

ORGANIC AND INORGANIC CONTAMINANTS IN THE BAHLUI RIVER IN THE BUILT-UP AREA OF IASI CITY

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Abstract

The physico-chemical composition of Bahlui river water depends on number of factors such as: geochemical nature of river bed, rainfalls, as well as anthropogenic activities. This study highlights the seasonal dynamics of water quality due to the presence of organic and inorganic contaminants in the urban sector of Bahlui river. The main tributaries of the Bahlui river, which cross through the Iasi city, are from the north: Rediu, Căcaina, Cîric, and from south: Nicolina, the last one being the longest tributaries the Bahlui river receives. There were taken samples during different seasons: summer, winter, autumn and spring, between December 2010 to October 2011, indicating a seasonal variation. The most important analysed physico-chemical indicators were: pH, electrical conductivity, turbidity, the chemical regime of oxygen (DO, chemical oxygen demand (COD) and biological oxygen demand (BOD), indicators of the mineralization degree (chlorides, sulphates, phosphates), hardness, alkalinity, organic and inorganic contaminants (heavy metals, nitrogen compounds - nitrate, ammonium). Laboratory analysis revealed that rivers entering the town with some original features, which then decays, reaching the river collector (Bahlui river) with different characteristics influencing quality. Concentration of contaminants in surface waters can vary depending on runoff caused by rainfall. The water from Bahlui River are affected by multiple pollution sources originating from industrial, residential and agricultural, located in densely populated areas. High turbidity levels are associated with the presence of a large number of microorganisms, reflected by the consumption of oxygen. Inorganic pollutants from human activities, such as former steel industry - CUG Iasi, affect the crossing river quality heavy metals being characterised by remaining action. For evaluation of both chemical variation as well as seasonal effect on the variables, box and whisker plots were performed. Connections among different sampling points were put into evidence by dendrogram, cluster analysis clearly grouped the monitoring sites in five regions with different pollution levels. The statistical evaluation of data yielded very useful information concerning water quality being a very useful tool for a better water resources management.

Keywords: Organic and inorganic contaminants, Iasi city, multivariate and cluster statistical analyze.

1. INTRODUCTION

Water resources contamination represent one of the major concern of the modern world, after scientific and technical development that generate numerous contaminants, organic and inorganic, with different action on environment, including surface waters, more vulnerable, due to the larger area of the river basin with different land-use and anthropic activities, that represent point and non-points contaminants sources for water.

Bahlui drainage basin is located in the north-east part of Romania, crossing more urban areas that represent a major source of contamination of the surface water, due to the spatio-temporal variability and main activities developed in each city, the largest being Iasi city. In this case, Bahlui river were frequently affected by the human activities as agriculture, industry, residential areas and others areas of the city. The monitored section has 14 km length, that is located in the third lower section of the river basin, before the confluence with Jijia river.

Water quality of the Bahlui river was studied over decades, including last decade in various studies, in accordance with legislation of the country and of the European Union, as member, highlight that the seasonal studies were not realized and not correlation between contaminants realized.

Recent studies of water quality reveal water quality degradation that fit in lower quality classes (Crăciun I. & all 2004, Giurma I. & all 2007, Benchea & all, 2010), different types of contaminants (organic – Neamtu & all, 2009, inorganic – Horaicu & all, 2009, Seliman & all, 2009, Oişte & Breabăn, 2011), studies realized for urban area of Iasi city. The impact of urbanized area were revealed in all studies, by the differences between first sampling point located before the city and the last point located after the river cross the city, the registered values being significantly higher, and also showing the influence of tributaries, specially of Nicolina river, that is the main Bahlui river tributary on the south of built-up area of Iasi city.

1.1 Methodology

Sampling points (figure 1) were established after field observations concerning the examination of the drains, minor riverbed morphology and uniform distribution for each urban area crossed by the river. The distance between points vary between 0.5 km and 1 km. After sampling, the water samples were analyzed in the department laboratory.

