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Water Quality Management of the Waters of the Romanian River Hârtibaciu

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ABSTRACT. This study aims at monitoring physico-chemical features of the waters of the Hârtibaciu River in Romania with a view to establishing its qualitative benchmarks. Using the waters of this river for agricultural purposes leads to the establishment of its physical and chemical features and its falling within the related quality group. This study has monitored general chemical indicators and specific chemical indicators in the waters of the Hârtibaciu River; the resulting values show that it falls within the $2^{nd}/3^{rd}$ quality group.

1. INTRODUCTION

Rivers are the main source of drinking and industrial water in Romania. They are characterized by flowing phenomena (which incfluences the amount of suspended or colloidal particles, physical and chemical features, the shape of the river bed, the variation of the water flow and level), the contact surface between water and atmosphere (which influences oxygenation capacity, daily and seasonal temperature variation) and the self-purifying capacity (Oprean et al. 2007, Iancu et al. 2013, Maher et al., 1999). A sustainable water management leads to the establishment of important benchmarks in order for water sources that are necessary for agriculture and for the perpetuation of fish and other aquatic living creatures to be used in proper conditions (Pylea et al. 2005).

Rivers are characterized by the presence of natural impurities. The specific structure depends on the soils along the river bed, the soils in the drainage basin, the waste waters discharged by various users and the capacity to dissolve atmospheric gases.

The rivers and tributaries present a lower degree of mineralization; the amount of dissolved mineral salts is under 400 mg/L and is made up of bicarbonates, chlorides, nitrates, phosphates, Sodium, Potasium, Calcium and Magnesium sulphates coming from the erosion of rocks, soil and precipitation.

Generally, metals represent both a soil (irrigations) and a water contamination problem. Thus, it is mandatory to include a close monitorization in their quality control strategy (Osibanjo et al. 2011, Singare 2011, Prabha et al. 1997, Sharma et al. 2004).

The main characteristic of watercourses is the variable load of suspended and colloidal particles (clays, sand, silica) and organic substances. When it rains, this load increases considerably (Oancea et al. 2007).

The discharge of effluents that are insuficiently treated has led to the alteration of watercourse quality and to the emergence of a wide range of impurifiers: non-rapidly degradable organic substances, sulphur, nitrate, phosphorus compounds, microelements (copper, zinc, lead), pesticides, organic chorinated insecticides, detergents etc. (Oprean et al. 2008, Oprean et al. 2013, Nyugen et al. 2005, Lee et al. 2000).

In several cases, high bacteriological impurities can be observed. Microorganisms, viruses, protozoa originate from the discharging of waste waters that were contaminated with human or animal waste, microorganisms from the ecosystem (Stegărus et al. 2013).

River waters have a self-purifying capacity, due to natural biochemical processes favoured by the contact between air and water; nevertheless, bacteriological contamination does not fade (Schriever et al. 2010, Medema et al. 2006).

Self-purification or natural purification refers to all the natural purification processes through which water is restored to the qualitative level before it was polluted. Environmental, chemical, physical and biological factors facilitate the process of self-purification.

2. MATERIALS AND METHODS

Water samples taken from 6 places (noted P1, P2, P3, P4, P5, P6) between the city of Agnita and the commune of Nocrich (Transylvania, Romania).

The physico-chemical analysis focused on the following parameters; the methods employed are in accordance with Order no. 161/2006 - Normative regarding the classification of surface waters to establish the ecological status of water bodies.

- CCOCr, (SR ISO 6060/1996)
- CBO₅, (SR EN 1899/1,2-02,03,DIN 38409-87)
- CCOMn, (SR EN ISO 8467-01)
- dissolved O₂ (SR EN ISO 25814-99)

One parameter that plays an important part in water analysis is the Chemical Oxygen Demand (COD). This determination offers precious information on the level of water pollution with organic matter.

