

HISTORICAL ASSESSMENT OF ATMOSPHERIC PERSISTENT ORGANIC POLLUTANTS DEPOSITIONS IN MUNTINU GLACIAL LAKE, SOUTHERN ROMANIAN CARPATHIANS, BASED ON RADIONUCLIDE-DATED SEDIMENTS

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ABSTRACT. This study aims to assess the pollution history of persistent organic pollutants (POP) in lake Muntinu, Carpathian Mountains, Romania. Gamma spectrometry was used to measure ²¹⁰Pb and ¹³⁷Cs radionuclides in order to determine the age of sediment layers. The target compounds were isolated from sediment samples by ultrasound-assisted extraction method, followed by purification of extracts using open-column chromatography. 16 polycyclic aromatic hydrocarbons (PAHs), 20 organochlorine pesticides (OCPs) and 12 polychlorinated biphenyls (PCBs) were analysed in each dated sediment layer using gas chromatography coupled with mass spectrometry or electron capture detector. The results show that, over the past 100 years, POP concentrations from sediment samples ranged from 2.53 to 156.27 ng/g for PAHs, from 1.78 to 71.12 ng/g for OCPs, and from not detected to 76.03 ng/g for PCBs. PAHs diagnostic ratios such as Σ LMW/ Σ HMW, ANT/(ANT+PHE) and FLT/(FLT+PYR) show that the main source of PAHs in the sediment is of pyrogenic nature, especially from biomass and coal combustion. The sources of OCPs and PCBs could not be determined due to the lack of data obtained. However, the study demonstrates that the analysis of POP residues in sediments is a suitable method for reconstructing the history of surface water pollution.

Keywords: *Historical pollution, Polycyclic aromatic hydrocarbon, Organochlorine Pesticide, Polychlorinated biphenyl, radionuclides dated sediment.*

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INTRODUCTION

Persistent organic pollutants (POPs) are chemical compounds considered of high interest in environmental studies due to their high persistency and high toxicity. These pollutants are the main subject of the Stockholm Convention, in which all the partners involved have reached a conclusion that these pollutants possess toxic properties, they have long half-lives, are very resistant to degradation, they can bioaccumulate, they can volatilize and be transported over long distances. Given the fact that they are very toxic, these compounds represent a health risk to both human and other beings. Thus, in 2001, with the initiation of the Stockholm Convention, a number of 12 compounds and classes of compounds were banned. The so called “dirty dozens” were the following: Aldrin, Chlordane, DDT, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene (HCB), Mirex, Toxaphene, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). As of 2022, a number of 28 compounds and classes of compounds complete the list of prohibited substances [1].

Among persistent organic pollutants, Organochlorine pesticides (OCPs) and Polychlorobiphenyls (PCBs) are prohibited to be used in most countries, but there are exceptions and they are still being used locally in underdeveloped or developing countries. In the category of OCPs, the most frequently mentioned are: HCHs, DDTs, and chlorinated cyclodienes.

HCH (hexachlorocyclohexane) is solid white chemicals of synthetic nature having four common isomers: α -, β -, γ -, δ -HCH. The most used and well known from them is the γ -HCH isomer, also known as Lindan, which was considered a very potent insecticide for the protection of crops. Although HCH have been banned for decades, they are still used in some countries for treatment against scabies and body lice [2]. Given the fact that γ -HCH isomer is considered the most toxic of class, most of the studies focus only on its detection, neglecting the other isomers. The appropriate way would be to focus on each of them, since they are all found in the environment. From the acute exposure point of view, γ -HCH isomer is the most toxic for mammals, followed by α -, δ - and β - isomers. In terms of chronic exposure, β -isomer has the highest level of toxicity, followed by α -, γ - and δ -HCH isomers [3].

DDT 1,1,1-Trichloro-2,2-bis(4-chlorophenyl)ethane was developed at the end of the 1930s and it is one of the most well-known modern synthetic insecticides. This compound is better known as p,p'-DDT (4,4' DDT) and it is used together with its accompanied substitution isomer 1,1,1-Trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane, or o,p'-DDT (2,4' DDT). Due to its effectiveness, it was once heavily used for pest control in agriculture, forestry and to control mosquito-borne malaria in the 20th century. Like the other

categories of persistent organic pollutants, DDT has persistent stability, high capacity of bioaccumulation, strong toxicity, and it can be carried at long distances from the application areas [4], representing a major concern on human health. Common DDT metabolites are DDE (2, 4'- and 4,4' DDE) and DDD (2, 4'- and 4,4' DDD). 4,4' DDT, was considered to be the most important chlorinated insecticide ever marketed [5]. 4,4' DDE and 4,4' DDD are metabolites of DDT, which share the same characteristics but are considered to be less toxic than its parent.