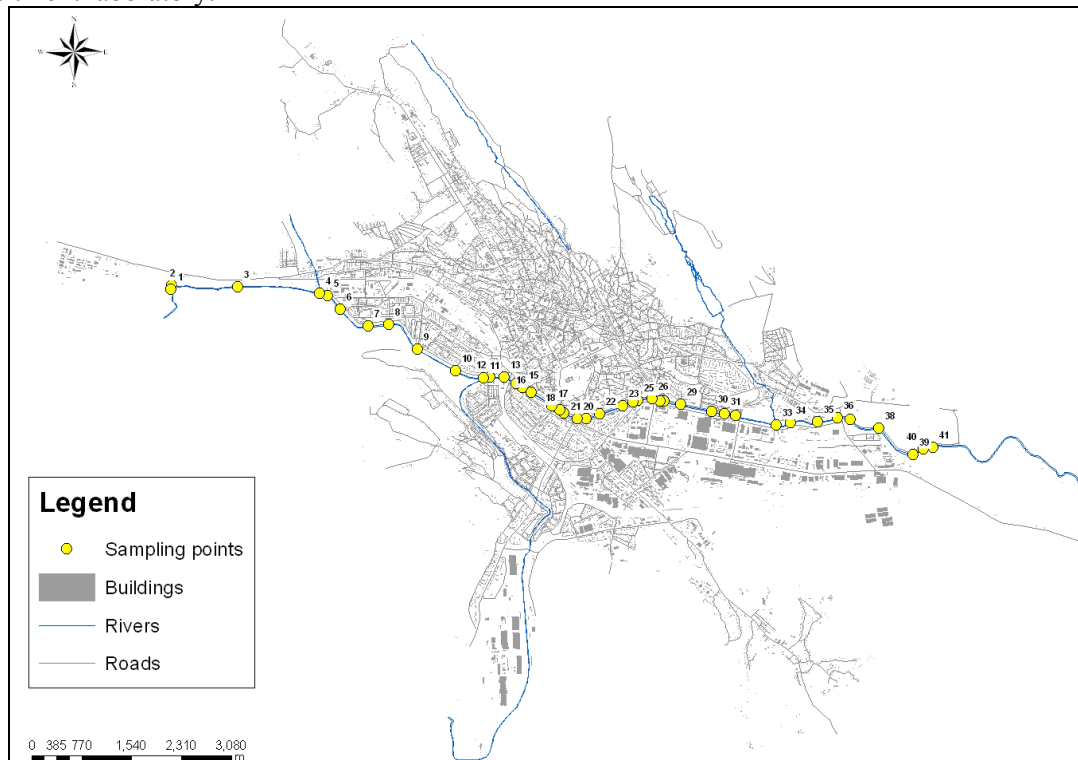


Figure 1. Sampling points location of Bahlui river

More physical and chemical parameters that interact with organic and inorganic contaminants, as pH, electrical conductivity, turbidity, the oxygen regime (DO, COD – CCO Mn oxygen consumption and BOD); chlorides, nitrates, as well as heavy metals.

The pH, electrical conductivity and chlorides measurements were made by potentiometric methods with a Multi 350i/SET WTW multiparameter instrument. For dissolved oxygen levels and biological oxygen demand, Winckler method were used and for chemical oxygen consumption the potassium permanganate method by titrimetric determination. Spectrophotometric method were used, according to ISO standard, with phenoldisulfonic acid for nitrates and for calibration plot, were used reference solutions with concentrations between 5-50 $\mu\text{g/mL}$, using a Shimadzu UV 1601 spectrophotometer at a wavelength of 410 nm for nitrates, and heavy metal ions were analyzed using atomic absorption spectrometry in air acetylene flames in the hydrochloric solution obtained after the digestion (ICPA-Bucharest methodology).

Results were statistically analyzed, for characterization and interpretation which involve processing a large number of data. Multivariate statistical analysis is a powerful instruments in order to identifying similarities and dissimilarities among the variables existing in the water (Giridharan L., & all. 2009).

In this study data was evaluated using cluster analysis. Hierarchical cluster analysis represent an straight technique that performs the identifying natural groups from data. Using the Ward's method it is possible to classifies the results into clusters based on their nearness obtained through Euclidian distances. The final product created is represented by a dendrogram. To generate the dendrogram XLSTAT software were used, showing the correlations established between the studied indicators, highlighting the organic and inorganic contaminants and it variation.

1.2 Results and discussions

The results for the variation during the seasons are summarized for each parameters in the box-and-whisker plots in figure 2 to 7. In these plots, the edges of a box are the quartiles, the horizontal center line is the median, and the horizontal thin black lines are the maximum and minimum values.

