carbon atoms is replaced with one atom of nitrogen, oxygen, or sulfur, which are called heterocyclic aromatics or polycyclic aromatic compounds (PAC) (Boehm, 2005).

These compounds have different physical and chemical features on account of their molecular mass, which has an influence on their movement and fate in the environment. For oils and oil derivatives in water, processes such as solubilization, evaporation, biodegradation, and photo-oxidation take place in the first hours after the spill (Fingas, 2005). Exposing these compounds to light and contact with other chemicals affects the toxicity of PAH mixtures or individual PAHs. Also, the concentration and the structures of PAHs have an influence on the magnitude of the toxicological effects, carcinogenicity, mutagenicity, and genotoxicity (Logan, 2007).

The physico-chemical properties, the way PAHs interact with the environment and its organisms are strongly correlated with the number and the position of their aromatic rings (UNEP, 1992). So, the higher the number of aromatic rings, the higher will the melting and the boiling points be, which will result in a lower solubility in water, lower vapor pressure, and a hydrophobic nature, leading to affinity for organic materials and deposition in sediments (Lourenço et al., 2023).

There is a list comprising of 16 priority PAHs chosen by the U.S. EPA which includes some of the parent PAHs which are most frequently detected in environmental monitoring. The 16 selected compounds are: naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FL), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benz[*a*]anthracene (BaA), chrysene (CRY), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[123-*cd*]pyrene (IPYR), dibenzo[*ah*]anthracene (DbahA), and benzo[*ghi*]perylene (BghiP) (**Table 7**) (U.S. EPA, 2025a), and all of them are also included in EPA’s Priority Pollutant List (U.S. EPA 2025b).

Table 7. Characteristics of the 16 priority PAHs

Name	**Priority list**[a]	**MF**[b]	**MW**[b]	**NR**[b]	**bp (°C)**[b]	**Environmental Distribution**[b]
Naphthalene	E, U	$C_{10}H_8$	128	2	218	Particle gas phase
Acenaphthylene	U	$C_{12}H_8$	152	2	280	Gas phase
Acenaphthene	U	$C_{12}H_{10}$	154	2	279	Gas phase
Fluorene	B, U	$C_{13}H_{10}$	166	2	295	Particle gas phase
Phenanthrene	U	$C_{14}H_{10}$	178	3	340	Particle gas phase
Anthracene	E, U	$C_{14}H_{10}$	178	3	342	Particle gas phase
Fluoranthene	E, U	$C_{16}H_{10}$	202	3	375	Particle gas phase
Pyrene	U	$C_{16}H_{10}$	202	4	393	Particle gas phase
Benz[*a*]anthracene	C, U,	$C_{18}H_{12}$	228	4	400	Particle gas phase
Chrysene	C, U,	$C_{18}H_{12}$	228	4	448	Particle gas phase
Benzo[*b*]fluoranthene	C, E, U,	$C_{20}H_{12}$	252	4	481	Particle gas phase
Benzo[*k*]fluoranthene	C, E, U	$C_{20}H_{12}$	252	4	480	Particle gas phase
Benzo[*a*]pyrene	C, E, U,	$C_{20}H_{12}$	252	5	496	Particle gas phase
Indeno[123-*cd*]pyrene	C, E, U,	$C_{22}H_{12}$	276	5	536	Particle phase
Dibenz[*ah*]anthracene	C, U	$C_{22}H_{14}$	278	5	524	Particle phase
Benzo[*ghi*]perylene	C, E, U	$C_{22}H_{12}$	276	6	550	Particle phase

[a] Specific PAHs which are enlisted in priority pollutants lists: C - considered carcinogenic (Stout & Emsbo-Mattingly, 2008), E – European priority pollutant as defined by the European Commission (2001), U – U.S. EPA 16;

[b] Source: PubChem, 2025a; MF- molecular formula; MW- molecular weight; NR- number of aromatic rings; bp – boiling point.

1.3.1. Sources of PAHs

Their occurrence in the environment can be made from natural and anthropogenic processes, with similar compounds being introduced in the environment by both methods, thus leading to the necessity of using proper diagnostic tools in order to establish and differentiate the sources (Boehm, 2005).

