Quality Assessment of Some Freshwater Resources Located in Bucharest and Surrounding Areas

I. Water Quality Assessment of Herastrau, Pantelimon and Mogosoaia Lakes

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The quality assessment of the aquatic environment from some freshwater resources situated in Bucharest and Ilfov County - Romania has been performed in an extended study and data obtained will be presented in several papers. This first paper presents a case study on water quality assessment of the Mogosoaia, Herastrau and Pantelimon Lakes, lakes built on the Colentina River. Two water and sediment sampling campaigns were conducted in the summer and autumn 2016, 29 specific parameters were determined for water samples and heavy metals content for sediment samples. The obtained results for water samples allowed the classification of lakes water in quality classes and the heavy metals values for sediments were compared to the standards of chemical quality, according to the national legislation M.O. 161/2006. Furthermore, for an overview of water quality, the Water Quality Index (WQI) method was used, where the indicators were grouped into two categories: the first category took into account 18 quality parameters (WQI-1) and the second considered heavy metals content (WQI-2).

Keywords: Water quality parameters, Water Quality Index, Water pollution

Water quality is a global issue as it is considered a key factor in ensuring human health [1-3]. The increase of the degree of urbanization, industrial progress and the diversification of the chemical structure of products has led to pressures on water resources [4]. The disruption of natural equilibrium of an aquatic ecosystem due to natural and anthropic causes may have unpredictable effects on the evolution and existence of that ecosystem. The freshwater ecosystem is an essential element for the survival of living organisms and for providing numerous goods and services, such as: drinking and irrigation water, industrial activity, fishing and recreation [5, 6], therefore its contamination with different chemical contaminants is one of the main environmental issues nowadays [7]. Anthropic activities (agriculture, industry and urban activities that may generate heavy metals, pesticides, nutrients and other pollutants) are the major pollution sources for the freshwater ecosystems [8]. Thus, monitoring of water quality is a requirement for the efficient management of water resources and preservation of aquatic biodiversity [9, 10].

For the assessment of water quality, a series of physicochemical indicators may be considered. At national level, according to the legislation, the indicators for the characterisation of water quality are classified in 5 main groups: thermal regime and acidification (temperature (T) and hydrogen ion concentration (pH)), oxygen regime (dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD)), nutrients (ammonia (NH₄-N), nitrates (NO₃-N), nitrates (NO₂-N), total nitrogen (TN), phosphates (PO₄-P), total phosphorus (TP), Chlorophyll a (Chl a), salinity (conductivity (EC), filterable residue (TDS), chloride (Cl), sulphates (SO₄²⁻), sodium (Na⁺), calcium (Ca²⁺), magnesium (Mg²⁺)), specific toxic pollutants of natural origin (total chromium (Cr), copper (Cu), zinc (Zn), arsenic (As), barium (Ba), selenium (Se), cobalt (Co), lead (Pb), cadmium (Cd), iron (Fe), mercury (Hg), manganese (Mn) and nickel (Ni)) and other relevant chemical indicators (phenols, methylene blue active substances (MBAS), halogenated organic compounds (AOX)) [11].

Water temperature is one of the most important characteristics of an aquatic system as it has major influence on biodiversity of aquatic species, on the concentration on dissolved oxygen, on the chemical and biological processes and on the stratification and density of water [12, 13].

Hydrogen ion concentration influences the photosynthetic activity of aquatic plants, the dissociation of salt molecules in water favouring the action of some toxic substances, the respiration of aquatic organisms, etc. [13].

Oxygen regime. Oxygen and carbon dioxide are the prevalent gases in river water, and their concentration varies based on their solubility. Dissolved oxygen is an indicator of the equilibrium between the generating oxygen processes and oxygen consuming processes and it is affected by a series of factors, such as: oxygen depletion, sources of oxygen and other water quality parameters [13, 14]. DO and BOD are indicators of pollution caused by organic matter and affect the self-cleaning of water [15]. The available studies have proven that DO is a limiting factor as regards the life of aquatic organisms and causes the populating of the aquatic ecosystems [16]. Chemical oxygen demand is an important parameter in the assessment of organic pollution and represents the quantity of substances that may be oxidised: it may be analysed with methods employing potassium dichromate (CODₗ) or potassium permanganate (CODₘₚ) [17].

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Salinity. The main metallic cations dissolved in water are sodium, potassium, calcium and magnesium, while carbonates, chlorides and sulphates are among the most important anions. Conductivity is a rapid method for determining the dissolved substances, and high values of conductivity are an indicator of high concentrations of dissolved ions in water [18].

