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The Danube River water quality characteristics in the Braila Town

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Abstract. Various physico-chemical characteristics of the Danube River water in Braila Town were studied during the summer, autumn and winter of 2008 year, for three sampling points. The parameters like pH, hardness, chloride, fluoride, ammonium and metallic ions (calcium, magnesium, chromium, iron, and copper) were analyzed in order to assess the water quality for Danube River. The major problems for Danube River water quality in Braila Town were identified to be the presence of copper and iron, in concentrations which placed sometimes the water in 5th class of quality, and the high concentrations of ammonium ion.

Keywords: Danube River, water quality, pH, hardness, chloride, fluoride, ammonia, metallic ions.

1. Introduction

The Danube River, second largest river in Europe in length and discharge of water, has been from many years an invaluable resource for navigation purposes. Another uses of the Danube River are: drinking water source in many locations, irrigation, fisheries, hydroelectric power production, industrial uses, tourism and recreation. The Danube River is too often the final destination for waste disposal, which created problems of water quality and quantity. Water quality in the Danube has improved during the last decade, but further improvement is still needed [1]. The main pollution problems are the excessive volumes of nutrients (nitrogen and phosphorus) entering the river, mainly from agricultural fertilizers and not adequately threatened municipal sewage [2]. Discharges of organic micro-pollutants and ionic metals in the river create the major problems, including water pollution, groundwater and soil contamination [3].

Braila is a city in Muntenia, Eastern Romania, a Danube River harbour and the capital of the Braila County. Located in a field of Delta fertile land, in Braila County are practiced intense agriculture and animal breeding, which may cause a high level of copper and nutrients in Danube River.

To assess water quality is usually used the ecological state of surface waters, a combination of physical, chemical and biological indicators [4]. To evaluate the water quality, we used the Romanian legislation. For the assessment of water ecological state are used five classes of quality, and for water chemical state are established two states: the good chemical state and the bad chemical state [5].

In our study about Danube River, it was previous analyzed the Danube River water quality in Constanta County (Rasova, Harsova, respective Cernavoda area) [6, 7, 8].

In the present research, we analyze the Danube River water quality across Braila Town.

2. Experimental

Experimental results were obtained using three samples from three sampling sites in the sequence (from upstream to downstream): (**1**) passage ferryboat; (**2**) discharge of water from swimming pool; (**3**) harbour.

Water samples were collected in Teflon bottles from the left side of the river, during the 2008 year, respective in summer (August), autumn (October) and winter (December). Samples were filtered to remove particulate material, and were kept refrigerated at 4^{o}C, away from light, prior to analysis.

The studied parameters are: pH, fluoride, chloride, ammonium, total hardness and some metallic ions.

Chloride ion, calcium and magnesium ions, and total hardness were determined using usually titrimetric methods; pH, ammonium and fluoride ions were determined by potentiometric methods.

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For pH measurements was used a portable pH-meter and for the measurement of fluoride and ammonium ions concentration were used ion-selective electrodes (I. S. E.). Calibration of potentiometer was detailed in a previous paper [6]. The calibration curve was linear for F^- between 10^{-5} and 10^{-2} mol/L and for ammonium ion between 10^{-6} and 10^{-2} mol/L.

The total concentrations of some metallic ions in Danube River water were determined using the molecular absorption spectrometry in visible. In order to increase the sensitivity of the analytical determination, we used the method of the standard addition [9, 10]. The method of the standard addition is applied when the compounds to be determined are in low concentration and the chemical matrix is not constant in the samples to be analyzed. The precision of iron, copper and chromium determination was evaluated under the optimum conditions; the effects of pH, temperature, complexation time, reagent amounts were studied [10, 11].

For the measurement of studied heavy metals by molecular absorption spectrometry, a DR-2800 spectrophotometer from Hach Company was used.

3. Results and Discussions

The variations of studied parameters in Danube River water are represented in Figures 1 - 10.

3.1. pH

Since pH can be affected by chemicals in the water, pH is an important indicator of water that is changing chemically. Pollution can change water's pH, which in turn can harm animals and plants living in the water. Slightly alkaline pH is preferable in waters, as heavy metals are removed by carbonate or bicarbonate precipitates [12].

