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Distribution of the heavy metals in the soil and water matrix, a space-time overview from a lakes protected area

CATALIN MANEA^{1,2*}, NARCIS CLAUDIU SPINU^{1,2}, MIHAIELA DRAGHICI¹

¹National Research and Development Institute for Industrial Ecology - ECOIND, Ramnicu Valcea Branch, 182 Stirbei Voda Street, 240588, Romania

²Politehnica University of Bucharest, Splaiul Independentei 313, Bucharest, postal code 060042, Romania

*Corresponding author: catalin.manea@incdecoind.ro

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Abstract

The aim of this study was to evaluate the quality of environmental factors of soil and water in a protected area in Romania, namely the Preajba-Facai lake system in Dolj County. Highlighting the evolutionary aspects of the analysed quality parameters (20 physical-chemical indicators) on a spatial-temporal scale in order to establish geochemical thresholds is the final result of a larger project. The presented results were obtained through seasonal monitoring over a period of 3 years, which involves water and soil sampling and subsequent laboratory analysis. The results obtained were interpreted in relation to the legislation in force and through a more suggestive evaluation by calculating the pollution indices: the global pollution index (IPC) for water and the Nemerov synthetic soil contamination index. Following the field visits, additional information was brought, which contributed to a good knowledge of this region. The area, although protected, is influenced by the anthropogenic factors, which have a negative impact on the environment. In some cases, non-conformities were identified and validated through the analysis performed.

Keywords: *assessment, protected area, soil, water, heavy metals*

INTRODUCTION

Geochemical studies are a priority in many countries, considering the importance of applying the obtained results from some geochemical databases [1-7].

Research is being done in order to develop pollution indexing methods; for residential or agricultural areas, geochemical maps that illustrate the environmental risk index or graphs indicating the values above the admissible levels, in relation to the specific legislation are created [8].

In Europe, spatial and temporal variability is observed more in precipitation volume compared to temperature variations. In Northern Europe, precipitation has increased, especially in winter, while precipitation has decreased in Southern Europe, especially in summer. Protected areas cover biodiversity and ecosystems of high conservation value. In addition, these areas provide a variety of services (ecosystem services), both direct and indirect, to our societies and economies. The increase in average annual temperature would affect the current protected areas that hold certain species and the possibility of the disappearance of these species in the coming decades. Declines of certain species directly affect the maintenance of biodiversity which can lead to a decline in species and habitat diversity [9].

The human population growth intensified land use and increasing habitat fragmentation threaten global ecosystems and protected areas. It is of major importance to include the potential impact of

climate change on the design of future nature conservation strategies and the implementation of protected area management [10].

Objectives to stop the loss of biodiversity would be restoring the necessary habitat, reducing greenhouse gas concentrations and promoting/adapting society to climate change [11-17].

The abiotic factor that most strongly influences the physical, chemical and biological processes of the soil is considered the relief that is specific to each individual area [18-19].

In this context, the purpose of the present study was to obtain a series of geochemical thresholds, to monitor and highlight the relevant aspects of the soil and water.

The choice of the studied area was based on an integrative conceptual model that highlights the to The area is distinguished by a wide variety of flora and fauna specific to lake areas similar to the Danube Gorge Lake Complex, a miniature delta made by the Nera River at its discharge into the Danube, a reserve that gathers hundreds of rare specimens of flora and fauna, topographical, climatic and biological characteristics, compared evolutionarily on a temporal scale.

EXPERIMENTAL PART

The main characteristics of the studied area

The data of the report refer to the investigation and evaluation of the quality of the soil and surface waters on the Preajba-Facai lake system located in a protected area in Romania. Figure 1 shows the location of the area and sampling points for the Preajba-Facai lake complex.

