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Physicochemical Assessment of Water Quality in Nicolina River

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Abstract. Nutrient regime is related to the variation during the seasonal changes, especially the temperature modifications, land-use transformation and other physico-chemical parameters variation, influenced by main activities outside and inside the Iaşi city. Nicolina river is the main Bahlui river tributary on the south of buildup area of Iasi city, and it has one of the most important influence in Bahlui river water quality, due to different characteristic of the areas it cross: rural area, industrial area, and the area with individual and collective houses. This paper presents the regime of the NH₃, NH₄ and PO₄ during the dry and wet season (December, April and June), of the samples taken from the Nicolina river (15 samples), the changes imposed by the seasonal variation being obvious. Field observations were conducted to study the Nicolina river in order to establish sampling points, followed by sampling and lab analyses of the physico-chemical indicators, like pH, electrical conductivity, turbidity, oxygen regime, hardness, alkalinity as well as heavy metals. Form all data the most relevant variation have been on the nutrients regime due to natural and anthropic sources. The Arc GIS 9.3 software were used for illustrated spatial distribution of obtained data followed by some correlations based on cluster analysis, that highlight the influence of human activities within the buildup area and the succession of seasons, the amounts of NH_3 , NH_4 and PO_4 becoming almost doubled, passing from the class II and III to class III and IV.

Keywords: Nicolina river, nutrient regime, land-use, GIS, cluster analyze

INTRODUCTION

Water resources represent one of the most important natural resource for any urban area, including Iaşi city built-up area that is a major contributor to surface water quality modification. According to the law 60/2000/EC Water Framework Directive and other directives and laws in the field of water, it was necessary to extend the approach regarding the water, knowing this modifications it will be possible to reduce the impact of the human activities on river water quality, anthropical sources representing one of the major sources for nutrients – agriculture, industry and sewage treatment system.

Nicolina river is the main Bahlui river tributary on the south of buildup area of Iaşi city, it has a length of 20 km, but the monitoring section is about 7.5 km, and the river basin area of 117 km², the study cover only 11.48 km2, that means the third lower section of the river basin. Multi-flow environment is 0.477 m^3 /s, which is determined at hydrometric station in the area Nicolina II district of the city of Iaşi (Seliman C. et al., 2009). Also are representative the climatic data for the city, due to the influence on surface water: 9.72° C the multiannual temperature average at Iaşi station and the 787 mm/m2 the multiannual precipitations at Bârnova pluviommetric point of Nicolina.

The present work is part of a larger study regarding surface water quality in urban area of Iaşi city. The major objective is to obtain a database, that can be useful for future studies and extended for entire built-up area of Iaşi city.

This article present the results of nutrient regime from Nicolina river between winter of 2010 and summer of 2011, (December, April and June) the seasonal variation being observed. Processing the obtained data classification of the Nicolina River water into quality classes were made, which is very useful for determining the status of water quality from the nutrient regime point of view.

Nutrient regime knowing is very important in order to keep within the bounds the amount of NH3, NH4 and PO4, do not exceed the allowable concentrations, that would cause nitrogen and phosphorus enrichment, succeed by water eutrophication with negative consequences on water quality and aquatic life.

The quality of Bahlui river surface water and its tributaries was the subject for another studies realized until now by Benchea R. et al., 2010, Seliman C. et al., 2009, Neamtu M. et al., 2009, Dumitru S., 2006, Giurma I. et al., 2007, Crăciun I. et al., 2004, but the sampling points were to rare to show in detail the human impact in urban area of the Iaşi city.

MATERIALS AND METHODS

Sampling points (15 samples) were established after field observations concerning the examination of the drains, of the minor riverbed morphology. The distance between points is 1.8 km in industrial area, and 0.7 - 0.8 km in urban area occupied by houses, because the human activities are there more harmful for the environment including the surface water. After sampling with a special device from the middle of water course, in different seasons (cold, warm and transitional) and stored in polyethylene bottle with 2000 ml capacity, the samples were analyzed in the lab.

More physical and chemical parameters that interact in nutrients regime have been determined: physical and chemical indicators (pH, electrical conductivity, turbidity, the oxygen regime (DO, COD – CCO Mn oxygen consumption and BOD); indicators of the degree of mineralization (chlorides, sulfates, phosphates, nitrates), physical and chemical selective indicators (hardness, alkalinity), including NH3, NH4 and PO4 concentrations, as well as heavy metals.

The pH and conductivity measurements were made by potentiometric methods with a Multi 350i/SET WTW multiparameter instrument. For dissolved oxygen levels, Winckler method were used. Spectrophotometric method were run for nutrients, according to ISO standard, with phenoldisulfonic acid for nitrates (NO3), Nessler reactive and Seignette salt for ammonium (NH4), and phosphates (PO4) is based on an ammonium molybdate reaction.