For analysed samples, the average pH values range from 7.14 to 7.86 in the Danube River water (Fig. 1) and do not exceed the limits, according to Romanian water classification scheme (6.5 - 8.5) [5]. These values are typical for natural surface waters, being optimum for most organisms.

In all studied sites the pH decreased from August to December, because of natural factors (like biological activity cycle) and also of anthropic factors (e.g. the domestic sewage and agricultural run-off, which are usually alkaline in nature, due to the presence of ammonium compounds). The smallest water pH in site **2** can be correlated, especially in summer, with the discharging of chlorinated water from swimming pool.

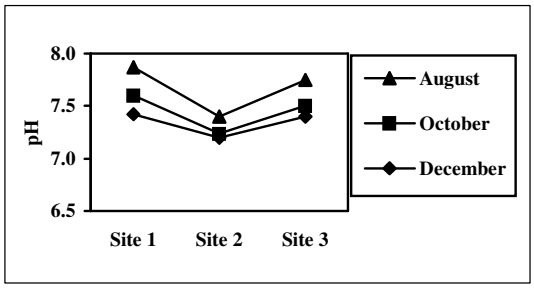

Fig. 1. Variation of pH in the water of Danube River, Braila Town, in 2008 .

3.2. Salinity

High concentrations of dissolved salts in water compromise its use for domestic and agricultural purposes with recommended maximum levels dependent upon the end-use. An excess of Cl^- in inland water is usually taken as an index of pollution [13].

The surface waters with chloride concentration below 25 mg/L belong to the first class of quality and waters with chloride concentration of 25 – 50 mg/L belong to the second class of quality [5].

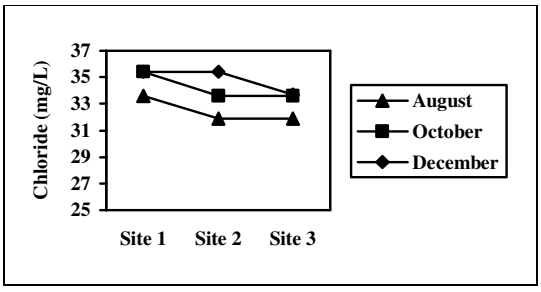

Fig. 2. Variation of chloride concentration in Danube River water, Braila Town, in 2008.

For all the determinations, the chloride concentration was between 30 and 40 mg/L (Fig. 2), the Danube River water in Braila Town being of second quality class, and the highest chloride concentrations being determined in winter. In

August, all the samples of water had the smaller chloride concentration, probably because the samples were collected during a period of raining.

The high concentration of chloride ion in water may be due to the natural factor, the soils in Braila County being known as salted soils.

3.3. Fluoride ion

Fluoride exists naturally in water, the source of most fluoride in natural fresh-water resources being various rocks and minerals in bedrock and sediments. Although fluoride has a beneficial effect within a range of low concentrations, at higher concentration has adverse effects. In generally, the river water contains below 0.1 mg/L [14].

The obtained fluoride concentrations in investigated samples (Fig. 3) have been found between 12 – 13 µg/L.

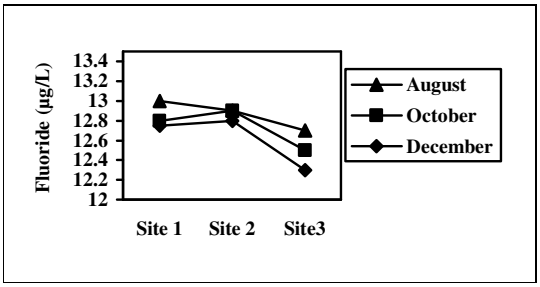

Fig. 3. Variation of fluoride concentration in the Danube River water, Braila Town, in 2008.

It was concluded that there were not major changes along the river and/or during the seasons, in the studied areas the concentration of fluoride ion being almost constant in time.

3.4. Hardness

Hardness may be defined as the sum of polyvalent cations present in water, the most common such cations being calcium and magnesium. The degree of hardness depends on the type and amount of impurities present in the water. Hardness also depends on the amount of carbon dioxide in solution. Carbon dioxide influences the solubility of the impurities that cause hardness. The most common sources of water hardness are calcium and magnesium salts [15].

Hardness is usually expressed in terms of the equivalent calcium carbonate or calcium oxide. One German degree, or one degree of General Hardness (dGH), is defined as 10 milligrams of calcium oxide per litre of water (17.848 milligrams of calcium carbonate per litre of water, or 17.848 ppm) [16].