Most commonly, PAHs sources are classified into natural sources such as combustion of organic material (Wang et al., 2023; Guerrerro et al., 2019), or from volcanoes (Kozak et al., 2017; Tomasek et al., 2021), but they are mainly originated from anthropogenic sources such as industrial activities (Cao et al., 2022; De Almeida et al., 2018), and vehicle emissions (Bakeas et al., 2011; McCaffery et al., 2020), with other examples of PAHs that are produced for commercial use, such as naphthalene, fluorene, anthracene, phenanthrene, fluoranthene, and pyrene (Franck & Stadelhofer 1987).

The most well-known classification of PAHs is by the temperature of their formation, which can be of petrogenic or pyrogenic origin, either formed naturally or anthropogenic. Boehm, 2005 classifies the formation of PAHs according to the temperature at which they are formed:

- PAHs created relatively fast, in a matter of days or even a few years, at a low temperature (<70°C) by the transformation of organic matter after the deposition in sediments;
- slow formation of PAHs at a moderate temperature (100-300°C) by the formation of fossil fuels and coal, recognized as **petrogenic PAHs**;
- PAHs created rapidly, at a high temperature (>500°C) by incomplete (low oxygen) combustion (pyrolysis) of organic materials, performed either naturally (combustion of forests and grass) or anthropogenically (combustion of fossil fuels), often recognized as **pyrogenic PAHs**;
- PAHs created naturally by biosynthesis of individual compounds performed by plants and animals, method recognized as **biogenic or diagenetic PAHs**.

i) Petrogenic PAHs

Sources of petrogenic PAHs include reservoirs of petroleum and coal formed over geological time, namely, when the biological organic matter is converted to petroleum or coal, both being known as fossil fuel. Several aspects such as temperature, pressure, burial conditions, biodegradation, and subsurface migration have a great influence on the chemical transformation of organic matter into fossil fuels. All these aspects influence the molecular complexity, composition, and physical properties of crude oil, coal, and the PAH structures from fossil fuels (Boehm, 2005).

Many of the individual PAHs can be produced naturally during the processes of fossil fuel creation, but the PAHs that are most commonly found in fossil fuels have between 2 and 6 aromatic rings. The main components of petroleum are the well-known 16 parent PAHs from the U.S. EPA list, and a large number of alkylated PAHs, as alkylated PAHs exceed the abundance of the parent compounds, this aspect being in fact the main feature of petrogenic PAHs (Boehm, 2005).

ii) Pyrogenic PAHs

During high temperature processes from natural and anthropogenic activities, there are organic compounds which somehow escape the complete combustion, compounds known as pyrogenic PAHs. Pyrogenic PAHs are in large part produced during combustion of wood, fossil fuels, and internal combustion of engines. Other activities include high temperature processing of coal, residues being rich in pyrogenic PAHs and are known as coal tars (Boehm, 2005).

Many PAHs are generated via processes of low temperature combustion, being released in the form of exhaust and solid residues, prevalent in aquatic environment. They reach the aquatic environment mostly by atmospheric deposition or by rain washout (Stogiannidis & Laane, 2015).

The high temperatures involved tend to destroy the alkylated PAHs, thus, the main feature of pyrogenic PAHs is the dominance of parent compounds, therefore, PAHs which are produced at high temperature such as fast pyrolysis or combustion processes are significantly different from PAHs produced by petrogenic processes, being abundant in compounds with more than 3 aromatic rings, having mainly compounds from 4 to 6 aromatic rings (Boehm, 2005).

The number of PAHs which are produced from pyrolytic activities may vary, depending very much on the combustion conditions, temperature, oxygen, and the fuel type (Westerholm et al., 1988). The composition of PAHs which are produced from the combustion of fossil fuel or biomass is highly dependent on the conditions of combustion, the content of oxygen being the determining factor of the final number of PAHs being produced. Nevertheless, for the determination of the composition of pyrogenic PAHs from combustion processes, it seems that temperature is the most important factor, as lower temperature combustion generates alkylated PAHs, while higher temperature combustion supports the production of parent compounds (Boehm, 2005).

2. Methodologies for reconstructing pollution history

2.1. Historical pollution

Historical Pollution often describes the interaction between some important factors in the evolution of mankind, such as industrial and technological development. The constant evolution of these major factors has increased production activities which later had a strong impact on the environment and ecosystems. The constant evolution of science and knowledge also had harmful effects on the environment and inevitably also on human life, and legislation regarding the impact and control of these industrial and technological activities on the environment has developed over time. Therefore, the legislation could not keep up with the rapid pace of development. In a more simplistic manner, historical pollution could be explained as the present environmental damage as a consequence of the pollution created from industrial activities products extended over long periods of time (Centonze & Manacorda, 2017).