Methoxychlor has been widely used as a replacement of DDT, due to its lower persistence level in the environment [6].

Endosulfan is an organochlorine insecticide, composed out of α - and β - isomers. It is often produced as a mixture of α - and β - isomers in ratios of 2:1 or 7:3. It has been used worldwide to control leaf-eating pests such as bollworms and aphids. [7].

Chlordane and chlordane related compounds have been heavily used in the past in order control termite and cutworm populations. Due to its persistence and distribution in environment, it has been classified as persistent organic pollutant and as active endocrine disruptor organochlorine pesticide [8]. Technical chlordane is classified as cyclopentadiene pesticide and is a mixture of 140 compounds, the most abundant of its components being *cis*-chlordane and *trans*-chlordane. The peak of its production was in the 1970s and it is estimated that almost 50% of the technical chlordane ever produced is unaltered in the environment [9].

Aldrin and dieldrin are two very common insecticides used for protection against soil insects like worms, beetles and termites. They were used heavily between 1950s and 1970s. Dieldrin is a metabolite of aldrin, it shares the same toxicity as its father being found in environment and human tissues, but is easier metabolized by animal and plants [10]. Endrin and endrin aldehyde are OCPs from the same class like aldrin, mainly used against insects, rodents and some species of birds. It was heavily produced and used from the 1950s to 1970s, very toxic, with a half-life that can range up to 12 years [11]. Endrin aldehyde is a degradation product of endrin and little is known about its properties.

Heptachlor is chlorinated cyclodiene, class which derives from cyclopentadiene, mainly used to control insect pests like termites and soil borne insects. It was intensely used from the early 1950s until the end of 1970s, very soon getting banned in most countries. Heptachlor can be oxidized to heptachlor epoxide, which is considered more toxic and persistent than its parent, and even after decades since its banning, heptachlor and its residue can still be found in the environment [12, 13].

Polychlorobiphenyls (PCBs) are chemicals of organic nature consisting of 209 chlorinated compounds discovered in the 19th century and first

synthesized in 1929. They are divided into groups and are based on the number of chlorines atoms. Each group has a 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. The most commonly used form of referring to PCBs is by using the numbering system and lists PCBs from PCB 1 (mono-Cl) to PCB 209 (deca-Cl) [14].

These types of compounds have most often been used in production of industrial oils, plastic additives and different types of paint. Like OCPs, PCBs are considered a danger for the environment being very persistent and toxic, so their production has been stopped from the late 1970s. They were included in the first list of the Stockholm convention from 2001, the so called "dirty dozen" [14].

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds which consist in two or more aromatic fused rings. In the environment, the most common PAHs compounds that are found contain two to seven fused benzene rings [15].

They are present in the environment since prehistoric times from naturally produced activities such as fires and volcanoes [16], but also derive from other industrial activities, indicating anthropogenic pollution such as incomplete combustion of fossil fuels [17].

These compounds are subjected to degradation mechanisms such as oxidative and photolytic reactions. PAHs that derive from anthropogenic sources reach the atmosphere either by adsorption onto particles or by gaseous state, so they can be easily transported over long distances by wind and air currents, where they deposit on water or solid materials like soils and sediments [18].

The analysis of POPs in sediment and soil samples involves their extraction and analysis by chromatographic methods. The most used techniques for extraction is Soxhlet extraction [19, 20], ultrasound assisted extraction [19, 21, 22] or accelerated solvent extraction (ASE) [20]. For the analysis, gas chromatography coupled with mass spectrometry [17, 19-21] or selective detectors like electron capture detector (ECD) for halogenated compounds [20, 21] are the most used techniques. High performance liquid chromatography coupled with fluorescence detector is also used for PAHs analysis [22].

Due to the high persistency of POPs in environmental factors such as water, soil, and sediments, these compounds are used as tracers of historical pollution from the last hundred years, and this kind of study is combined with the analysis of river and lake sediments using radionuclides for the dating process. Using this methodology, information can be obtained about the incidence and intensity of the use of these compounds in agriculture and industry.