All the water samples had total hardness between 9 and 10^0G (Fig. 4), which means there are soft waters [16]. The total hardness of the studied water samples increased from summer to winter.

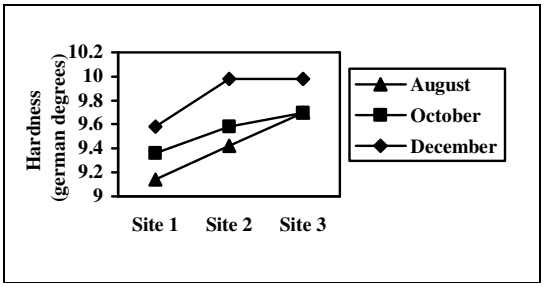

Fig. 4. Variation of hardness of Danube River water, Braila Town, in 2008.

3.5. Metallic ions

In order to analyze the quality of water, the concentrations of some representative (calcium and magnesium) and transitional metallic ions (chromium, iron and copper) were also determined.

Calcium. Calcium, an essential element for living organisms, occurs in water naturally. One of the main reasons for the abundance of calcium in water is its natural occurrence in the earth's crust. Rivers generally contain 1 - 2 mg/L calcium, but in lime areas rivers they may have calcium concentrations as high as 100 mg/L. The calcium ion influences aquatic organisms concerning metal toxicity. In softer water, membrane permeability in the gills is increased. Calcium also competes with other ions for binding spots in the gills. Consequently, hard water better protects fishes from direct metal uptake. Various calcium compounds may be toxic [14].

In all analyzed samples, the calcium concentration is bellow 50 mg/L (Fig. 5), the water being of first quality class.

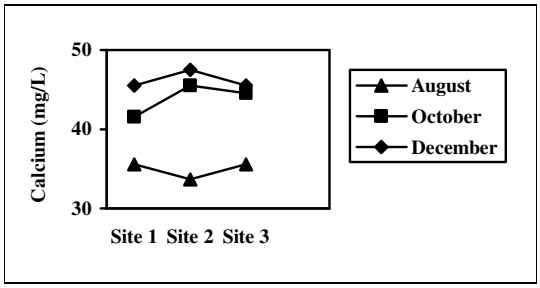

Fig. 5. Variation of calcium ion concentration in the Danube River water, Braila Town, in 2008.

Also, the concentration in all sites has decreased from winter to summer, in accordance with the variation of hardness.

Magnesium. Magnesium, an essential nutrient for plants as well as for animals, is washed from rocks (dolomite, magnesite, etc.) and subsequently ends up in water, being also responsible for water hardness. Rivers contain approximately 4 mg/L of magnesium and a concentration of 30 mg/L is recommended for drinking waters [13].

Magnesium has many different purposes and it also ends up in the environment from fertilizer application and from cattle feed [14]. The surface waters with magnesium concentration between 12 and 50 mg/L belong to second quality class [5].

All the analyzed samples had the magnesium concentration between 15 and 24 mg/L (Fig. 6), the water being of second quality class. The higher magnesium concentration was determined for site **3** in summer. The magnesium concentration decreased from summer to winter, probably due to natural factors, like the natural cycle of vegetation.

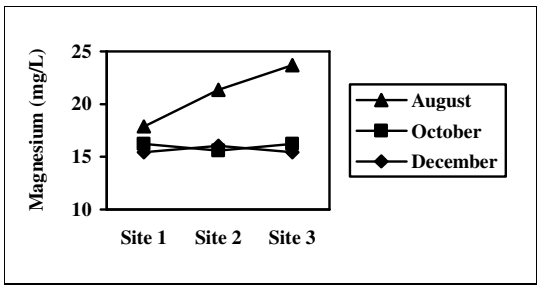

Fig. 6. Variation of magnesium ion concentration in the Danube River water, Braila Town, in 2008.

Iron. Iron is one of the most common elements found in nature, accounting for at least 5% of the earth's crust and just about all water supplies contain some measurable amount of iron. Iron stains and contaminates anything it contacts. The resulting stains are usually yellowish-brown to reddish-brown, but may be gray to black in the presence of some organics. Iron may also cause undesirable odours and tastes in water [14]. A concentration of total iron in water between 1.0 and 2.0 mg/L is assigned to 4th quality class and over 2.0 mg/L to 5th quality class [5].