Organic contaminants presence is revealed by the oxygen regime in surface waters, studied in three parameters: dissolved oxygen, biological oxygen demand after five days and chemical oxygen consumption. First parameter, dissolved oxygen (fig 2) mean value for all period 9.82 ± 0.36 mg O₂/L show that it fit in first quality class, with seasonal variation, with higher values on winter, when the rate of decomposition of organic substances were lower, high flow and low temperatures, and lower values on summer when were registered the opposite situation. It is important for respiration by aquatic animals, decomposition, and various chemical reactions that consume oxygen, and can be harmful by the small amount, due to fluctuating levels seasonally and over a 24-hour period.

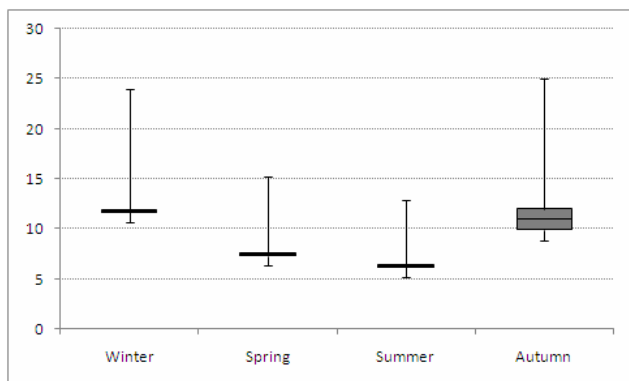


Figure 2. Box-and-whisker diagram for dissolved oxygen and seasonal variation

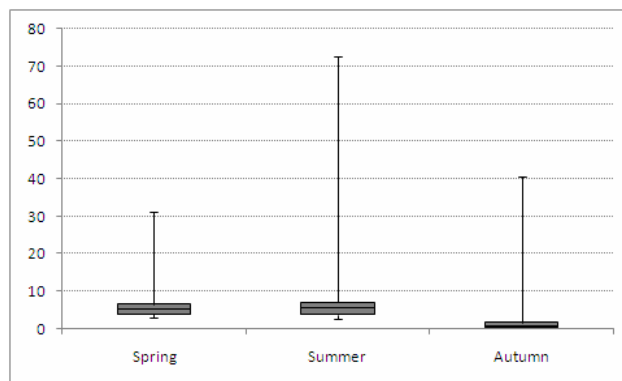


Figure 3. Box-and-whisker diagram for biological oxygen demand after five days and seasonal variation

Second parameters, biological oxygen demand after five days (fig 3) represent the amount of dissolved oxygen needed by aerobic biological organisms from the water to break down organic material present in a given water sample at certain temperature over a specific time period. Mean value 6.83 ± 5.86 mg O₂/L fit into third quality class, with fluctuation during the season, with higher values on summer, according to the larger number of aquatic organisms existing in the water. It can be also related to the nitrates content of water body that contribute to high BOD levels, because they are plant nutrients and can cause plant life and algae to grow quickly.

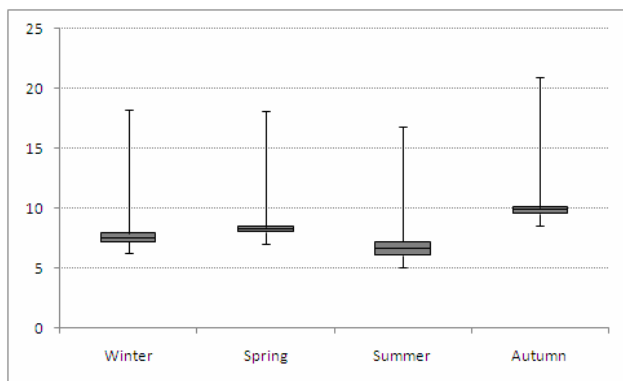


Figure 4. Box-and-whisker diagram for chemical oxygen consumption and seasonal variation

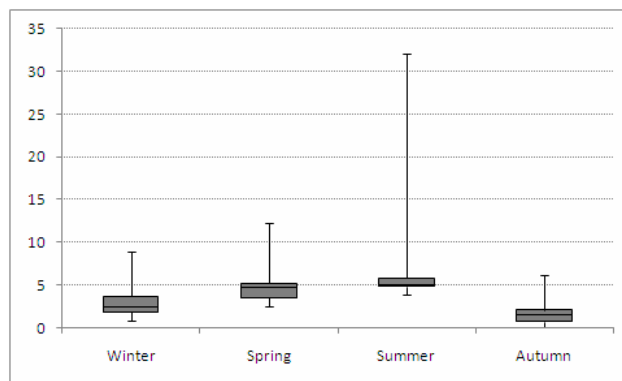


Figure 5. Box-and-whisker diagram for nitrates and seasonal variation

The last parameter chemical oxygen consumption (fig 4) indicates the amount of oxygen consumed per liter of solution, that for Bahlui river was 8.81 ± 0.45 mg O₂/L, fitting in second quality class, excepting the autumn, when the mean values exceed 10 mg O₂/L., fitting in third quality class, being related with higher temperatures that favored by the survival of many aquatic organisms.