The aim of this study was to evaluate the historical pollution with POPs of an alpine lake (Lake Muntinu, located in the Southern Carpathian Mountains), as well as to identify the sources of POPs pollution. To the best of our knowledge, this is one of the first studies carried out in Romanian alpine lakes on this subject.

RESULTS AND DISCUSSION

POPs concentration in sediment layers

A number of 20 sediment layers samples with a thickness ranged between 0.5 and 1.5 cm resulted from the sectioning of 60 cm of collected sediment were selected. For our study we took into account only the first 18 centimeter which corresponds to a period from 2018 in the first centimetre to 1905 along 18th centimeter. Below the 18th centimeters are layers of sediments older than the 20th century, which can be hundreds, maybe thousands of years old. These layers were not included in this study because their age exceeds 100 years. Each layer was subjected to the radionuclides dating method previously described by Begy et al. [23] in order to establish the age of the layer.

Subsequent, each sediment layer was subjected to GC analysis in order to determine the variation of the concentration of each class of POPs over the last 100 years.

The obtained results show that the concentration of POPs in the sediment layers varied during the last century, the layers with the highest POP concentration correspond to the period between 1945 and 1990, known as the period of greatest industrialization in Romania (Figure 1).

Different maxima can be identified for each class of compounds that can be associated taking into account the errors of sediment dating with some events or with the development of Romanian society in the last hundred years. Thus, for PAHs, four maxima can be identified corresponding to the years 1920, 1942, 1965 and after 1987. If we look at the past, 1920 corresponds to the period of the First World War, 1942 to the Second World War, 1965 to the beginning of coal mining in the Jiu Valley and after 1987, the period of the opening of the Transalpina road.

If we take into account that at a distance of approximately 30 km is the city of Petroșani, which has a very rich history in the mining industry, and at a distance of approximately 60 km is the city of Hunedoara, one of the most important steel centres in Romania, we can consider that along with the few other small industrial towns and villages in this region are the main contributors to the high levels of PAHs in the sediment of Lake Muntinu.

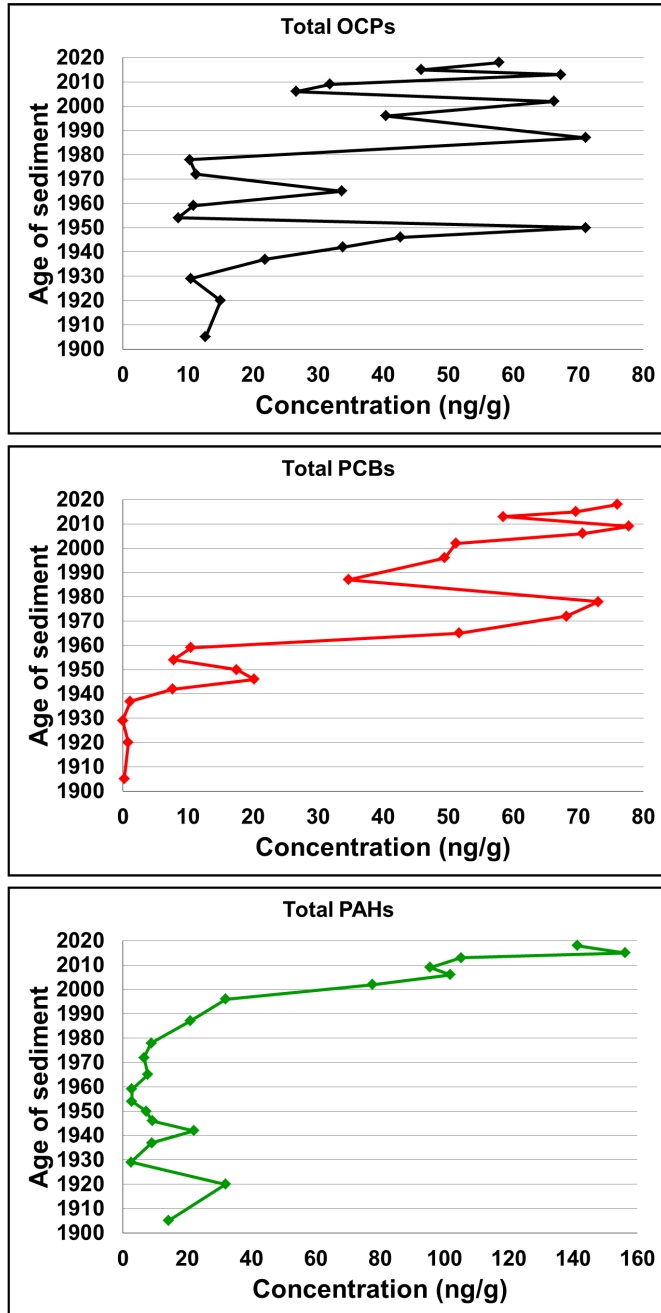


Figure 1. Variation of OCPs, PCBs and PAHs concentration, in the core sediment of Lake Muntinu over the past 100 years