The iron concentration had a large variation in analyzed period, with a decrease from summer to winter in all studied sites. In summer, the increasing of temperature decrease the concentration of dissolved oxygen, therefore the oxidation of soluble Fe(II) to insoluble Fe(III) compounds is slow and the concentration of soluble iron is higher.

Maximum iron concentration was determined in site **3** and minimum in site **2** (Fig. 7).

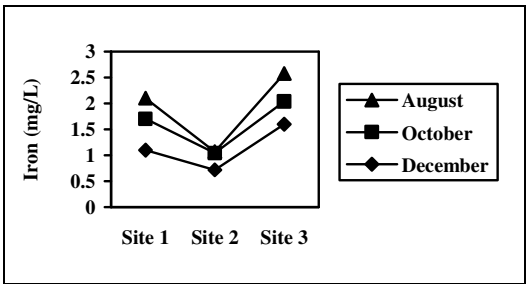

Fig. 7. Variation of total iron concentration in the Danube River water, Braila Town in 2008.

In summer, the water from sites **1** and **3** are of 5th class, and in autumn and winter are of 4th class. The highest concentration in the site **3** (Braila Harbour) and less in the site **1** (the passage ferryboat) can be associate with anthropic factors. The water from site **2** (swimming pool) has the lowest concentration of iron (3rd class of quality), in all the seasons.

Chromium. Chromium does not occur freely in nature. The main chromium mineral is chromite. Chromium compounds can be found in waters only in trace amounts. The element and its compounds can be discharged in surface water through various industries. Natural sources of water contain very low

concentrations of chromium. Rivers contain approximately 1 μg/L of chromium, although strongly increased concentrations are possible. It is a micronutrient (or essential trace element). It occurs in several forms, or oxidation states. The two most common are chromium (VI) and chromium (III), depending on pH. In natural waters, trivalent chromium is most abundant [14].

The concentration of chromium can be correlated with the presence of Fe(III) and pH, because both Cr(III) and Cr(VI) can strongly sorbs to iron hydroxide solids forming particulate Cr(III) and Cr(VI)[17], with the decreasing of chromium concentration in water.

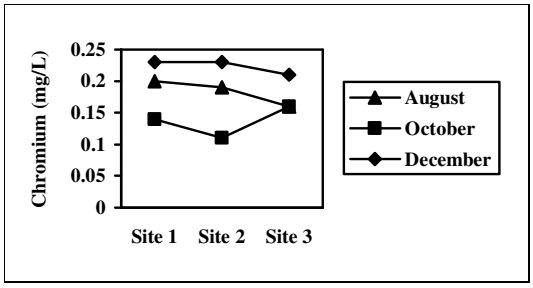

Fig. 8. Variation of total chromium concentration in the Danube River water, Braila Town, in 2008.

The total chromium concentration is of 0.1 – 0.25 mg/L for 4th class surface water and over 0.25 mg/L means that the water has a bad chemical state [5]. The concentration of total chromium in water was lowest in October, increasing to August and then to December. All the analyzed samples had concentration of total chromium between 0.11 and 0.23 mg/L and belong to 4th quality class (Fig. 8). Being a micronutrient, the chromium concentration can be also correlated with biological cycles.

Copper. Copper occurs naturally in rocks, soil, waters, sediments, air, and also in plants and animals. It is an essential element for all known living organisms, including humans. The levels of copper in surface and groundwater are generally very low. Copper can be released into the environment by both natural sources and human activities and it is very widespread in the environment. High levels of copper may come from fertilizers, septic systems, animal feedlots, industrial waste, and food processing waste [14].

The copper concentrations over 1.3 μg/L denote a bad chemical state and the detected quality classes of surface water, referred to copper are: 2nd class (20 - 30 μg/L), 3rd class (30 - 50 μg/L), 4th class (50 – 100 μg/L) and 5th class (over 100 μg/L) [5].

The highest concentration of copper was in summer, in site **2**, and, except site **3**, the copper concentration decreased from summer to autumn and winter (Fig. 9).

The higher concentrations of copper, determined in site **2**, where the water from swimming pool discharges in Danube River, can be correlated also with the water lowest pH. The atypical variation in site **3**, in comparison with the other two sites, may be due to the greater influence of anthropic factor in the harbour.