- nitrogen, in the form of ammonium, is the basic indicator that highlights the degree of organic nitrous pollution of wasterwaters. It is determined in accordance with SR ISO 7150/1-00, nitrates are determined in accordance with SR ISO 7890-3/2000 and nitrites in accordance with SR ISO 26777/06.
- heavy metals (As, Ba²⁺, Cd²⁺, Cu²⁺, Cr⁶⁺, Hg²⁺, Pb²⁺)

Heavy metals are natural compounds that cannot be broken down or destroyed; in high concentrations, they are toxic and dangerous. Metals get in the human body in the form of cations (iron, manganese, cobalt, copper, molybdenum, zinc) and light metals (potassium, calcium, magnesium and sodium).

The above-mentioned metals were determined through the agreed method SR EN ISO 15586/2004 "Water quality - Determination of trace elements using atomic absorption spectrometry with graphite furnace".

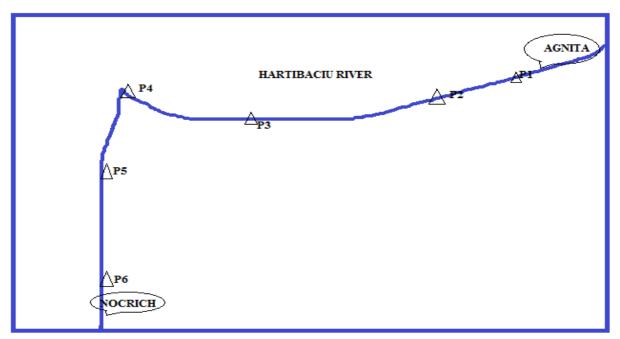


Figure 1. Hârtibaciu River on the segment Agnita-Nocrich with the places where the water samples were taken

3. RESULTS AND DISCUSSIONS

As shown in Figure 2, the determined amounts of ammonium fall between 1.98 mg/L at collection point P3 and 2.79 mg/L at collection point P6; the maximum values fall within the quality group. Nitrates recorded concentrations between 13.67 mg/L at collection point P3 and a maximum of 22.11 mg/L at collection point P6. Nitrites recorded a minimum value of 1.17 mg/L at collection point P3 and a maximum of 3.01 mg/l at collection point P1. The values recorded by the "nutrient" group fall within the quality group of surface waters.

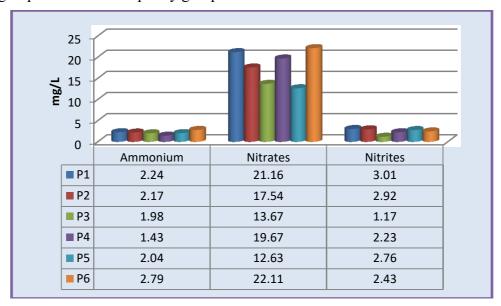


Figure 2. Concentrations of ammonium, nitrates and nitrites recorded in the six water collection points on the Hârtibaciu River

The indicators of Oxygen regime (Figure 3) recorded the following values: dissolved oxygen recorded values between a minimum of 4.83 mg/L at collection point P4 and a maximum of 5.13 mg/L at collection point P6. The results of the biochemical oxygen demand recorded values between 6.19 mg/L at collection point P1 and 7.34 mg/L at collection point P2. Collection points P3 and P6 recorded close values that oscillate around 7.17 mg/L and 7.12 mg/L respectively. The CCCOMn values recorded were 12.52 mg/L at collection point P2, 12.58 mg/L at collection point P5 and a maximum of 13.61 mg/L at collection point P3, respectively 13.44 mg/L at collection point P6. In what regards the chemical oxygen demand determined through the potassium dichromate method showing the concentration of organic substances in the waters of the Hârtibaciu River, it recorded a minimum value of 15.92 mg/L at collection point P4 and a maximum value of 18.65 mg/L at collection point P6. Intermediary values were recorded at collection points P2 (18,45 mg/L) and P3 (18,34 mg/L), values close to the maximum and to 16.23 mg/L at collection point P1, respectively 17.44 mg/L at collection point P5.