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For OCPs the highest peaks correspond to the period 1950, 1965, 1987, 2013, while for PBCs the period 1946, 1978, 2009. The period from 1950 to 1990 is known as the period of intensive development of agriculture and heavy industry in Romania which could be an explanation of the higher amount of OCPs and PCBs found in the analysed layers sediment.

On the other hand, the peaks in 2009 and 2013 could be correlated with the increase in human activity in the area with the start of the rehabilitation works of the transalpine road and implicitly with the opening of the ski resorts.

PAHs distribution and sources

The total PAH concentration in sediment core ranged from 2.53 to 156.27 ng/g, the highest levels being in the upper layers, 2015 layer (156.27 ng/g) and 2018 layer (141.34 ng/g) (Table 1).

Table 1. Concentrations of OCPs, PCBs, PAHs and PAHs isomeric ratios Σ LMW/ Σ HMW, ANT/(ANT+PHE), FLT/(FLT+PYR) according to the ages of sediment layers.

Age of sediments	Total OCPs*	Total PCBs*	Total PAHs*	Σ LMW/ Σ HMW	ANT/(ANT+PHE)	FLT/(FLT+PYR)
2018	57.86	76	141.3	0.69	0.4	0.79
2015	45.90	69.6	156.2	0.75	0.45	0.64
2013	67.30	58.5	105.1	0.45	0.55	0.79
2009	31.84	77.8	95.61	0.24	0.52	0.61
2006	26.65	70.7	101.8	0.13	0.35	0.77
2002	66.28	51.2	77.67	1.26	0.41	0.7
1996	40.47	49.5	32	1.32	0.39	0.7
1987	71.12	34.7	20.95	0.78	0.3	0.65
1978	10.28	73.1	8.89	0.66	0.5	0.86
1972	11.28	68.2	6.61	0.02	-	-
1965	33.64	51.7	7.79	1.29	0.29	1
1959	10.85	10.5	2.81	0.06	-	-
1954	8.52	7.8	2.81	0.04	-	-
1950	71.12	17.5	7.26	0.99	0.46	-
1946	42.66	20.2	9.15	0.98	0.24	0.61
1942	33.81	7.65	22.11	2.51	0.46	1
1937	21.89	1.13	9.02	1.48	0.2	-
1929	10.48	nd	2.53	0.04	-	-
1920	15.04	0.83	31.9	1.44	0.48	0.68
1905	12.71	0.24	14.19	3.09	0.36	1

*ng/g dry sediment, "-" not estimated, nd – not detected

Several diagnostic ratios were used in order to have a better estimation of the sources of PAHs from sediment cores. One of them was the ratio between low molecular weight PAHs (Σ LMW) which represent the ones with 2 or 3 rings and with high molecular weight PAH, (Σ HMW) which are the PAHs that have between 4 and 6 rings (Σ LMW / Σ HMW). A ratio lower than or equal to 1 it indicates a pyrogenic source (combustion processes and volcanoes), while a value greater than 1 indicates a petrogenic source (fossil fuels, oil and coal) [17, 22].

Other isomeric ratios used were Anthracene/ (Anthracene+ Phenanthrene), [ANT/(ANT+PHE)]; and Fluoranthene/ (Fluoranthene+ Pyrene), [FLT/(FLT)+PYR)] [17, 22]. A ratio ANT/(ANT+PHE), less than or equal to 0.1, indicates a petrogenic source, and greater than 0.1, a pyrogenic nature. A ratio of FLT/(FLT+PYR) less than 0.4, it indicates PAHs deriving from oil products, between 0.4 and 0.5 attests a source of PAHs from fossil fuels burning, and higher than 0.5 are a characteristic of natural sources such as biomass and coal burning [17, 22].

According to our results the values of the Σ LMW/ Σ HMW ratio from Lake Muntinu ranged between 0.02 and 3.09. 13 out of 20 samples were below 1, which indicates that sources are mostly of pyrogenic nature (Figure 2).

