THE INFLUENCE OF POLLUTION MONITORING PARAMETERS IN CHARACTERIZING THE SURFACE WATER QUALITY FROM ROMANIA SOUTHERN AREA*

D. FLORESCU[1], R.E. IONETE[1], C. SANDRU[1], A. IORDACHE[1], M. CULEA[2]

[1] National R&D Institute for Cryogenics and Isotopic Technologies, Uzinei Str. 4, RO-240050, Rm. Valcea, Romania, E-mail: dianaflorescu@icsi.ro; E-mail: roxana@icsi.ro; E-mail: sandru@icsi.ro; E-mail: andreea.iordache@icsi.ro
[2] Univ. Babes-Bolyai, Dept. Of Physics, I. Kogalniceanu, RO-3400 Cluj-Napoca, Romania E-mail: monica.culea@phys.ubbcluj.ro

Received September 10, 2010

Characterization of seasonal changes in surface waters quality is an important aspect in evaluating temporal variations of rivers pollution due to natural or anthropogenic inputs of point/non-point sources.

The present paper aims to evaluate the water quality parameters, in three main potential pollutant sources along the Arges, Olt and Jiu rivers and to extract those parameters that are most important in assessing the water quality.

Surface water quality data for 12 physical and chemical parameters collected from 3 different points/rivers thereby before, after and from a main city on the rivers were analyzed during the springtime of years 2010.

Key words: environment, surface water quality, chemical analysis, water parameters

1. INTRODUCTION

Surface water quality encompasses a wide range of conditions that are part of the aquatic environment in a water stream. In turn, the aquatic environment provides diverse habitat and a clean water supply for aquatic life, wildlife and humans.

There is no single or simple measure for water quality. Water may be tested for a few characteristics or numerous natural substances and contaminants, depending on the need. This can be done using traditional methods, such as collecting representative water samples from a water body and analyzing them to an analysis laboratory or on-site by hand-held electronic meters.

* Paper presented at the 11th International Balkan Workshop on Applied Physics, July 7–9 2010, Constanta, Romania.

1.1. FACTORS THAT INFLUENCE THE WATER QUALITY

Many factors influence water quality including climate and precipitation, soil type, geology, vegetation, groundwater, flow conditions and human activities. The greatest impacts are usually from point sources associated with the discharge of treated wastewater from municipalities and industries. In recent decades, in Romania there is a significant and ongoing improvement of wastewater treatment technology that has reduced the impact of point source pollution to rivers.

Extensive land-use activities like agriculture, mining and urban development can also significantly impact water quality. This pollution from non-point sources may include sediment, nutrients and toxic contaminants.

Certain pollutants originating from urban, industrial and/or agricultural activities can also be transported long distances by atmospheric processes, and deposited directly onto land and water stream within a drainage basin. Acid rain is one of the best known examples of this type of impact. This long-range transport can also include soil minerals, nutrients and numerous man-made chemicals.

The imposed quality standards for surface waters/rivers have to be related with the river usage type. For example, the drinking water implies higher standards than the water used for industrial or agricultural purposes.

Water quality monitoring data are compared over time, from place to place, and to expected conditions, in order to evaluate impacts on aquatic ecosystems. The data are also compared to surface water quality Romanian guideline (Normative benchmarks for surface water quality classification No. 10/2002), to evaluate the suitability of the water for specific uses. Such guidelines are usually based on toxicity studies or conditions which support the intended use. Water quality is deemed to be acceptable when the values are within the guidelines.

1.2. STUDY MAIN AIM

Urban and industrial development along the river basins has subjected the rivers to an increased stress ultimately leading to water pollution and environmental damaging. In its endeavor to protect and manage the environment, ICIT Rm. Valcea, by its Research Department, has started several environmental monitoring programs, one of them being applied to the characterization of surface waters quality in the Romanian Southern area. Based on collected data (physical and chemical parameters), water quality is determined by comparing with relevant standards.

This study is part of a program that aim to assess and establish a “baseline” data on the water quality of these rivers in order to characterize the river quality and identify changes or trends in water quality over time, to identify the types of pollutants discharge into the rivers and the possible sources of pollutants and also to gather information for decision makers for follow-up actions to maintain and improve the water quality of the rivers.

2. MATERIALS AND METHODS

The water quality monitoring program was carried out on three main rivers from the Romania South, water samples being collected in areas with high pollution potential.