Nutrients regime. In aquatic ecosystems, the main biogenic elements are nitrogen compounds (nitrites, nitrates, ammonia and total nitrogen), phosphorus ions (phosphates, total phosphorus) and Chlorophyll a. The increase of nutrients content in natural waters favours the occurrence of the eutrophication process - excessive growth of algae and other aquatic plants [19, 20]. Despite the progress in controlling the primary pollution within the municipal and industrial wastewater treatment plants, the secondary pollution, such as eutrophication, aggravated continuously during the last years and became a significant issue as regards the biodiversity of freshwater ecosystems [21].

Pollutants of natural origin. The environmental contamination with metals and metallic compounds is an important global issue due to their toxicity and bioaccumulation potential [22]. The presence of heavy metals in the environment is mainly due to industrial and agricultural activities, and also to wastewater discharge [23]. The pollution of aquatic ecosystems with this type of pollutants may reduce the biodiversity of the ecosystem [12, 24].

Other relevant chemical indicators. The presence of phenols in surface water is caused by the effluents resulting from various sources such as chemical industry, oil refineries, and dry distillation of wood or municipal wastewater discharge [25]. Detergents play an important role in reducing water quality and they may result from the discharge of wastewater from residential areas, agricultural leakages or different industrial effluents [26].

The present case study is focused on the quality assessment of the waters and sediments from Mogosoaia, Herastrau and Pantelimon II Lakes, lakes built on the Colentina River, the first two located in Bucharest and the last in Ilfov County.

Experimental part
Study area and sampling
The three studied lakes, Mogosoaia, Herastrau and Pantelimon II, are part of a chain of 15 lakes formed along the Colentina River, a tributary of the Dambovita River with a total length of 98 km, of which 37.4 km within the city of Bucharest [27, 28]. The first stage of water and sediments quality assessment study was the two sampling campaigns conducted in July 2016 (CI) and September 2016 (CII), respectively. In order to evaluate the transversal fluxes of pollutants, two sampling sections were established for each lake, respectively the inlet (SI) and the outlet (SII) of the lake, the initial letter of the lake being also assigned to each section. Therefore, for the Mogosoaia Lake the sample sections were SI-M and SII-M, for the Herastrau Lake, SI-H and SII-H and for the Pantelimon Lake, SI-P and SII-P (Fig. 1).

Water samples were collected in polyethylene recipients (3 L) from approximately 30 cm under the water surface and were kept at 4°C during their transportation to the laboratory, according to an internal sampling procedure elaborated in agreement with the in force standards [29-32]. In situ measurements were performed for the determination of unstable parameters: temperature, pH, conductivity and dissolved oxygen.

Sediment samples were collected in polyethylene recipients, previously washed with detergent and rinsed with distilled water, according to an internal sampling procedure developed in agreement with the in force standards [33].

The determination of quality parameters
The following 29 physicochemical parameters were determined for water samples: T, pH, EC, turbidity, DO, CODcr, CODmn, BOD, TDS, Cl-, Ca2+, Mg2+, Na+, NH4-N, NO3-N, NO2-N, TN, TP, PO4-P, phenol index, MBAS, Cd, Pb, Cu, Cr, Ni, Zn, Mn, Fe. For sediment samples, the following heavy metals were determined: Cd, Pb, Cu, Cr, Ni, Zn and Hg. All reagents used for the determination of the physicochemical parameters were of analytical purity and their determinations were performed using standardized methods of analysis [34-52].

Calculation of Water Quality Index Method (WQI)
An overview on the quality of monitored water was obtained through the calculation of the Water Quality Index (WQI), when a number of n physicochemical quality parameters are reduced to a single number [53]. WQI was calculated from the point of view of using the surface water for human consumption [54]. In the present case, the...
grouping of the parameters in two categories was performed: Group 1 (easily treated parameters) included 18 parameters: pH, EC, DO, COD\textsubscript{cr}, COD\textsubscript{mn}, BOD, TDS, Cl\textsuperscript{-}, Na\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{-}-N, NO\textsubscript{3}\textsuperscript{-}-N, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, TN, TP, PO\textsubscript{4}\textsuperscript{-}P, phenol index, MBAS and Group 2 (heavy metals) included: Cd, Pb, Cu, Cr, Ni, Zn and Fe. For WQI calculation the following equations have been applied [54-57]:

\[ WQI = \frac{\sum_{i=1}^{n} Q_i W_i}{\sum_{i=1}^{n} W_i} \]  
\[ Q_i = \frac{100 \left( V_i - V_0 \right)}{S_i - V_0} \]  
\[ W_i = \frac{1}{S_i} \]

where: \( Q \) = sub-index for \( i \)-th water quality parameter, \( W \) = weight associated with \( i \)-th water quality parameter, \( n \) = number of water quality parameters, \( V_i \) = estimated concentration of \( i \)-th parameter in the analysed water, \( V_0 \) = the ideal value of this parameter in pure water (\( V_0 = 0 \), except \( \text{pH} = 7.0 \) and \( \text{DO} = 14.6 \) mg/L) and \( S_i \) = recommended standard value of \( i \)-th parameter.