From the ratios of ANT/(ANT+PHE) and FLT/(FLT+PYR) the results suggest that the PAHs present are of biomass and coal combustion (Figure 3). The results confirm our hypothesis that the sources of PAHs in the sediments of Lake Muntinu are the result of atmospheric deposition from the coal and steel industry in the neighboring cities. Moreover, with the opening of the Transalpina road, PAHs resulted from the combustion of fossil fuels are also an important source of PAHs.

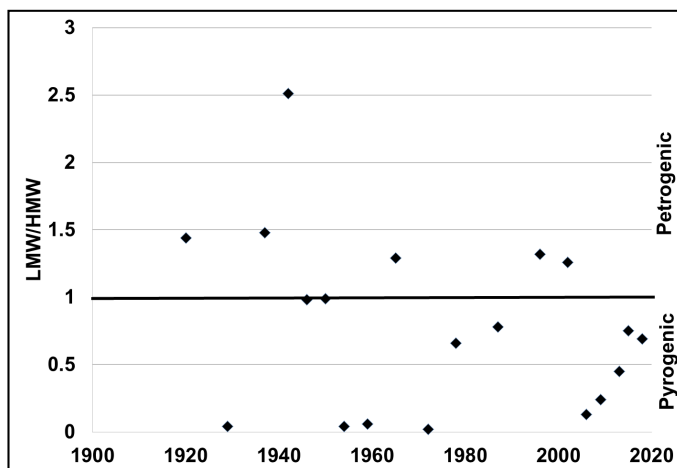


Figure 2. Isomeric ratios of Σ LMW/ Σ HMW versus the age of sediment

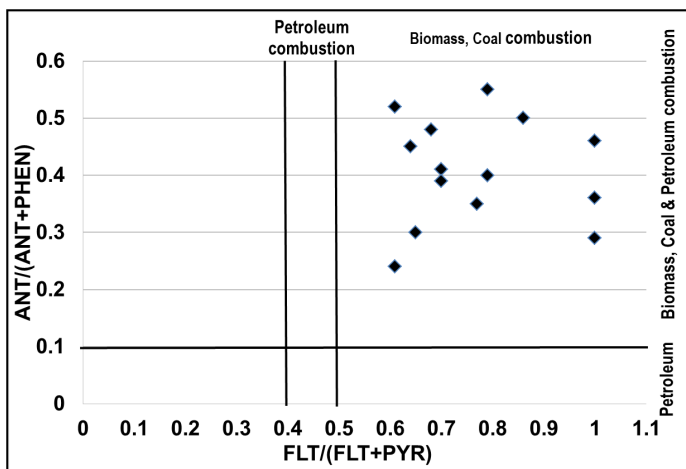


Figure 3. Isomeric ratios of ANT / (ANT + PHE) versus FLT / (FLT + PYR) in the sediment layers of Lake Muntinu

Organochlorines (OCs) distribution and sources

The concentration of OCPs ranged from 8.52 to 71.12 ng/g. The identified compounds were Heptachlor (<loq (0.01) to 19.75 ng/g), α -HCH (<loq to 62.93 ng/g) and Heptachlore exo-epoxide (<loq to 95.08 ng/g), which was the most common out of all the OCPs. Tecnazene, Hexachlorobenzene, γ -HCH, Quintozene, Aldrin, Heptachlor endo-epoxide, *trans*-Chlordane, 2,4'-DDE, α -Endosulfan, *cis*-Chlordane, Dieldrin, 4,4'-DDE, 2,4'-DDD, Endrin, β -Endosulfan, 2,4'-DDT, 4,4'-DDT were not detected in any of the samples. Unfortunately, due to the lack of data on individual OCPs, an estimate of their provenance cannot be made.

PCBs concentration tend to be at the same range as OCPs, the total concentration ranging from <loq (0.01) to 77.8 ng/g. The highest concentration detected was for PCB 52 with concentrations from <loq to 73 ng/g, and the lowest were for PCBs 138 with concentrations from <loq to 5.6 ng/g, and for PCB 194 with concentrations from <loq to 11.78 ng/g. PCBs -18, -28, -31, -44, -101, -114, -149, -153 and -180 were not detectable.

By comparing the total concentration of OCPs with the total concentration of PCBs it can be observed that the PCBs started to be used in 1965 while the use of OCPs stopped to be used in 1950 (Figure 4). The high concentration of OCPs from 1987 to 2018 can be explained by their high retention in environmental factors and their transport through air currents, but in the absence of data on the movement of air currents and precipitation in the studied area, this connection cannot be established.