Most important rivers from the southern Romania region, Arges, Olt and Jiu, are providing water for industry, agriculture and human use, but are also collecting treated and not treated wastewaters from different sources. The main pollutants near the collecting samples sites are ARPECHIM Pitesti, on Arges River, OLTCHIM Rm. Valcea and SODA Factory Govora on Olt River, and the coal mining Petrosani and Lupeni, on Jiu River.

2.1. EXPERIMENTAL

Surface water quality data for 12 physical and chemical parameters collected from 3 different points/rivers thereby before, after and from a main city on the rivers were analyzed during the springtime of years 2010.

The sampling sites were: (1) Catanele, (2) Pitesti, (3) Bascov – on Arges River, (4) Goranu, (5) Riureni, (6) Tatarani – on Olt River and (7) Braniste, (8) Craiova, (9) Isalnita – on Jiu River.

During sampling, the weather reports and river aspects were different. At first sampling campaign, in April 2010, the outside temperature, in Pitesti and around the city, was 11^0C, and the sky partly clear. At our arrival to Rm. Valcea, the next city from our sampling schedule, the temperature increased to 15^0C, the sky being clear with the sun up. In Craiova city, the weather conditions were the same as in Rm. Vilcea.

On the other hand, at the second sampling campaign, in May 2010, despite of the rainy weather of that month, that day was sunny, with unexpected temperature for that period of the year, between 21^0C and 25^0C.

The samples were collected in polyethylene bottle at depth between 0.20 ÷ 0.50 meters, the experimental part being made at ICIT Rm. Valcea – at Research Department Laboratories. These results are just a first part of a monitoring programme, the maiden work continuing with seasonal collected data in order to have significant patterns of change through the day and through the seasons for investigated rivers.

2.2. RESULTS AND DISCUSSIONS

The water quality in Arges, Olt and Jiu rivers, in the study sites, are influenced by the anthropogenic factor through activities such as extracting underground resources (minerals, salt), processes the resulting wastewater, wastewater discharges from households, chemicalization crops, etc. A significant changes to water quality is done by the chemical products/industry and mining activities.

The studied parameters were: temperature, pH, turbidity, particulate matters, electrical conductivity, dissolved oxygen, chloride ion, calcium ion, nitrate ion, fluoride ion, ammonia ion and total organic carbon. The potentiometric method was applied for parameters determination, except for determinations of suspended particulate matter were gravimetric method has been used. For measurements, ion selective electrodes from Horiba Company were used, on a multi-sample analyzer.

The Horiba analyzer measures the samples with a specific range for each parameter, as it follow: for pH - between 0 upH to 14 upH, for DO - between 0 ÷ 19.99 mg/L; for conductivity - between 0 ÷ 9.99 S/m; for turbidity - between 0 ÷ 800 NTU; to nitrate ion - 0.62 ÷ 62000 mg/L; to chloride ion - 0.4 ÷ 35000 mg/L; to calcium ion - 0.4 ÷ 40080 mg/L; to fluoride ion - 0.02 ÷ 19000 mg/L; to ammonia ion - 0.1 ÷ 1000 mg/L. This method has a wide application, to biological, agricultural, metallurgical, geological and environmental samples, after they were preliminary treated. The potentiometer method was used to analyze the parameters named below.

Temperature **–** the air and water temperature during sampling is an important factor that influenced the natural processes in rivers water. It affects especially the dissolution of oxygen, the pH and the salts dissolubility in water (Figure 1).