Inorganic contaminants analyzed reveal the presence of the heavy metals, nitrates and chlorides as main pollutants of the Bahlui river water.

Nitrates (fig 5) 4.54 ± 1.03 mg /L, mean values fit into second quality class, with higher values registered on summer, due to the rainy period that preceded the sampling and high levels of turbidity, that indicates large amount of sediments mobilized from the hilly arable land, including fertilizers with nitrogen used in agriculture.

Chlorides (fig 6) mean values 141.77 ± 17.89 mg /L fitting in third quality class, being conditioned by their dissolving from marine salts that have impregnated the geological substrate (Sarmatian sedimentary

rocks) and by washing the saline soils. From that reason the values registered on spring are higher from the synergic action of the rain and snow melting with the lack of vegetation, that cover the soils, fitting in fourth quality class, with values over 300 mg /L.

Heavy metals from the water were generally mobilized in larger amount when the pH is acid, under 6, that can explain the fact the levels of heavy metals registered were lower, and some elements were the limit of detection as Pb, Cd, Cr, being identified only five of them: Zn, Cu, Mn, Ni, Fe in April 2011, the only month of monitoring for heavy metals.

Figure 7 show the Zn values 1.02 ± 0.05 mg /L, Cu 0.99 ± 0.03 mg /L, Ni 1.02 ± 0.058 mg /L fitting in the first quality class, with higher values for Zn 0,053 mg/L from the soil that was contaminated with heavy metals, Zn, because the soils from Iasi county have Zn deficiency. Figure 8 reveal Mn values 1.056 ± 0.037 mg /L set into third quality class for Bahlui river, naturally occurring in soils. The values obtained for the Fe 1.524 ± 1.068 mg /L, reveal that the Bahlui river correspond to the third class.