The weightage unit (\( W_i \)) of each parameter was calculated a value inversely proportional to the standard (\( S_i \)), respectively the quality class I according to the national legislation (M.O. 161/2006) [11]. From the computed WQI values, waters are classified into five classes, namely excellent water - Class I (WQI<50), good water - Class II (50>WQI>100), poor water - Class III (100>WQI>200), very poor water - Class IV (200>WQI>300) and water unsuitable for drinking - Class V (WQI>300) [55, 58, 59].

Results and discussions

Water quality assessment

The assessment of the water quality sampled from the established sampling sections for the three lakes and the classification in quality classes was performed according to the national legislation [11]. The main quality indicator for thermal regime and acidification is the concentration of the hydrogen ions (\( \text{pH} \)). The values of \( \text{pH} \) recorded during the two sampling campaigns were within the limits provided by the aforementioned order. In the first campaign, the values of \( \text{pH} \) ranged between 7.31 - 7.62 and in the second campaign between 7.48 - 8.04. The thermal regime varied in the first campaign (summer time) between 24.5 - 26.4°C and in the second campaign (autumn time) between 19.8 - 20.1°C.

Figure 2 presents the quality classes for water quality derived from indicators of oxygen regime (COD\textsubscript{cr}, COD\textsubscript{mn} and BOD) geo-referenced for all 6 sampling sections of the studied freshwater ecosystems. The minimum value for DO was 7.14 mgO\textsubscript{2}/L was determined in SI-P in the first campaign, and the maximum value was 9.79 mgO\textsubscript{2}/L and determined in SII-P in the second campaign. The values for COD\textsubscript{cr} varied from 9.28 mgO\textsubscript{2}/L to 31.48 mgO\textsubscript{2}/L, for COD\textsubscript{mn} between 3.84 - 9.75 mgO\textsubscript{2}/L and the values for

**Table 1**

| Parameter | Methods |
|-----------|---------|
| T         | Thermometric |
| pH        | Potentiometric |
| EC        | Turbidimetric |
| Turbidity | Standard reflux dichromate method |
| COD\textsubscript{cr} | Standard permanganate method |
| COD\textsubscript{mn} | Incubation, Winicke titration |
| BOD       | PO\textsubscript{4}-P |
| DO        | Phenol index |
| Cl\textsuperscript{-} | MBAS |
| Ca\textsuperscript{2+} | Atomic absorption spectrometry |
| Mg\textsuperscript{2+} | |
| TN        | |

Fig. 2. Water quality classes for the indicators COD\textsubscript{cr}, COD\textsubscript{mn} and BOD geo-referenced for each sampling section.
BOD have recorded a minimum of 1.54 mgO₂/L in the SI-M section and a maximum of 7.67 mgO₂/L in the SII-P section.

From the analysis of figure 3, it may be noticed that for the Mogosoaia Lake, the oxygen consumption determined by the dichromate method (CODₐ) recorded values specific to the quality Class II for water samples collected in CI and values specific to Class III of water quality for the water samples collected from section SI-M. Also, the values for BOD in CII were within the Class III of water quality. For the Herastrau Lake, the values of CODₐ were within the quality Class II. For the Pantelimon II Lake, the values obtained in CI were within the quality Class II and for CII, the values for CODₐ and BOD were within the quality Class III.

From the point of nutrients regime, the values for NH₄-N varied in the range 0.15 mgN/L (SI-P, CII) - 0.95 mgN/L (SII-H, CI). The presence of the ammonium ion in natural water may be due to the decomposition of organic substances in anaerobic conditions and in the presence of bacteria or to the reduction of nitrite ions. The values of NO₂-N ranged between 0.01 - 0.30 mgN/L, generally, the higher values being determined in the autumn (CII). The values of NO₃-N determined in the 6 sampling sections varied in the range 0.01 - 0.09 mgN/L and within the quality class I for all three studied lakes. The analysis of total nitrogen showed a great variation of the concentration range for all 6 sampling sections (0.82 mgN/L in the SI-M section and 3.69 mgN/L in the SII-P section). As to the values of PO₄-P and TP, they ranged between 0.02 - 0.31 mgP/L and respectively 0.05 - 0.36 mg/L, with maximum values for section SI-M, CII. Figure 3 shows the quality classes for the 6 sampling sections in both sampling campaigns.

According to figure 3, the values recorded for the Mogosoaia and Pantelimon Lakes were specific to quality Class IV for nitrites content and quality Class III for phosphates (the Mogosoaia Lake) and ammonia (the Pantelimon Lake). The values for nitrites were also reported by Ionescu et al. (2012) [60]. For the Herastrau Lake, values specific for the quality Class III were recorded only for ammonia. Figure 4 shows the quality classes for the indicators relevant to salinity (TDS, Cl⁻, SO₄²⁻, Ca²⁺, Mg²⁺, Na⁺).