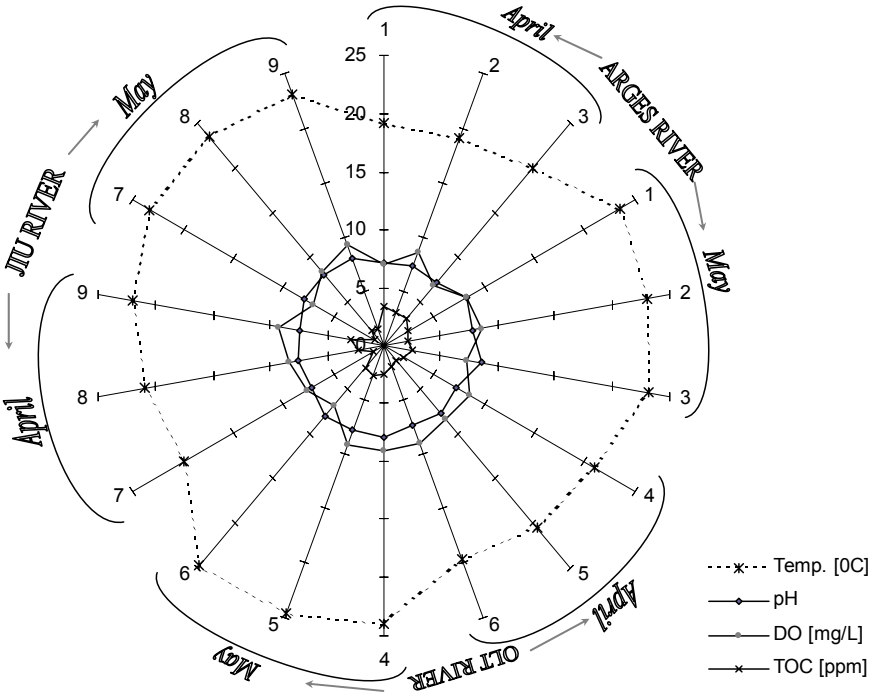

Fig. 1 – pH, DO, TOC variation with temperature.

pH **-** pollution can dramatically change the water pH. Being affected by the geology of water source, atmospheric inputs and/or chemical contaminants, the pH becomes an important indicator for water quality.

For the analyzed samples, the water average pH values were in the range of 7.07 and 8.5, didn't exceeding the limits, according with the Romanian classification scheme (6.5 ÷ 8.5). These values are typical for natural surface water, being optimum for most organisms. The increase of pH from April to May 2010, was caused also by the natural and anthropogenic factors.

Conductivity **-** the water ability to carry an electrical current, indicates the physical presence of dissolved chemicals in water. The measurement of the water's conductivity can provide a clear view of the concentration of ions in the water. An increased conductivity can be the result of released heavy metals ions from water pollutants. A higher conductivity reflects higher water pollution. The measured values for our samples were in the range of 237 μS/cm (on Arges River – site 1) and 960 μS/cm (on Olt River – site 5), didn't exceeding the limit value for drinking water.

Turbidity – consists from suspension inorganic matter, dispersed organic substances, microscopically microorganisms, etc. in water.

The value of total suspension particulate matter is particularly important to characterize the rivers water. According to water volume and specific gravity, particles are in separated form, as deposit (sedimentary), or floating on water surface (floating).

There is an increase of suspension particulate matter on Olt River and Jiu River (Figure 2), at the interact with the chemical industry and mining activity, in the studied area.

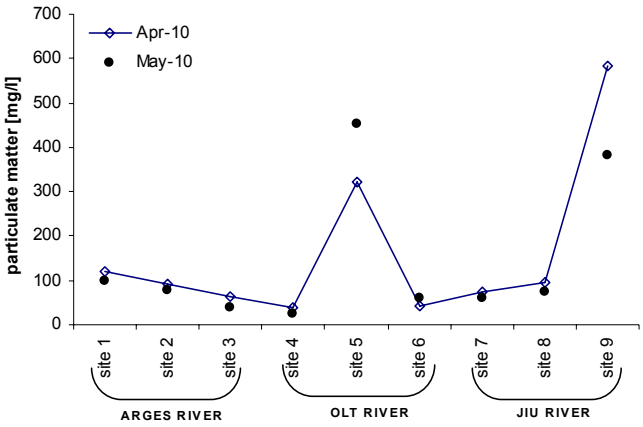

Fig. 2 – Suspended Particulate Matter concentration.

DO (dissolved oxygen) - essential for river self-purification. Oxygen depleting substances could be natural materials, such as plant matter (*e.g.* leaves and grass) as well as human-made chemicals. Other natural and anthropogenic

substances may cause turbidity (cloudiness) which blocks light and disturb plant growth, and clogs the gills of some fish species.

Organic constituents are significant in river chemistry for the effect that they have on dissolved oxygen concentration and for the impact that individual organic species may have on aquatic life. Any organic and degradable material utilizes oxygen as it decomposes. Where organic concentrations are elevated the effects on oxygen concentrations can be significant and as conditions get extreme the river bed may become anoxic.

The measured value for DO, according with the water quality Romanian guideline, fit the water quality in the studied area in classes I and II.

TOC (total organic carbon) **-** organic matter plays a major role in aquatic systems being measured as total organic carbon. It affects biogeochemical processes, nutrient cycling, biological availability, chemical transport and interactions. Has also, direct implications in the planning of wastewater treatment and drinking water treatment.