This concept of historical pollution is a relatively recent approach and emerged as a need for awareness of the negative effects of industrial development in relation to the prospects for improving and reducing environmental impact. (Centonze & Manacorda, 2017).

2.2. Persistence of a substance

"*The term "persistent chemicals" hereby refers to any synthetic organic chemical species that is stable in the environment for long periods of time and causes unintended effects on the environment and health of wildlife and humans*" (Loganathan & Lam, 2011).

Internationally, environmental persistence of a chemical is measured in half-life (Loganathan & Lam, 2011), persistence also being defined as a chemical with environmental half-life of more than two months in water or more than six months in soil or sediment (Jayaraj et al., 2016).

The half-life ($t_{1/2}$) is described as the amount of time necessary for the disintegration of a certain compound and reaching half of its initial concentration. Explained in a more formal manner would be, "*the required time for the decay rate of a sample of unstable nuclei to decrease by a factor of 2*" (Arfken et al., 1984).

An important term used when discussing about the persistence of a chemical is bioaccumulation. Bioaccumulation is a phenomenon which describes the retention and assimilation of contaminants from external environmental sources, it presents the result of a dynamic balance between processes such as distribution, excretion, and assimilation of a substance in a certain organism. A very important step for the bioaccumulation to occur is the rate of contaminant assimilation, which must be higher than the clearance rate. If the assimilation rate is equivalent to the clearance rate, a state of equilibrium is reached. The equilibrium concentration of a certain substance present in the organism tissue is determined using bioaccumulation factor (BAF). This method is the result of the ratio between a certain compound's tissue concentration to its concentration in the environmental matter which is in equilibrium with that organism (Lourenço et al., 2023; Neff, 2002).

Also, bioavailability is another important factor in determining the persistence of a chemical, phenomena which could be defined as "*the extent to which a chemical can be absorbed or adsorbed by a living organism by active (biological) or passive (physical or chemical) processes*" (Neff, 2002). A certain chemical is considered bioavailable when it has a certain form in which it can react or bind with a surface coating of a living organism. Additionally, that certain chemical not only does it have to react with the tissues of living organism, but it must also produce certain biological responses (Neff, 2002).

Considering the persistence of some organic compounds and their tendency to bioaccumulate in environmental factors, this data can be used to estimate the history of environmental pollution, in the absence of measurement data, by using layers of lake sediments whose age can be estimated by dating methods, respectively measuring the concentrations of POPs in these sediment layers by modern instrumental techniques. This methodology that combines radioactive dating of sediments and analysis of POPs residues in dated sediments has been used in various studies worldwide (Arinaitwe et al., 2016; Bigus et al., 2014; Cai et al., 2016; Chalmers et al., 2007; Combi et al., 2020), the results obtained providing valuable information regarding the anthropogenic impact on the environment. Moreover, the data obtained from these measurements can be used for a series of statistical approaches aimed at estimating the source of POPs in environmental factors. The aspects related to the methodology used in the present thesis, estimation of the history of pollution of some lakes, and the identification of pollution sources are presented below.

2.3. Methods for sediment dating

Analyses of sediment cores have been used for many years in the determination of sedimentation rates and attributing calendar dates for various sediment depths. Radioactive measurements can provide information for time periods ranging from a few months to hundreds of years. Using this type of chronological results, different characteristics of water bodies can be studied, such as sediment deposition, dredging operations, and especially useful for the study of buried toxic substances. Certain water bodies, such as long waterways, are often loaded with historical contaminants from various industries over time, these toxic substances being buried progressively into the sediments, later becoming a record of a form of contamination. This type of chronological information is also useful in observing the migration or degradation of buried substances (Jeter, 2000).

^{210}Pb (lead-210) method is considered a viable method for the determination of sediment ages, offering the best response to quiet deposition areas such as lakes, bays, and swampy areas (Jeter, 2000). This method is used for the determination of relatively young and undisturbed sediment cores, usually for periods between 100-150 years (Appleby and Oldfield, 1983). Aspects related to this method are presented below.