To construct the calibration plot, were used reference solutions with concentrations between 5-50 μ g/mL. We measured the optical density of the solutions using a Shimadzu UV 1601 spectrophotometer at a wavelength of 410 nm for nitrates (NO3) respectively 430 nm for ammonium (NH4) and 650 nm for phosphates (PO4).

The results were represented according to the classification of data into classes establish by ISO for NO3, NH4 and PO4 and by the Order 16/2006 approving the Norms for surface water quality assessment in order to asses the ecological status of water bodies. At the end were obtained more graphs with all sample points and the quality class that fit each value and finding the cause, separately for each season.

Cluster analyze shows us the relations between data obtained for each points and their spatial distribution, some correlations between positions and other spatial characteristics like land use or main type of buildings being put into evidence. To generate the dendrogram JMP Statistics 7 were used showing the final correlations between the studied indicators, highlighting the nutrient regime and it variation.

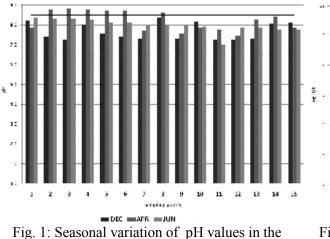
RESULTS AND DISCUSSIONS

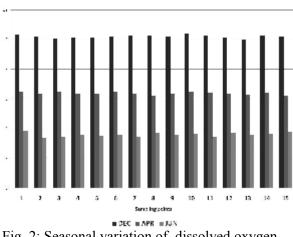
Nutrients regime is evaluated by including values in quality class for each point according to the Order no. 161/2006.

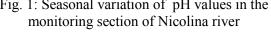
The indicators analyzed for highlight the nutrients regime and its seasonal variation can be correlated with pH, dissolved oxygen and conductivity and also with the spatial distribution of the type of houses and land-use, especially of the points situated near by the confluence with the Bahlui river, after receiving the effluents from drains situated in this area, where the individual houses are predominating.

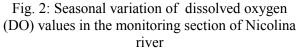
Physico - chemical indicators

The pH values (fig. 1) – show that the value did not fit in the limits provided by the law, exceeding the value 8.5, the alkaline character of the water is significantly higher for the first six points only April and over 8, also in June. The spatial distribution of pH ranging from 7.666 ± 0.4346 in December to 8.2168 ± 0.5031 in April and 7.97817 ± 0.32982 in June. The seasonal variation of pH values observed in this study is in agreement with results of previous studies.









Dissolved oxygen is vital to aquatic life, as it is needed to keep organisms alive, being in direct correlation with temperature and development of biodiversity.

Fig. 2 reveal that at the low temperature and the absence of the vegetation the higher level of DO have been recorded ($10.22 \pm 0.1019 \text{ mg/L}$), compared with the summer period when the lowest value was found ($3.61 \pm 0.1457 \text{ mg/L}$). Oxygen is removed from the water as organic matter decays.

The electrical conductivity (fig. 3) is the indicative of the total dissolved solids (TDS, inorganic chemicals) in the water. In this case the seasonal variation is between 780.345mg/L in summer to 1224.95 mg/L in winter period.

Higher conductivity values indicates that more material is dissolved material, especially on winter, when the weather and the small flow are major factor in higher conductivity values.

The average conductivity is between 1162.61 μ S/cm in June and 1749.93 μ S/cm in December with a minimum of 1090.6 μ S/cm and a maximum of 1830.84 μ S/cm.

All these indicators have an important relevance in nutrients regime, for the reason that the water acts both as a dilution medium as well as for the nutrients dispersion, influencing strongly the water quality.

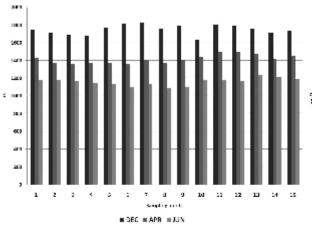
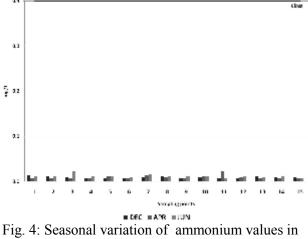


Fig. 3: Seasonal variation of electrical conductivity values in the monitoring section of Nicolina river



the monitoring section of Nicolina river

Nutrients regime indicators

In small amounts the nutrients are indispensable for the existence of aquatic life, but higher concentrations are harmful, including NO_3 , NH_4 and PO_4 , causing the reducing of oxygen level in water being consumed by the overdeveloping vegetation. The nutrients sources can be: point sources – industrial units, waste dumps, drains, animal dejections and non-point sources – agriculture, industry emissions, urban area etc.