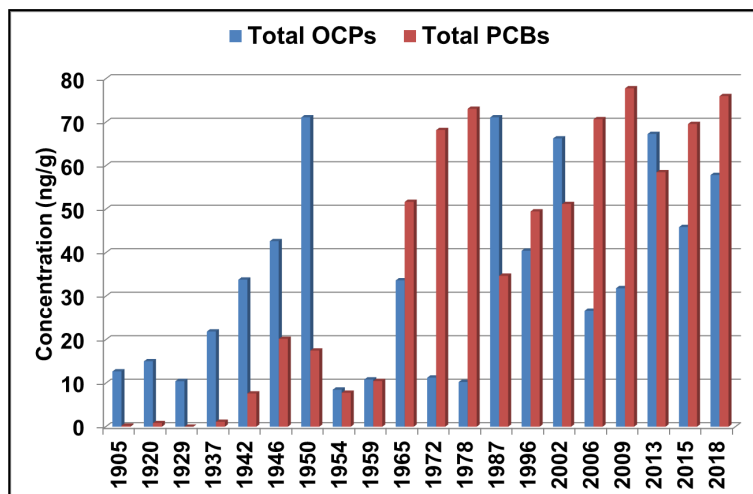


Figure 4. Comparison between total OCPs concentration and total PCBs concentration in sediment layers over the past 100 years

CONCLUSIONS

The lack of monitoring data for POPs in the environment over the last century makes it quite difficult to establish policies to reduce these pollutants in the environment, respectively to assess the health risk due to its exposure. This study provides valuable information about pollution with three classes of POPs of a region of Romania in the last 100 years through their analysis in the aquatic core sediments of an alpine lake.

The results of the study show that the concentrations of these pollutants are directly related to human activities in the studied area and even if human settlements are relatively far away, pollutant emissions can affect areas at high altitudes. Thus, PAHs (range 2.53 - 156.27 ng/g) have pyrogenic pattern showing that they are generated by combustion and not by the spills of petroleum products. The OCPs (range 1.78 - 71.12 ng/g) could be connected with agriculture, while PCBs (range not detected - 76.03 ng/g) with industrial activities.

Moreover, even if the sources of POPs could be identified through the use of isomeric ratios, more studies are needed for a clearer understanding of the anthropogenic contribution to environmental pollution. In summary, this method is a good way to determine a historical deposition of POPs, and also to evaluate toxicological potential and their distribution in the environment.

EXPERIMENTAL SECTION

Area of study and samples collection

The glacial lake Muntinu is situated in Vâlcea county at an altitude of over 1900 meters, very near Transalpina road, at approximately 2 km away, and the nearest urban area of the city of Petrosani at about 30 km away (Figure 5). The maps presented in figure 5 were built using the ArcMap 10.8 software starting from the information from the database and created by vectorization and downloading information from GPS. The coordinates of the sampling point are 45°21'58"N and 23°39'14"E. This lake has no any tributaries, and it was formed naturally by precipitation and by the melting of glaciers.

Sediment sample was collected at the point of the lake discharge using a gravity corer of stainless steel material, with a sampling tube of 60 cm. Before the analysis, the samples were pre-treated and prepared in accordance with Begy et al. study [23].