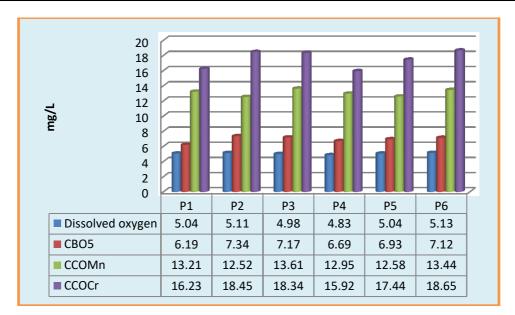


Figure 3. Concentration of dissolved oxygen and biochemical oxygen demand identified in the six water collection points on the Hârtibaciu River

Figure 4 shows the values referring to the metals determined in the waters of the Hârtibaciu River; these values contribute to its falling into the related quality group. We can notice that arsenic recorded values between 7,2 μ g/L, (P5) and 12 μ g/L (P4). P1 recorded a value of 8,3 μ g/L, close to that of P3 - 8,1 μ g/L. Barium recorded the following values: P1-79,21 μ g/L<P5-81,21 μ g/L, P6-66,72 μ g/L <P2-77,12 μ g/L, and P4-12,3 μ g/L<P3-45,73 μ g/L. We can see barium reached a maximum level of 81,21 μ g/L and a minimum value of 12,3 μ g/L.

The values recorded in the case of an important indicator, cadmium, were situated between $27\mu g/L$ at collection point P4 and a maximum of 0,69 $\mu g/L$ at collection point P6. Values close to those recorded at collection point P6 were measured at collection point P1, i.e. 0,67 $\mu g/L$. At collection points P2 and P3 we recorded values of 0,47 $\mu g/L$, respectively 0,55 $\mu g/L$.

Hexavalent chromium identified in the six water samples taken from the Hârtibaciu River recorded values between 2,8 μ g/L - P5 and a maximum of 6,9 - P4. Values 20% lower than the maximum were measured at collection point P2 and values 38% lower at collecting point P1. Copper, a metal that is permanently identified in surface waters recorded values of 3,8 μ g/L in samples P3 and P6 and 5,4 μ g/L in P1 and respectively 5,9 μ g/L in P5.

The maximum copper values recorded were 3 μ g/L in the sample taken at collection point P4 and 7,6 μ g/L the one taken at collection point P2. Mercury presented sub-unit values in all the samples, i.e. between 0,45 μ g/L and a maximum of 0,91 μ g/L. Intermediary values were recorded in the samples taken from collecting points P1-0,56 μ g/L, P3-0,83 μ g/L, P4-0,72 μ g/L. Lead, a metal that is highly toxic for the soil and the human body, recorded values between 22,1 μ g/L in sample P4 and 46,7 μ g/L in sample P5. Values close to the maximum were also recorded at collection point P1, where the amount was 46,6 μ g/L. At collection point P3, the amount of lead was 10% lower than at collection point P2.

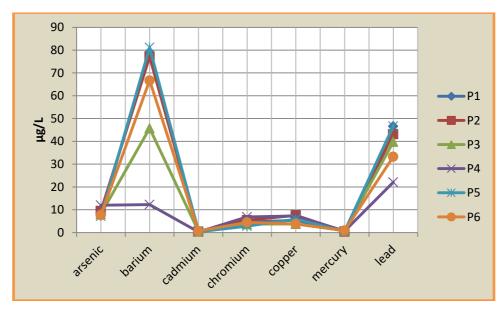


Figure 4. Concentration of metals in the six water collection points on the Hârtibaciu River

4. CONCLUSIONS

From the point of view of nutrients, the values measured in the waters of the Hârtibaciu River fall within the 2nd quality group, which means they are recommendable for agricultural purposes.

Oxygen regime indicates a high concentration of organic matter; from this point of view the waters fall within the 3rd quality group. This can also be explained by the lack of sewerage systems upstream of the city of Agnita, as nearby villages frequently discharge household waste into the outfall.

The metals do not pose a danger to the quality of these waters, also given the lack of a high level of industrialization in the area; according to the values recorded, the waters fall within the 2^{nd} quality group.

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