Ammonium (fig. 4) values are very small, with higher levels registered on summer, the source is non point – the agriculture and the hills leakage, but the influence is not harmful, the water fit in the first quality class.

The values can be correlated with the pH values, for all seasons – low values in the winter and highest values in the summer (0.00912 mg/L to 0.0119 mg/L.

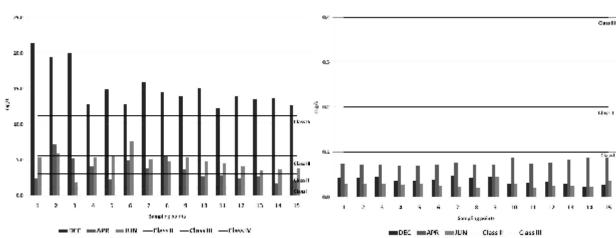
Nitrates levels (fig. 5) are influenced by the use of the fertilizers in the agriculture land in the build-up area of the city, but most of all outside the city, in the rural area.

In the winter are registered higher value $15.15 \pm 2.87 \text{ mg/L}$ (due to the lower rate of decomposition of organic substances and high level at dissolved oxygen) fitting in the fifth quality class, and smaller values in the warmer period - spring $3.57 \pm 1.54 \text{ mg/l}$ (due to the increased biogenic processes) fitting in the third quality class (Benchea et al., 2010).

In summer can be observed higher values 4.77 ± 1.54 mg/L, but it fit still in third quality class, excepting point six that becoming fourth class, probably caused by the heavy rain that preceded the sampling operation, when the leakage was higher and the soil was uncovered.

It can be also highlight the anthropic influence, because the first ten samples registered the higher values in every season, that cross an overcrowded area with collective and individual houses, and smaller in last five samples, located nearby former industrial unit – SC Fortus Iaşi. The high value of the sixth sample point show that in the rainy periods the sewage water is evacuated directly in the river. That trend can be confirm in April when the first ten points match to the third quality class and the last points correspond to the second quality class. The winter values can be related to the high values of the dissolved oxygen and conductivity, and low values for the pH, the situation being reverse in the summer.

Phosphates the other nutrient regime indicator analyzed (fig. 6) has small values, can be classify in the first water quality class, but it can revealed seasonal variation that can be correlated with the pH values, that are higher in the spring.



The main source is animal faeces spread in the spring on the arable land and fertilizer runoff, used outside city.

Fig. 5: Seasonal variation of nitrates values in the Fig. 6: Seasonal variation of phosphates values in monitoring section of Nicolina river

the monitoring section of Nicolina river

Land use and nutrients regime

The degree of pollution depends on the material, the physical and chemical nature of the material discharged, water depth and hydrographic conditions. The land - use (fig. 7) in the studied area (1279 ha) is very relevant as a result of the anthropic impact of the activities and habitation itself. It was analyzed how the land is actually used, some correlations with sample points position and the obtained values for each indicator being observed.

The land use of the built-up area shows that the houses occupy more than 50% of the area (25% collective houses and 30% individual houses), 22% by the industrial area (SC Fortus Iași) and 16% by vegetation - the forest (10%) covering Cetățuia hill and a small part of the Galata hill, being replaced by the individual houses and green spaces (6%) located in the collective houses area.

The activities developed inside the city influence the surface water quality, especially at the first seven sampling points (fig. 8) situated near the confluence with Bahlui river where are registered the highest values for all indicators show that the anthropic influence of the individual houses with gardens where the subsistence agriculture is practiced.

The human impact is reducing in the collective houses area (points 8 -11), but it has still an influence caused by the sewage that collect the wastewater and flows in the river, especially in the rainy period.

The impact of the industrial area (points 12-14) is very reduced thanks to the decrease of the activity in the main unit, an significant polluter of the environment, including surface water before 1989.

The last point is located before the industrial area, and show the characteristics of the water before crossing build-up area of the south of Iasi city