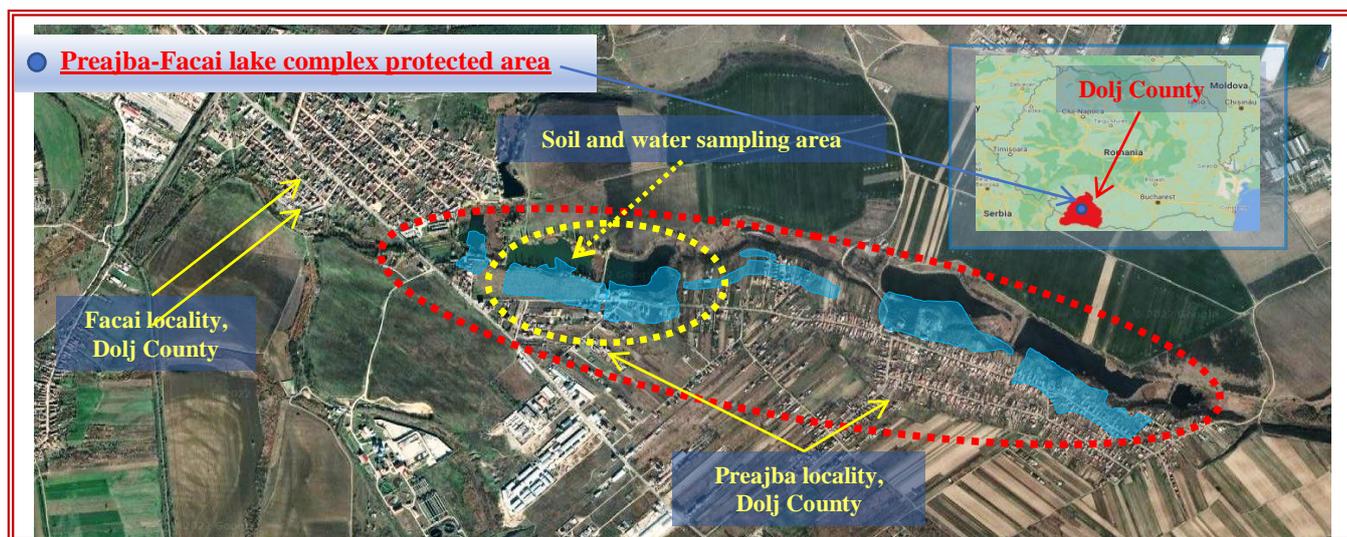


Fig. 1. Location of the protected area and sampling points for the Preajba-Facai lake complex (source of processing map: Google Earth, 2022)

The natural area is located in the central-eastern part of Dolj County, in the north of Preajba village, in the immediate vicinity of the DN55 national road, which connects the residence of the County, to the port of Bechet. The studied area was declared a protected area in 2000 and covers an area of 28 hectares, representing a lacustrine complex. The complex consists of five ponds, arranged in steps, permanently fed by strong springs. The ecological peculiarity of the area consists in a diversity of continental aquatic ecosystems (springs, streams, rivers, lakes and swamps), situated in a relatively small geographical space, each of them presenting specific characteristics to biocenoses, plant and animal populations. The flora and fauna of the reserve are specific to freshwater wetlands and their variety and abundance is favored by the abundance of water.

Surface water and soils sampling

All sampling points were precisely located with a GPS type Montana 610 Garmin, the data are presented in Figure 2. In addition, a number of sampling points located in areas outside the outer perimeter of the protected area were chosen to highlight anthropogenic pressures on the protected

area. A soil auger kit from Burkle and a telescopic spoon from the same supplier were used for surface water sampling.

Two surface water samples (A1, A2) and eight soil samples (S1 – S8) were collected from the Preajba-Facai lake complex. Table 1 shows the sample type and GPS coordinates of the sampling points.

Sampling techniques and methods of analysis have been performed in accordance with applicable national standards. The samples were uniquely labeled, properly preserved and brought to the laboratory for analysis in the same day.

The equipment used for the experimental studies was calibrated prior to testing, in accordance with applicable laboratory procedures.