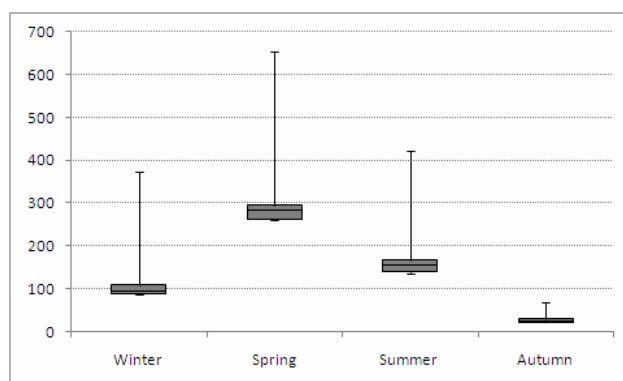


Figure 6. Box-and-whisker diagram for chlorides and seasonal variation

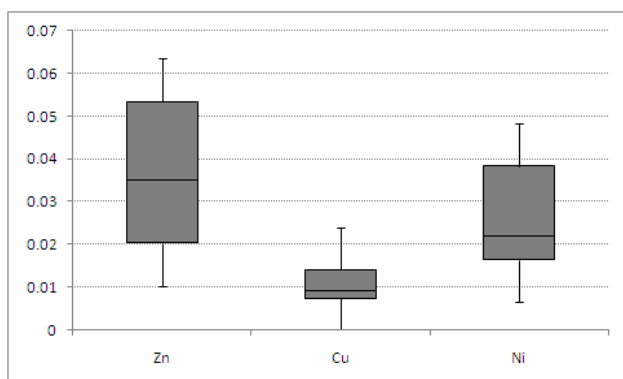


Figure 7. Box-and-whisker diagram for heavy metals – Zn, Cu, Ni for April 2011

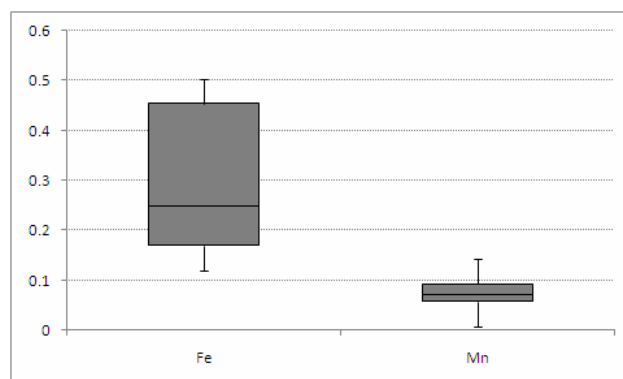


Figure 8. Box-and-whisker diagram for heavy metals – Fe, Mn for April 2011

To identify the relationships among the analyzed parameters and their possible sources was rendered a dendrogram (Fig. 9) where all parameters were grouped into five statistically significant clusters. According to order no. 161/2006 the water quality of Bahlui river in the built-up area of Iasi city belongs to the IVth and Vth quality class. Based on present analysis the IVth quality class corresponding to a highly polluted water (32 samples) can be divided in 4 subdomains based on pollution sources. Cluster 1 (14 samples) is characterized by an moderate impact of urban runoff, agricultural and domestic effluent due to the geographical position between west city entrance to the confluence with Nicolina river. Cluster 2 (9 samples) reveal an increased pollution generated by industrial and domestic effluents. This region cross the central part of the city, characterized by a developed residential area with both block of flats and houses. Cluster 3 (5 samples), crossing a specific zone consist of residential neighborhood on the right side and semi-industrial platform with pilot laboratory of Technical University with industrial and domestic effluents more concentrated. Sites 26, 27, 32 correspond to the confluence with Cacaina and Ciric rivers, predominantly domestic leakage. Cluster 4 comprising the remaining 4 samples from IVth quality class with sites 28, 29, 31, lies in a former industrial area, with mostly industrial effluents. Station 42 alone comes under this category and is mainly influence by the waste treatment outflowing. Cluster 5, overlapping with the Vth quality class (powerful polluted), is comprises suburban and urban areas where both types of effluents flow directly into river with the consequences on degrading water quality.

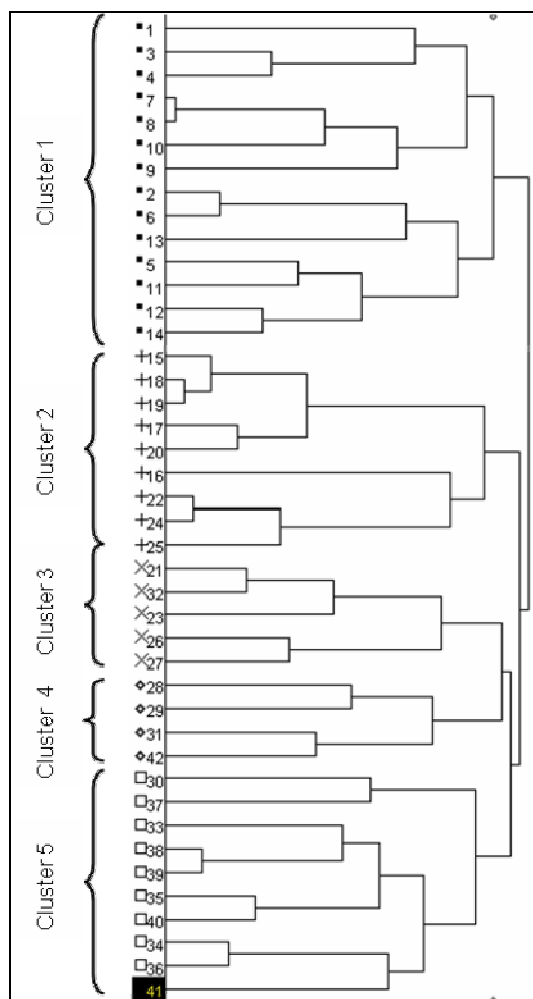


Figure 9 Dendrogram of relation among seasonal river water samples

CONCLUSIONS

The analyze of the organic and inorganic contaminants highlight the following:

- Organic contaminants represents the main problem, revealed by oxygen regime indicator and inorganic ones, especially trace elements (Fe and Zn) and nitrates content increasing represent a real problem, with a seasonal obvious variability
- Land use has an important role to understand the seasonal variation of the analyzed indicators, by the changes of the arable land and by the distribution of the main type of buildings and other functional areas.
- Cluster analysis of the obtained data put into evidence the establishment of five clusters that illustrate the functional areas of the city crossed by the Bahlui river: Dendrogram with cluster points, being obvious the anthropogene influence of the urban area, with special influence of industrial area of the city in cluster 5.

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