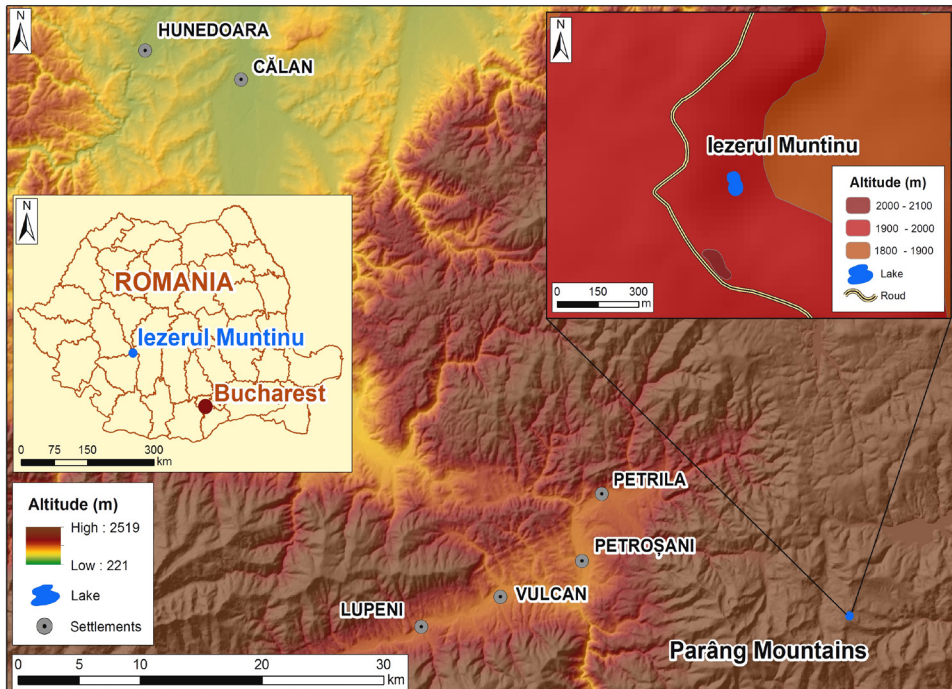


Figure 5. Map illustrating the geographical position of Lake Muntinu (Iezerul Muntinu)

Chemicals and reagents

For the qualitative and quantitative analysis, standard mixtures of different types of POPs were used. OCPs standard solution in concentration of 2000 µg/mL in hexane:toluene (1:1 v/v) (EPA CLP Organochlorine Pesticide Mix), and containing 20 compounds: Tecnazene, α-HCH, Hexachlorobenzene, γ-HCH, Quintozene, Heptachlor, Aldrin, Heptachlor exo-epoxide, Heptachlor endo-epoxide, Trans-Chlordane, 2,4'-DDE, α-Endosulfan, Cis-Chlordane, Dieldrin, 4,4'-DDE, 2,4'-DDD, Endrin, β-Endosulfan, 2,4'-DDT, 4,4'-DDT was provided by Supelco (Merck Romania SRL, Bucharest, Romania). PCBs mix congeners in concentration of 10 µg/mL, in heptane, containing a number of 12 PCBs: -18, -28, -31, -52, -44, -101, -114, -149, -153, -138, -180, -194 was obtained from Supelco (Merck Romania SRL, Bucharest, Romania). For PAHs, the standard solution with a concentration of 500 µg/mL, in acetonitrile:toluene mixture (92:8 v/v) was purchased from Restek (Restek Corporation, Bellefonte, United States), The mixture certified as CRM EPA Method 8310 PAH Mixture, contains a number of 16 compounds such as: Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenz[a,h]anthracene, Benzo[g,h,i]perylene, and Indeno[1,2,3-cd]pyrene.

For the quantification of OCs and PCBs, PCB-30 and PCB-155 were used as internal standards. As for PAHs, a surrogate standard (IS1) containing 4 deuterated compounds such as: Naphthalene-d8, Anthracene-d10, Fluoranthene-d10 and Perylene-d12, was used to assess the extraction recovery and another one (IS2) containing 3 deuterated compounds: Acenaphthene-d10, Phenanthrene-d10 and Chrysene-d12 for quantitative analysis of PAHs respectively.

For the extract purification step a purification open column containing from bottom to top silica, alumina and granular anhydrous sodium sulphate (200-300 mesh, Merck, Germany), activated at 450°C in a furnace for 6 h was used. For extract desulphurization, copper of < 425 µm size and 99.5% purity (Sigma-Aldrich, Merck, Germany), activated with hydrochloric acid (1 N) was used. The reagents used in the analysis were acetone, acetonitrile, dichloromethane, and hexane, acquired from Merck (Germany) and were all HPLC purity graded.

The Milli-Q water prepared using a Milli-Q-Plus ultra-pure water system from Millipore (Milford, MA, USA) was also used.

Instrumentation

The analysis of POPs was carried using Gas Chromatography, and depending on the nature of the compounds of interest, two types of analysis were carried-out. Gas chromatography-mass spectrometry (GC-MS) was used for the analysis of PAHs and gas chromatography – electron capture detector (GC-ECD) for OCPs and PCBs.

For PAHs analysis a Focus gas chromatograph equipped with a DSQII mass spectrometer operating in electron impact ionisation (EI) mode (70 eV), and a TriPlus Autosampler (Thermo Electron Corporation) was used. A capillary column model TR-5 MS (30 m x 0.25 mm i.d., 0.25 µm film thickness, Thermo) was used for the separation of the compounds, using a gradient temperature program of 60°C with holding time of 1 min, from 60 to 130°C with 10°C/min, from 130 to 300°C using 3°C/min and a holding time of 5 min at 300°C. Helium (99.999%) was used as a carrier gas with a flow rate of 1.2 mL/min. The identification of PAH compounds was achieved using the selected ion monitoring (SIM) mode and the comparison of relative retention times between sample and the standard solution. X-Calibur software was used for the acquisition of data.