2.3.1. The cycle of ^{210}Pb (lead-210) in nature

Elemental lead is present in two valences, one is $^{+}$2, while the other is $^{+}$4. The inorganic lead is usually found in divalent states. It has 35 isotopes, with 4 of them being the main isotopes present in environmental matter, namely, ^{208}Pb (52%), ^{206}Pb (24%), ^{207}Pb (23%), and ^{204}Pb (1%), all of them having different concentrations in rock formations (Encinar & Moldovan, 2005).

^{204}Pb is the only one of them that is a primordial isotope and has natural abundance, while the other three are decay compounds from ^{238}U, ^{235}U, and ^{232}Th (Baskaran et al., 2014). Of all 35 isotopes of lead, only three have long half-lives, the rest have half-lives of hours, even seconds. The three mentioned isotopes are ^{205}Pb ($T_{1/2}$ = 17.3 million years), ^{202}Pb ($T_{1/2}$ = 52.500 years), and ^{210}Pb ($T_{1/2}$ = 22.2 years) (Encinar and Moldovan, 2005).

^{210}Pb is an isotope of Pb, having natural radioactivity, and it can be found as traces in most soils, as it is a part of the natural decay series of ^{238}U (uranium-238) (**Figure 4**). It has a second source of appearance in the environment, being produced as fallout from the atmosphere by the radioactive decay of the rare gas ^{222}Rn (radon-222), having a constant fallout onto the earth's surface in small quantities. ^{222}Rn has a short half-life of 3.8 days, decaying into short-lived parent isotopes of ^{210}Pb (Jeter, 2000).

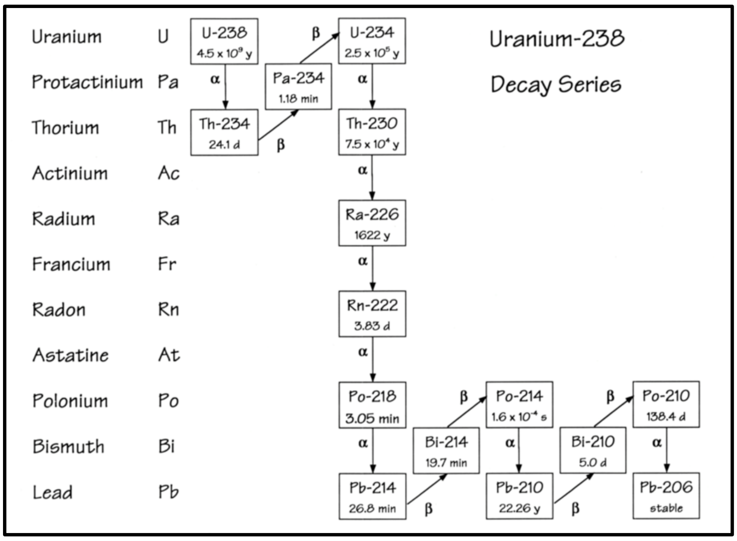

Figure 4. Decay scheme for ^{238}U. Assigned decay time expressed in years (y), days (d), minutes (m), and seconds (s) (source: Andrews & Chang, 2014)

^{210}Pb decays via *β*- and *γ*-emissions, with a small amount of the decays occurring at ground level, and most of the decays (80.2%) are a result of excited nucleus, stabilized by low energy gamma rays and internal conversion of electrons, which will lead to the formation of ^{210}Bi (bismuth-210) isotope. ^{210}Bi has a low half-time ($T_{1/2}$ = 5.01 days), and its decay will lead to the formation of ^{210}Po (polonium-210), later leading to the formation of the stable ^{206}Pb (**Figure 5**) (Mabit et al., 2014).

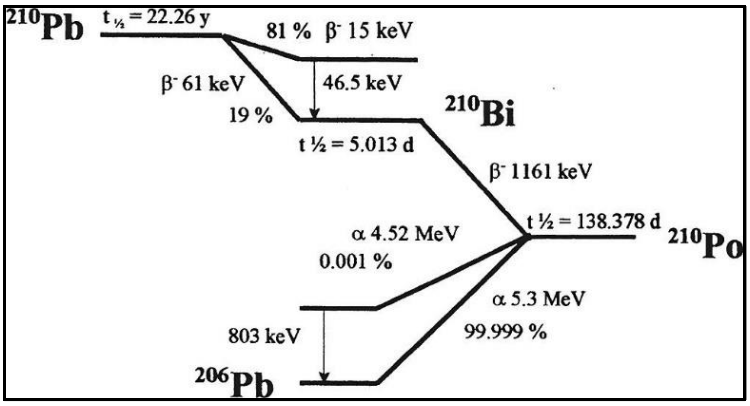

Figure 5. Decay scheme for ^{210}Pb (source: Nachab & Hubert, 2012)

This isotope reaches a lake reservoir both directly from rain, indirectly from run-offs, or from the decay of ^{222}Rn, being deposited in the mud interface by both sedimentation and exchange processes. ^{210}Pb which is formed in the interior of the sediment by the decay of ^{226}Ra (radium-226) is often named supported ^{210}Pb and it is assumed to be in equilibrium with the ^{226}Ra isotope (Appleby, 2001).