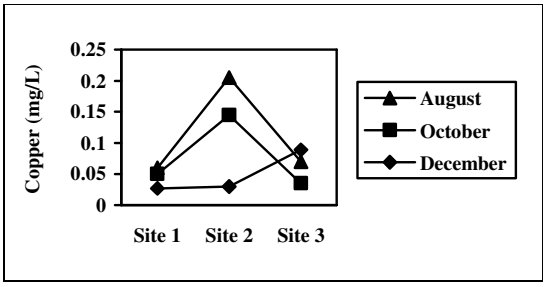

Fig. 9. Variation of copper concentration in the Danube River water, Braila Town, in 2008.

In Braila County are practiced agriculture and animal breeding, which maybe cause a high level of copper in Danube River, in summer the concentration being higher after agricultural treatments in spring.

The presence of some metallic ions in the Danube water in concentrations higher than normal values is a permanent problem, not only in Braila County [6,7,18]. The high concentration of these metals may be correlated with the general trend in Danube basin (mining and/or agricultural activities, etc.), not only to the local pollution sources (like agricultural treatments for copper, naval activity for iron).

3.6. Nutrients

Nutrients like nitrogen and phosphorus are necessary for healthy waters, but high levels of nutrients can cause a number of problems, ranging

from nuisance algae blooms and cloudy water to threatening drinking water and harming aquatic life. Total nitrogen, ammonia nitrogen and nitrate nitrogen are the main nutrients enriched in water body. The highest priority environmental challenge in the Danube basin is eutrophication. This problem is now also the priority issue for the Black Sea [19].

The total emissions of nitrogen in the Danube basin today are approximately 1.6 times higher than the levels in 1960. The main sources of nitrogen emissions into Danube are urban settlements, agricultural emissions caused by fertilizer and manure application, the deposition of oxidized nitrogen which is emitted mainly by combustion process in industry and traffic [19].

Ammonium is a nutrient for plants, but ammonia is poisonous for fishes when it's concentration is higher than 0.2 mg/L; at low values of pH, in water is found mostly ammonium ion. The tests are measuring the sum of NH_4^+ and NH_3. Sources for ammonium are mainly fertilizers and urea [20].

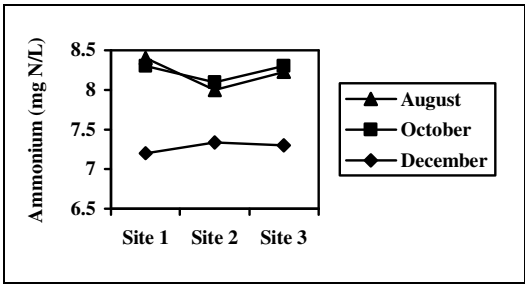

Fig. 10. Variation of N-NH_4^+ concentration in the Danube River water, Braila Town, in 2008.

The surface water with ammonium nitrogen concentration over 3.2 mg N/L belongs to the 5th class of quality. In all the determinations (Fig. 10), the ammonium nitrogen concentration is high, probably due to the organic matter dissolved in water, including the samples in the 5th class of quality.

The ammonium concentrations had a small tendency to increase from summer to autumn and decreased to winter substantially, in accordance with the vegetation cycle. The ammonium concentration in water can be correlated also with pH and temperature, which influence the equilibrium between ammonium ion and ammonia. The consequence of high ammonium concentrations may be an increasing amount of algae.

4. Conclusions

The quality of the Danube River water across Braila Town is affected by both natural and anthropic factors.

Thus, the presence in water of nutrients, like ammonium and iron ions, and micronutrients, like some metallic ions, can be associated with the biogeochemical cycles, but also with the agricultural and industrial activities. In two of the studied sites the naval activity is important, and as result the iron concentrations are higher.

The concentration of ammonium and metallic ions in water can be correlated also with the temperature of water, the concentration of dissolved oxygen, the pH, etc. The presence of other metallic ions also influences the equilibrium between soluble and insoluble metallic compounds.

The major problems for the Danube River water quality in Braila town were identified to be the high concentrations of copper, iron and ammonium, general characteristics for the water in the Danube River basin, which is hazardous to be assigned to a local major pollution issue.

5. References

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