As for OCPs and PCBs, the analysis process was performed by GC-ECD, using a gas chromatograph model Trace GC equipped with a ⁶³Ni electron capture detector, and a TriPlus Autosampler (Thermo Electron Corporation). For separation, a capillary column model HP-5MS (30 m × 0.25 mm i.d., 1.0 µm film thickness, Agilent) was used. The gradient temperature program was 70°C to 180°C at a rate of 25°C/min, from 180 to 200°C at 1°C/min, from 200 to 260°C at a rate of 2°C/min, and from 260 to 300°C at 5°C/min with a holding time of 5 min at 300°C. The carrier gas was nitrogen (99.99%) with a constant flow rate of 2 mL/min. The temperatures of the injector and detector were set at 270°C and 300°C. Identification of OCPs and PCBs compounds was based on the retention time of the standard mixtures. Acquisition of data was performed using Chrom-Card software.

Dating of sediments

Sediment samples have been collected using a gravity corer of stainless steel material, with a sampling tube of 60 cm. Before the analysis, the samples were pre-treated and prepared in accordance with Begy et al. study [23].

Using The CRS (Constant Rate of ²¹⁰Pb Supply) mathematical method by Appleby, 2001 [24], we determined the age and depth of the sediment column.

Gamma spectrometry was used for the analysis of radionuclides, using a HPGe detector from ORTEC, model GWL-120-15 type with a resolution of 2.08 keV for 1.33 MeV ⁶⁰Co and 1.1 keV for 122 keV ⁵⁷Co gamma lines. The detection limits for the radionuclides were the following: 7 Bq/kg for ²¹⁰Pb,

0.3 Bq/kg for ^{137}Cs and 0.5 Bq/kg for ^{226}Ra [25]. The associated dating errors are: one year for the period 2006-2015, two years for 1996 – 2006, three years for 1972 – 1996, four years for 1954 – 1972, five years for 1942 – 1954 and six years before 1942.

Extraction and purification of POPs

Extraction and clean-up procedure for POPs was performed in accordance to Barhouni et al. [21], but with small modifications. Approximately 4 g of homogenized dry sediment samples were placed into a 50 mL centrifuge tube and spiked with 100 ng each of multistandard mixture PAHs (IS1) and 20 ng PCB-30. 20 mL of acetone: hexane mixture (1:1, v/v) was added; the tube was capped and sonicated for 20 min in an ultrasonic bath. The mixture was centrifuged for 5 min at 4400 rpm and the solvent extract was transferred in a glass round flask of 100 mL. This procedure was repeated for two more times with 20 mL fresh solvent mixture. The final extract which contained all three extracts combined was concentrated to approximately 2 mL via rotary evaporation, mixed with 1 g of activated copper and left overnight for desulphurization. The following day, 10 mL of *n*-hexane was added, the copper was decanted away from the flask, and the extract was concentrated to approximately 2 mL with rotary evaporator and subjected to purification procedure.

For the purification step, a silica-alumina chromatograph column (15 mm i.d., made of glass) which contained from bottom to top, 3 g activated silica, 3 g activated alumina, and 1 g dehydrated Na_2SO_4 was used. This column was washed with 20 mL of *n*-hexane before use.

The ~2 mL concentrated extract was loaded onto the purification column and the target compounds have been eluted with 20 mL of *n*-hexane and 40 mL of *n*-hexane: dichloromethane (DCM) solution (80:20, v/v), concentrated to approximately 2 mL, dry evaporated under nitrogen stream and redissolved with 0.2 mL *n*-hexane:DCM solution (80:20, v/v). Before analysis, each sample was spiked with 100 ng each PAHs multistandard mixture (IS2) and 20 ng PCB-155.

The extraction and analyses procedure were validated in our previous study [21] using certified reference materials EC-3 (PAHs, PCBs and OCPs in marine sediments from Niagara River in Lake Ontario). The obtained recoveries ranging from $68.8 \pm 5.6\%$ to $110.1 \pm 2.9\%$ for PAHs, and from $89.8 \pm 10.7\%$ to $117.2 \pm 14.1\%$ for POCs and PCBs respectively [21].

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