In literature, the excess of supported ^{210}Pb is referred to as unsupported ^{210}Pb, and its source is primarily from atmospheric input. This isotope is the basis of this dating method, primarily due to its resistance in the environment, and its input, which is constant and does not migrate within the sediment, therefore, the unsupported ^{210}Pb will slowly decrease with depth, due to the radioactive decay law (**Figure 6**). Due to anthropogenic and natural effects, the total unsupported ^{210}Pb activity undergoes an exponential decay with depth, which assumes a uniform sedimentation rate over a period of 150 years (Simsek & Cagatay, 2014).

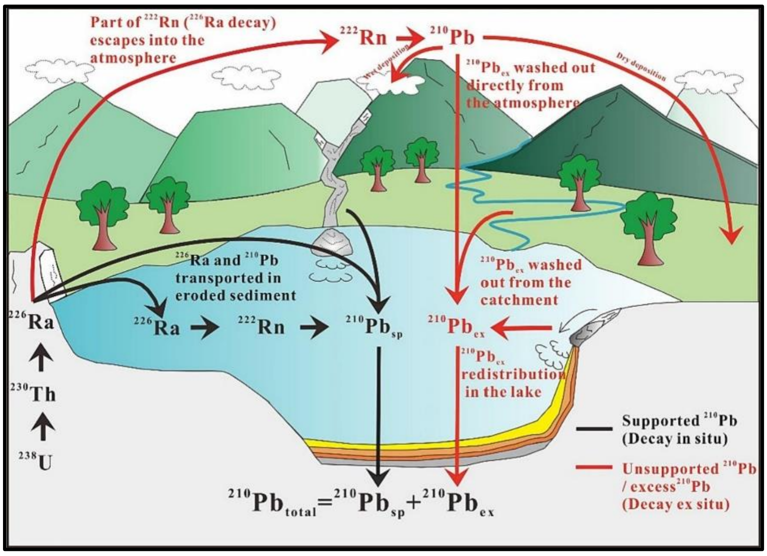

Figure 6. The pathways of ^{210}Pb in environment and marine sediments (source: Zhang & Xu, 2023)

2.3.2. Chronological studies using the ^{210}Pb dating method

The ^{210}Pb radionuclide is the most widely used for dating various solid materials ranging from one year to 200, being used in a wide range of fields such as limnology, biology, geology, geochemistry, speleology, etc. (Baskaran et al., 2014). This method is based on the activity of this radionuclide in sediments, which, having been deposited 22.3 years ago (the half-life of ^{210}Pb), would result in a presence of only half the amount which was initially deposited (Appleby & Oldfield, 1978).

In lake sediments, ^{210}Pb activity has two sources, one source is obtained from the sediment column by the decay of ^{222}Rn, which is called supported ^{210}Pb, and the second source is the unsupported/excess ^{210}Pb from the atmospheric fallout, also called excess of ^{210}Pb. For a proper determination of age and depth of sediments, both supported and unsupported concentration of ^{210}Pb must be measured. The unsupported/excess can be obtained by the concentration of ^{226}Ra, as they would be in radioactive equilibrium, and it is determined by its subtraction from the total concentration of ^{210}Pb. If the sediment accumulation rate and the erosion process are constant, then it is assumed that each sediment layer should have the same levels of unsupported/excess of ^{210}Pb, its concentration declining exponentially, resulting in a scale of linear profile (Appleby and Oldfield, 1983).