Although salinity indicators illustrate the presence of naturally occurring substances and are not pollution indicators, their classification in quality classes was performed in this paper and values specific to the quality classes I-II were obtained. The values of conductivity and turbidity in the 6 sampling sections ranged between 430 - 504 mS/cm, respectively 4.00 - 20.70 NTU.

As to the regime of toxic pollutants of natural origin, the total concentrations of the following heavy metals were determined: Fe, Mn, Zn, Cu, Pb, Cr, Ni and Cd. As seen in figure 5, the values for the concentrations of Cd, Zn, Cu, Pb, Cr and Fe were specific to the Class I of water quality. The
values for Ni were specific to quality Class II for the Pantelimon Lake. The values for Mn were specific to Class I-II of water quality for the Mogosoaia and Herastrau Lake, and to Class I-III of water quality for the Pantelimon Lake. Figure 6 shows the quality classes for phenol index and MBAS.

From figure 6, it may be noticed that the values of MBAS were within the quality Class I in both sampling campaigns. The values of phenol index in CI were within the quality class I for all 6 sampling sections, while the values obtained in CII were within the Class II of water quality for all the sampling sections, except for SII-P, for which the values were within the quality Class III.

Assessment of Water quality based on Water quality Index (WQI)

For the calculation of WQI, the indicators were classified in two groups: Group I included 18 physicochemical water quality indicators (pH, EC, DO, COD Cr, CODMn, BOD, TDS, Cl, Na+, NH4-N, NO3-N, Ca2+, Mg2+, TN, TP, PO4-P, phenol index, MBAS) and WQI-1 was calculated (fig. 7) and Group II included heavy metals (Cd, Pb, Cu, Cr, Ni, Zn and Fe) and WQI-2 was calculated (fig. 8).

The values of WQI-1 varied between 54.72 (SI-H) - 177.99 (SII-P) for water samples collected in the first campaign and between 53.08 (SII-H) - 246.24 (SI-M) for water samples collected in the second campaign. As seen in figure 7, generally the quality of water collected in the
first campaign (CI) was within the good water class, except for SI-P which was within the poor water class. For the second campaign (CII), WQI-1 values specific to very poor water class were obtained for SI-M, and to poor water class for SI-P, while for the rest of the sections values specific to good water class were obtained.

From the point of WQI-2 values (heavy metals), variations between 18.93 (SII-M) - 45.06 (SI-M) were recorded for the first sampling campaign and between 12.71 (SI-P) - 43.29 (SII-H) for the second campaign. The values were within the first quality class, namely “excellent water” (fig. 8).

Assessment of sediment quality
Figure 9 shows the variation of heavy metal concentrations (Cd, Pb, Cr, Cu, Ni, Zn and Hg) from sediments and their comparative analysis with the chemical quality standards provided by the national legislation (M.O. 161/2006) [11].

The comparative analysis of the values of Cd, Pb, Cr, Cu, Ni, Zn and Hg determined in the sediment samples and the chemical quality standards provided by M.O. 161/2006 highlighted the following aspects: the values of Cd, Cr and Hg were lower than the quality standards; Ni showed slightly higher values in CI compared to CII and slightly exceeded the quality standard in SII-M; similarly, Zn showed higher values in CI and exceeded the quality standard in SII-H; the values of Cu exceeded the quality standard in SI-M and SII-H for the samples collected in CI and in SI-P for the samples collected in CII; the values of Pb exceeded the quality standard in SII-H for CI and insignificant exceeding was observed for SI-P and SI-P in CII. Since the values of the heavy metals were generally lower than...
the quality standards, they have no potential for developing pressures on the aquatic environments.

Conclusions

The quality assessment of the aquatic environment from some freshwater resources situated in Bucharest and Ilfov County - Romania was performed in an extended study and data obtained will be presented in several papers. For water samples, 29 quality parameters were determined and for the sediment samples, the heavy metals content was evaluated. The obtained results highlighted specific values to water quality class I-IV. Specific values for water quality class IV were recorded only for nitrates in water samples collected from the Mogosoaia and Pantelimon II lakes. Also, the values of WQI-I have fallen within the very poor water class for SI-M (CI2) and within the poor water class for SI-II-P (CI2). The quality assessment of the sediments highlighted slight exceeding in the case of Zn, Cu and Pb content for the samples collected from SI-H in the summer campaign (CI).

These results show the need of permanent monitoring of water quality for freshwater located in Bucharest and surrounding areas as a priority in the efficient management of these water resources and in timely adopting the required legislative measures.

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