Table 1. Sample type and GPS coordinates of sampling points

Sampling points	GPS coordinates	Sample type	Sampling points	GPS coordinates	Sample type
S1	44°16'13.24"N 23°49'35.37"E	soil	S6	44°16'17.73"N 23°50'31.43"E	soil
S2	44°16'13.39"N 23°49'39.69"E	soil	S7	44°16'7.57"N 23°50'59.72"E	soil
S3	44°16'13.07"N 23°49'46.19"E	soil	S8	44°15'56.32"N 23°51'24.47"E	soil
S4	44°16'11.94"N 23°49'49.60"E	soil	A1	44°16'12.43"N 23°49'43.69"E	water
S5	44°16'15.35"N 23°49'53.03"E	soil	A2	44°15'58.07"N 23°51'18.07"E	water

Methods applied

The methods used for the analysis of the studied indicators applied techniques such as: electrochemistry (multiparameter Thermo Scientific Orion Star A 215), gravimetry (Precise Balance XB, Memmert Oven), spectrometry (UV-Vis spectrometry - Specord 210 Plus and inductively coupled plasma optical emission spectrometry - ICP-OES Perkin Elmer Optima 5300DV). Analytical purity reagents were used for both water and soil characterization. The interpretation of the soil results was performed by comparison with the reference normal values in the specific legislation, respectively with the reference values for the traces chemicals in soil with sensitive land use, practically the most severe quality conditions established for land use [20, 21].

The threshold values and the limits for the ecological status classes of surface water bodies in the national legislation in force were used to interpret the results for the water samples [22].

For the surface water characterization, were analyzed the following indicators: pH, iron, aluminum, ammonium, nitrite, nitrate, cadmium, total chromium, copper, manganese, mercury, nickel, selenium, antimony, lead, zinc, COD, calcium, magnesium and sodium. For the statistical interpretation of significant water quality parameters, the global pollution index (CPI) was calculated [23].

The quality indicators analyzed for the soil were pH, humus, Kjeldahl nitrogen, iron, arsenic, barium, cadmium, cobalt, total chromium, copper, manganese, molybdenum, nickel, lead, selenium, antimony, vanadium, zinc and potassium. The evaluation of soil quality was carried out by reporting the concentrations of heavy metal results with the geochemical background value, obtaining soil pollution indices [24].

Statistical methods

The threshold values and the limits for the ecological status classes of surface water bodies in the national legislation in force were used to interpret the results for the water samples [20].

For the statistical interpretation of significant water quality parameters, the global pollution index (CPI) was calculated [21].

Pollution index according to CPI

The global pollution index (CPI) is used to assess the level of pollution in a given river basin by using monitoring statistics. The formula for calculating the CPI is presented as follows:

$$CPI = \frac{1}{n} \sum_{i=1}^n PI_i \quad (1)$$

where the CPI is the comprehensive pollution index;

n is the number of monitoring parameters;

PI_i = number of the pollution index i .

PI_i is calculated according to the following equation:

$$PI_i = \frac{C_i}{S_i} \quad (2)$$

where C_i is the measured concentration of the parameter in water;

S_i is the allowed limit concentration of the parameter according to environmental legislation CPI is classified into five categories:

1. Category 1: CPI from 0 to 0.20 (clean);
2. Category 2: CPI from 0.21 to 0.40 (sub clean);
3. Category 3: CPI from 0.41 to 1.00 (slightly polluted);
4. Category 4: CPI from 1.01 to 2.00 (polluted environment);
5. Category 5: $CPI \geq 2.01$ (highly polluted)

The interpretation of the soil results was performed by comparison with the reference normal values in the specific legislation, respectively with the reference values for the traces chemicals in soil with sensitive land use, practically the most severe quality conditions established for land use [22, 23].

The evaluation of soil quality was carried out by reporting the concentrations of heavy metal results with the geochemical background value, obtaining soil pollution indices [24].

The mathematical formula of the Nemerov comprehensive index method is:

$$PI_{Nemerov} = \sqrt{\frac{\left(\frac{1}{m} \sum_{i=1}^m Pi\right)^2 + Pi^2_{max}}{2}} \quad (3)$$

Pi is the single pollution index of a particular heavy metal, calculated as:

$$Pi = \frac{Ci}{Bi} \quad (4)$$

In which C_i represents the Heavy Metal (HM) content determined in the layer and B_i is the geochemical background value (the HM content in the parent material). Pi^2_{max} is the maximum value of a single pollution index of all HMs, and m is the number of heavy metals studied. [27]. In Table 4 it is presented the assessment of Nemerov synthetic contamination index applied to soil [27].