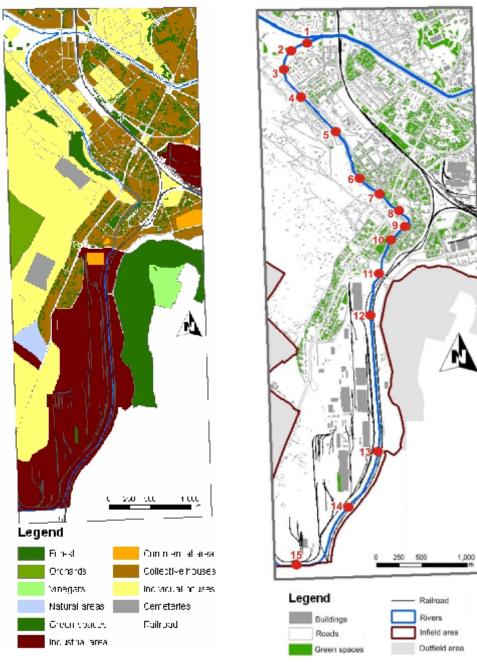


Fig 7: The land - use in the monitoring section of Nicolina river

Figure 8: The sample points in the monitoring section of Nicolina river

Nutrients regime in water of Nicolina River

The data base represent an instrument for statistical analysis, useful for establish possible correlations between sampling positions and nutrients values through multivariate methods. After application of such methods for all analyzed parameters and the criteria developed for the assessment of the correlation coefficient, groups of highly correlated water quality variables are identified.

Fig. 9 shows the cluster tree, the water quality variables are divided into 9 clusters, 3 of which are single-variable clusters. Two main groups of clusters were put into evidence, as follow:

The first group included the first seven sampling points were the human impact is more pronounced, by the individual houses predomination, especially the faeces pollution as well as other facts before mentioned

- The second group highlighted the lower values of the indicators caused both by industrial activity degradation as well as a better management of the habitation in collective houses.

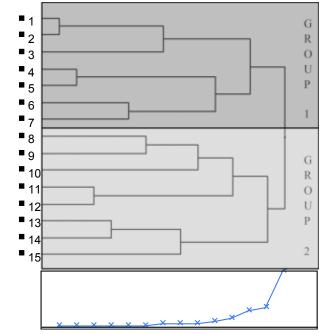


Fig 9: The dendrograme for the monitoring section of Nicolina river

This figure is very relevant because show exactly the anthropic impact of the urban area on the surface water quality in an extremely heterogeneous area of the city concerning the functionality, type of buildings, vegetation, and other urban elements distribution.

CONCLUSION

The analyze of the nutrients regime indicators and the seasonal transition variation highlight the following:

- From point of view of the quality classes for the nutrients regime, the nitrates content increasing represent a real problem, the fourth quality class being recorded.

- The seasonal variations indicates different trends like: NH_4 – low values on winter and higher in the summer, NO_3 - the reverse situation like NH_4 - due to the variation of the rate of decomposition of organic substances, highlighting also some correlations with the pH, dissolved oxygen and conductivity.

- 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 two equilibrated main clusters: the first one formed by 1-7 sampling points the other one built by 8 -15 points, being obvious the anthropic influence of the urban area occupied by individual houses.

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REFERENCES

1. Benchea R., Cretescu I., Macoveanu M. (2011). Monitoring of water quality indicators for improving water resources of Bahlui River, Environmental Engineering and Management Journal, Vol.10, No. 3, p. 327-332

2. Crăciun I., Mitroi A., Cercel P. (2004). The Quality Characterization of the Surface Water of the Bahlui Hydrographical Basin, Ovidius University

3. Cojocaru R. (2008). Nicolina river basin - Applied geomorphology study, Ph.D. Thesis, p. 173

4. Dumitru S., Nilca I., Mocanu V., Coteț V., Simota C. (2006) . The assessment of nitrates flux to the groundwater, using GIS, at a catchment and NUTS4 scale, Geographia Technica, 22 No. 2, p. 19-26

5. Giurma I., Crăciun I., Giurma C. (2007) The Analysis of the Impact of Storage Lake on Environment Using the Chemical Characterization of the Water Resources. Case Study Bahlui Basin River, Ovidius University Annals Series: Civil Engineering Volume 1, Number 9, p. 119 - 124

6. Crăciun I., Mitroi A., Cercel P. (2004). The Quality Characterization of the Surface Water of the Bahlui Hydrographical Basin, Ovidius University Annals Series: Civil Engineering Volume 1, Number 6, p. 281 – 286

7. Howden N., Bowes M., Clark A., Humphries N., Neal C. (2009). Water quality, nutrients and the European union's Water Framework Directive in a lowland agricultural region: Suffolk, south-east England, Science of the total environment, p. 2966 - 2979

8. Neamtu M., Ciumasu I., Costica N., Costica M., Bobu M., Nicoara M., Catrinescu C., Becker van Slooten K., De Alencastro L. (2009). Chemical, biological, and ecotoxicological assessment of pesticides and persistent organic pollutants in the Bahlui River, Romania, Environ Sci. Pollut. Res., (Suppl 1), p. 76–85

9. Seliman C., Plopa O., Damian C., Creţu M. (2009). Urban environment influence on the surface water quality in the city of Iaşi, , Lucr. şt., seria Agronomie, vol. 52, U.S.A.M.V. Iaşi, p. 461 – 466

10.*** Order no. 161/2006 – Normative regarding the classification of surface waters in order to establish the ecological status of water bodies