The equation used for the calculation of the unsupported/excess ^{210}Pb is the following:

$$^{210}\mathrm{Pb}_{\mathrm{ex}} = {}^{210}\mathrm{Pb}_{\mathrm{total}} - {}^{210}\mathrm{Pb}_{\mathrm{sup}} \qquad (1)$$

Where (Appleby, 2001):

- $^{210}\mathrm{Pb}_{\mathrm{ex}}$ is the unsupported/excess of ^{210}Pb;
- $^{210}\mathrm{Pb}_{\mathrm{total}}$ is the total concentration of ^{210}Pb;
- $^{210}\mathrm{Pb}_{\mathrm{sup}}$ is the concentration of supported ^{210}Pb (derives from the decay of the parent compound ^{226}Ra)

The analysis method which is most often used is gamma spectrometry, as it allows the simultaneous measurement of the radionuclides from the natural disintegration chains, such as ^{210}Pb, ^{226}Ra, ^{214}Pb, ^{235}U, and ^{238}U (Quintana et al., 2018). The chronologies resulted must then be validated using artificial radionuclides, most often being ^{137}Cs (cesium-137) and ^{241}Am (americium-241). The detection of ^{210}Pb is often combined with the detection of ^{137}Cs, in order to be sure and to obtain maximum chronology information. The results from the detection of ^{210}Pb are most often reported to the ^{137}Cs results from sediments, with the condition that the cesium profiles should be intact (Jeter, 2000). On the other side, ^{241}Am is considered less mobile in lake sediments than cesium, most often being used for the enrichment of ^{137}Cs dating, in case the cesium profile is disrupted (Arnaud et al., 2006; Appleby et al., 1991). Between 1954-1963, these two artificial radionuclides were heavily applied on surfaces around the globe as a result of high-yield thermonuclear weapons testing, therefore, they are used as markers in sedimentation records (Appleby, 2001). By measuring the surface distribution of ^{210}Pb and ^{137}Cs, both the erosion rates and soil redistribution can be estimated (Begy et al., 2021).

2.3.3. Age depth model (CRS)

Age depth model of the sediment column was built by applying the Constant Rate of Supply (CRS) mathematical model for ^{210}Pb deposition. For the calculation of ^{210}Pb dating results, there are usually two mathematical models considered practical, which are used constantly. First is constant rate of supply (CRS), and constant initial concentration (CIC) (Appleby and Oldfield, 1983).

CRS model is the most widely used (Appleby, 2001), and it assumes that the annual quantity of unsupported ^{210}Pb from the atmosphere that reaches the lake sediment is constant, the main source of ^{210}Pb in lakes derives from direct atmospheric fallout, and ^{210}Pb that reaches the sediment is influenced by post depositional processes and it undergoes changes according to the law of disintegration. More than 99% of the ^{210}Pb which is deposited on surface is trapped in the soil layers (Appleby and Oldfield, 1983).

Due to the occurring changes from the last 150 years, there have been massive changes in erosion processes and sediment deposition in lacustrine environments. Along with these changes, atmospheric Pb deposition may also vary with depth, and the logarithmic depth profile of ^{210}Pb becomes nonlinear with depth (Begy, 2009).

To calculate the age of a certain depth *i*, comparisons are made between the cumulative unsupported ^{210}Pb below depth *i* with the total unsupported ^{210}Pb in the entire sediment profile, all this by the integration of the concentration of supported ^{210}Pb, the bulk density and the thickness of each individual sediment layer. This is the way to obtain the mass sedimentation of each sediment layer and the age limits of the layers (Mabit et al., 2014). The sedimentation rate and the initial concentration of excess of ^{210}Pb (^{210}Pb$_{ex}$) can vary over time (Appleby, 2001).

The sediment accumulation deposit below layer *i* can be written using as the following equation:

$$A_i = A_0 e^{-\lambda t} \tag{2}$$

Age of layer *i* is calculated using the following equation:

$$t = \frac{1}{\lambda} ln \frac{A_0}{A_i} \tag{3}$$

The final step is the calculation of the mass accumulation rate for layer *i* using the following equation:

$$r_i = \frac{\lambda A_0 e^{-\lambda t}}{C_i} = \frac{\lambda A_i}{Ci} \tag{4}$$

Where (Appleby, 2001):

A_i - the inventory of ^{210}Pb of layer *i;*
$A_0 e$ - the inventory of ^{210}Pb excess of layer *i;*
λ - is the ^{210}Pb radioactive decay constant (0.03114 years^{-1});
t – age;
C_i – is the concentration of unsupported activity of ^{210}Pb of layer *i;*
r_i – mass accumulation rate.