Table 4. The assessment of Nemerov synthetic pollution index applied to soil

Class	NCI (P)	Pollution Level
I	$P \leq 0.7$	excellent
II	$0.7 < P \leq 1.0$	clean
III	$1 < P \leq 2.0$	slightly polluted
IV	$2.0 < P \leq 3.0$	moderately polluted
V	$P > 3.0$	heavily polluted

RESULTS AND DISCUSSIONS

Quality of surface water and soil from Preajba-Facai lake complex

Figure 2 illustrates the graphical representation of the quality indicators of the sampled water.

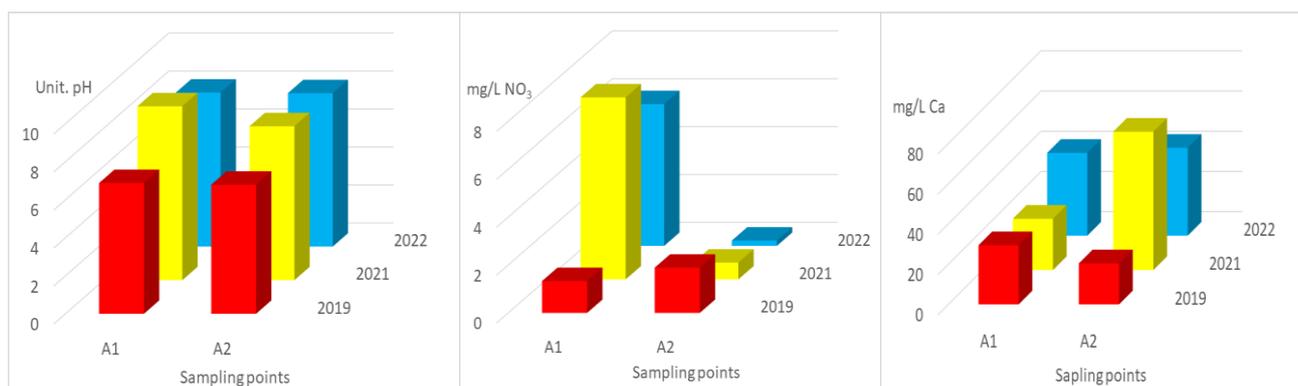


Fig. 2. Evolution of average values for quality indicators pH, nitrogen, calcium in the spring season of 2019/2021/2022 of the water

Regarding the results obtained, we mention the following: the pH values had a minimum of 6.79 pH units (2019) and a maximum of 9.15 pH units (2021). The normal range for pH imposed by legislation is 6.5 to 8.5. For the nitrogen parameter, the values ranged between 0.7 mg/L and 7.6 mg/L in the same year (2021), the values being between quality classes I and III for magnesium – 56.9 mg/L (2022) according to the legislation. Regarding the concentrations of the calcium indicator, they present a minimum of 20.4 mg/L in (2019) and a maximum of 68.8 mg/L in (2021) having the majority of the results only in quality class I [25].

Table 2 shows the values of the pollution indices by the method of calculating the global pollution index (CPI) obtained for the surface water quality parameters in the period 2019-2022 and the pollution category for the two sampling points [21].

Table 2. The values of the pollution indices by calculation of the global pollution index (CPI)

Parameter	Year	A1 – surface water		A2 – surface water	
		CPI	CPI Category	CPI	CPI Category
Nitrates	2019	0.44	CPI3	0.63	CPI3
	2021	0.68	CPI3	0.7	CPI3
	2022	0.53	CPI3	0.22	CPI2
Calcium	2019	0.58	CPI3	0.408	CPI3
	2021	0.51	CPI3	0.688	CPI3
	2022	0.82	CPI3	0.873	CPI3
Ammonium	2019	0.73	CPI3	0.51	CPI3
	2021	0.30	CPI2	0.05	CPI1
	2022	0.68	CPI3	0.737	CPI3
Nitrites	2019	0.63	CPI3	0.366	CPI3
	2021	0.46	CPI3	0.8	CPI3
	2022	0.59	CPI3	0.6	CPI3
Copper	2019	0.022	CPI1	0.014	CPI1
	2021	0.072	CPI1	0.072	CPI1
	2022	0.16	CPI1	0.135	CPI1
Nickel	2019	0.054	CPI1	0.041	CPI1
	2021	0.12	CPI1	0.12	CPI1
	2022	0.12	CPI1	0.12	CPI1
Lead	2019	0.034	CPI1	0.032	CPI1
	2021	0.2	CPI1	0.2	CPI1
	2022	0.2	CPI1	0.2	CPI1
Zinc	2019	0.025	CPI1	0.025	CPI1
	2021	0.31	CPI2	0.154	CPI1
	2022	0.039	CPI1	0.045	CPI1
COD-Mn	2019	1	CPI3	1	CPI3
	2021	0.026	CPI1	0.068	CPI1
	2022	0.5	CPI3	0.46	CPI3

Magnesium	2019	0.942	CPI3	0.911	CPI3
	2021	0.518	CPI3	0.988	CPI3
	2022	0.978	CPI3	0.526	CPI3
Sodium	2019	0.730	CPI3	0.699	CPI3
	2021	0.856	CPI3	0.898	CPI3
	2022	0.836	CPI3	0.872	CPI3

The other parameters analyzed in the water samples taken from this area have insignificant concentrations and for this reason were not interpreted.

The graphical representation of the soil quality indicators is presented in Fig. 3. The obtained results indicate the following conclusions: the pH value is between 5.9 (2019) and 8.86 (2021) pH units. The pH being in a slightly acidic range; the minimum obtained for the humus indicator is 0.24 % (2022) and the maximum is 1.99 % (2019), the concentrations of the lead quality indicator vary between 7.45 mg/Kg d.m. (2021) and 32.17 mg/Kg d.m. (2019), the results obtained being in normal values according to the legislation.

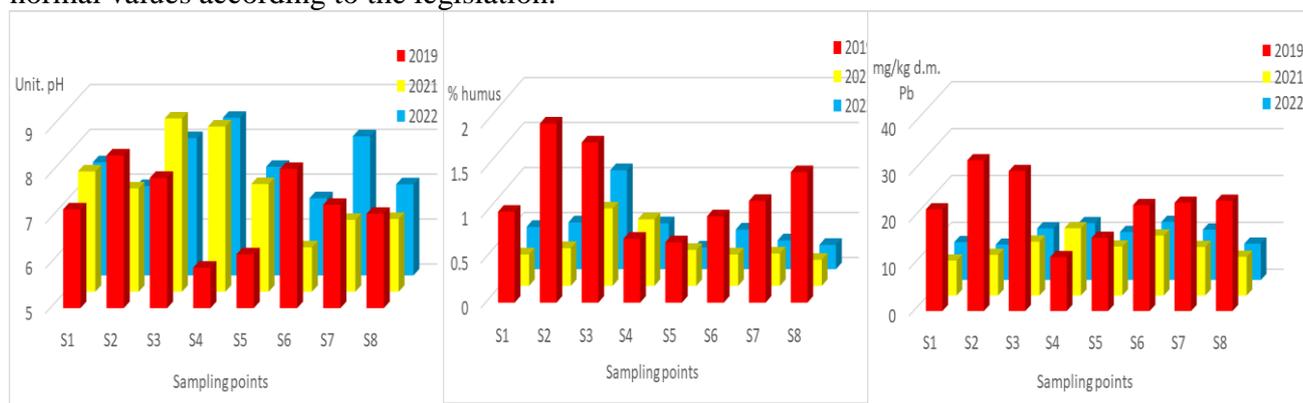


Fig. 3. Evolution of average values for quality indicators pH, humus, lead in the spring season 2019/2021/2022 of the environmental factor soil

After the analyzes carried out, no concentration values were identified that exceed the limit of sensitive use of the soil.

Table 3 shows the calculation of the soil pollution indices obtained for heavy metals in the period 2019-2022 and the pollution category for the eight sampling points [26].