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Annex 1

List of abbreviations used frequently used in the present doctoral thesis

^{241}Am	Americium-241 isotope
^{210}Bi	Bismuth-210 isotope
^{137}Cs	Cesium-137 isotope
^{202}Pb	Lead-202 isotope
^{204}Pb	Lead-204 isotope
^{205}Pb	Lead-205 isotope
^{206}Pb	Lead-206 isotope
^{207}Pb	Lead-207 isotope
^{208}Pb	Lead-208 isotope
^{210}Pb	Lead-210 isotope
^{210}Pb$_{ex}$	Excess of ^{210}Pb
^{214}Pb	Lead-214 isotope
^{210}Po	Polonium-210 isotope
^{240}Pu	Plutonium-240 isotope
^{226}Ra	Radium-226 isotope
^{222}Rn	Radon-222 isotope
^{232}Th	Thorium-232 isotope
^{235}U	Uranium-235 isotope
^{238}U	Uranium-238 isotope
μg	micrograms
ACE	Acenaphthene
ACY	Acenaphthylene
AET	Apparent effects threshold
ANT	Anthracene
ATSDR	Agency for Toxic Substances and Disease Registry
BaA	Benz[*a*]anthracene
BAF	bioaccumulation factor
BaP	Benzo[*a*]pyrene
BaP$_{Eq}$	Benzo[a]pyrene equivalent concentrations
BbF	Benzo[*b*]fluoranthene
BEDS	Biological effects database for sediments
BkF	benzo[*k*]fluoranthene
BghiP	Benzo[*ghi*]perylene
Bq/kg	Becquerel/kilogram
CC	Cis-chlordane
CIC	Constant initial concentration
CPAHs	Carcinogenic Polycyclic Aromatic Hydrocarbons
CRS	Constant rate of supply
CRY	Chrysene

CV	Coefficient of variance
DbahA	Dibenzo[*ah*]anthracene
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DLCs	Dioxin-like compounds
EqP	Equilibrium partitioning
ERL	Effects range low
ERM	Effects range median
FL	Fluorene
FLU	Fluoranthene
GC-MS	Gas chromatography coupled with Mass Spectrometry
GC-ECD	Gas chromatography coupled with Electron Capture Detector
HBCDD	Hexabromocyclododecanes
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HMW	High molecular weight
IARC	International Agency for Research on Cancer
ICH	International Conference on Harmonization
IPYR	Indeno[123-*cd*]pyrene
K_{OC}	Soil-water partitioning coefficient
K_{OW}	Octanol-water coefficient
LEL	Lowest effect level
LMW	Low molecular weight
LOD	Limit of detection
LOI	Loss on ignition
LOQ	Limit of quantification
m-ERM-Q	Mean effect range median quotient
MF	Molecular formula
Mp (°C)	Melting point
MW	Molecular weight
NAP	Naphthalene
NOAA	National Oceanic and Atmospheric Administration
NSTP	National Status and Trends Program
ng/g dw	nanograms/grams/dry weight
OCPs	Organochlorine pesticides
PAHs	Polycyclic aromatic hydrocarbons
PBDE	Polybrominated diphenyl ethers
PCBs	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzo-p-dioxins
PCDDF	Polychlorinated dibenzofurans
PEL	Probable effect level

PFOS	Perfluorooctane sulphonate
PFOSF	Perfluorooctane sulphonyl fluoride
PHE	Phenanthrene
POPs	Persistent organic pollutants
PYR	Pyrene
R^2	Linear correlation coefficient
RSD	Relative standard deviation
SD	Standard deviation
SEL	Severe effect level
SQGs	Sediment quality guidelines
$t_{1/2}$	Half-life
TC	Trans-chlordane
TCDD	*2,3,7,8*-tetrachlorodibenzo-*p*-dioxin
TEFs	Toxic equivalency factors
TEL	Threshold effect level
TEQ	Toxic equivalency quotient/Toxic equivalent
TOC	Total organic content
U.S. EPA	United States Environmental Protection Agency
WHO	World Health Organization

Annex 2

List of scientific publications and papers presented at scientific events based on the research conducted during the doctoral study

Scientific publications:

V.A. Pănescu, R. Begy, Gh. Roșian, M.C. Bruzzoniti, M.S. Beldean-Galea.

Historical assessment of atmospheric persistent organic pollutants depositions in Muntinu glacial lake, southern romanian carpathians, based on radionuclide-dated sediments.

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