Table 3. The calculation of the soil pollution indices obtained for heavy metals

Soil Samples	Year	HM											
		Cd		Cr		Cu		Pb		Ni		Zn	
		Pi	PL	Pi	PL	Pi	PL	Pi	PL	Pi	PL	Pi	PL
S1	2019	1.48	III	0.59	I	1.0	I	1.01	III	1.14	III	2.07	IV
	2021	1.4	III	0.22	I	0.4	I	0.35	I	0.5	I	0.39	I
	2022	1.25	III	0.22	I	0.4	I	0.35	I	0.5	I	0.39	I
S2	2019	2.84	IV	0.29	I	0.95	II	1.53	III	0.70	I	2.30	IV
	2021	3.6	IV	0.16	I	0.29	I	0.41	I	0.25	I	0.28	I
	2022	3.0	IV	0.16	I	0.29	I	0.41	I	0.25	I	0.28	I
S3	2019	2.18	IV	0.40	I	1.23	III	1.41	III	0.61	I	1.76	IV
	2021	2.8	IV	0.20	I	0.57	I	0.55	I	0.36	I	0.64	I
	2022	2.8	IV	0.20	I	0.58	I	0.55	I	0.37	I	0.64	I
S4	2019	1.96	III	0.76	II	1.19	III	0.56	I	1.07	III	2.06	IV
	2021	1.4	III	0.26	I	0.51	I	0.69	I	0.53	I	0.72	II
	2022	1.35	III	0.26	I	0.51	I	0.68	I	0.53	I	0.72	II
S5	2019	2.18	IV	0.86	II	1.25	III	0.74	II	1.24	III	2.17	IV
	2021	1.3	III	0.19	I	0.5	I	0.5	I	0.43	I	0.54	I
	2022	1.35	III	0.19	I	0.5	I	0.5	I	0.44	I	0.55	I
S6	2019	1.16	III	0.68	I	1.03	III	1.09	III	0.70	I	2.06	IV
	2021	1.45	III	0.21	I	0.5	I	0.59	I	0.58	I	0.42	I
	2022	1.5	III	0.21	I	0.5	I	0.60	I	0.58	I	0.42	I

S7	2019	1.2	III	0.70	I	1.11	III	1.10	III	0.85	II	1.51	III
	2021	1.5	III	0.16	I	0.36	I	0.495	I	0.41	I	0.33	I
	2022	1.65	III	0.16	I	0.36	I	0.49	I	0.40	I	0.33	I
S8	2019	1.92	III	0.66	I	0.99	II	1.15	III	0.78	II	1.72	III
	2021	1.3	III	0.17	I	0.30	I	0.41	I	0.32	I	0.24	I
	2022	1.25	III	0.17	I	0.30	I	0.39	I	0.32	I	0.24	I

* **Pi** - Pollution index; **PL** - Pollution Level; **HM** - Heavy Metal.

Evaluation of soil pollution indices led to the conclusion that the area falls into category IV - moderately polluted.

CONCLUSIONS

The present paper showed the results obtained following the monitoring of water and soil environmental factors in the Preajba-Facai lake complex, by applying formulas to calculate the quality indices. The assessment of the quality of environmental factors aims to identify sources of pollution and develop a strategy for the sustainable management of water sources, maintaining and promoting human health and other social aspects and economic growth.

The calculation of the CPI pollution index for surface water in the two sampling points frame the Preajba-Facai lake complex in category 3 - slightly polluted. The values of the CPI pollution index show variations depending on the season.

In the case of the soil environmental factor, the results of the concentrations of heavy metals determined in the eight investigated areas of the Preajba-Facai lake complex by means of the Nemerow contamination indices highlighted their inclusion in the III and IV quality classes, i.e. slightly polluted and moderately polluted. The non-compliant aspects of this protected area consist of: the lack of adequate management that does not ensure the security of the area and a controlled access, therefore areas of uncontrolled waste storage are identified. The lake area has a degraded appearance with visible traces of eutrophication.

The evaluation of the water and soil environmental factors in the studied protected areas is important for highlighting and quantifying the evolutionary aspects regarding their quality.

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