Total organic carbon is the amount of carbon bound in an organic compound and is used as a non-specific indicator of cleanliness or water quality. It has been recognized as an analytic parameter to measure water quality during the water purification process. Its origin in water comes from decaying natural organic matter (humic acid, fulvic acid, amines and urea) and from synthetic sources (detergents, pesticides, fertilizers, herbicides, industrial chemicals, and chlorinated organics).

Using TOC measurements, the number of carbon-containing compounds in a source can be determined. Knowing the amount of carbon in a freshwater stream is an indicator of the organic character of that stream. The larger the carbon or organic content, the more oxygen is consumed (Figure 3).

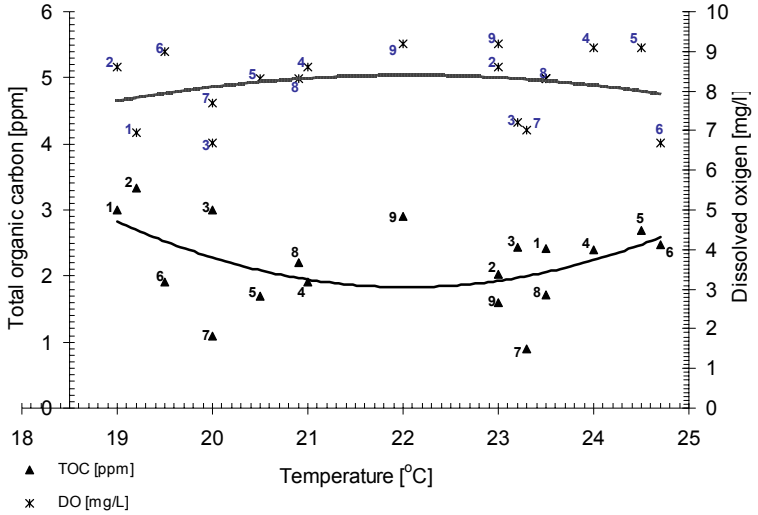

Fig. 3 – Correlation between DO and TOC, function on temperature.

A high organic content means an increase in the growth of microorganisms which contribute to the depletion of oxygen supplies. Industrial waste effluent may contain carbon-containing compounds with various toxicity levels. These situations can create unfavorable conditions for aquatic life, such as the depletion of oxygen and the presence of toxic substances.

Hardness – crucial parameter that characterize the final use of water, for different industrial branches, depending on Mg and Ca ions presence.

The main reason for abundance of calcium in water is its natural occurrence in the earth's crust. Rivers contain 1-2 mg/L calcium, but in lime rivers area 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.

From our study, an increase in calcium by the Olt River (Figure 4) can be observed, as an influence of OLTCHIM activities.

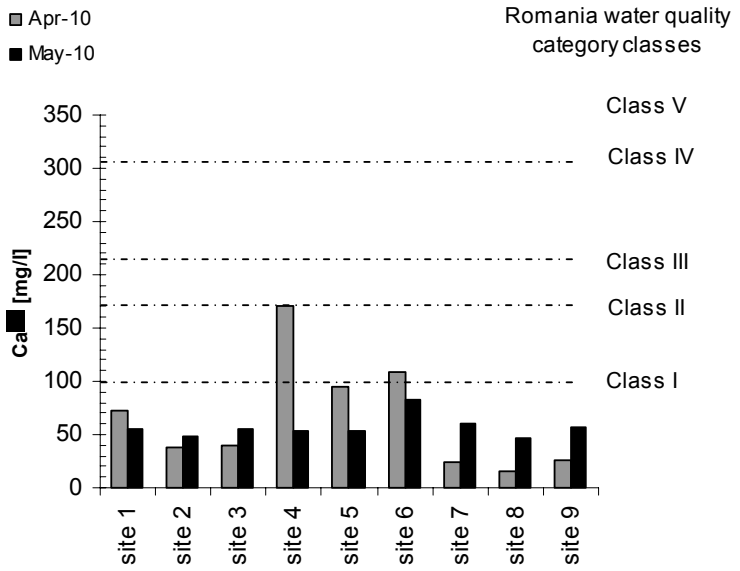

Fig. 4 – Calcium ion concentration.

Chlorides are not usually harmful to people; however, the sodium part of table salt has been linked to heart and kidney disease. Sodium chloride may impart a salty taste at 250 mg/L. High concentrations of dissolved salts in water compromise its use for domestic or agricultural purpose. An excess of Cl^- in inland water is usually taken as an index of pollution and can be provided across the sanitary and industrial waters.

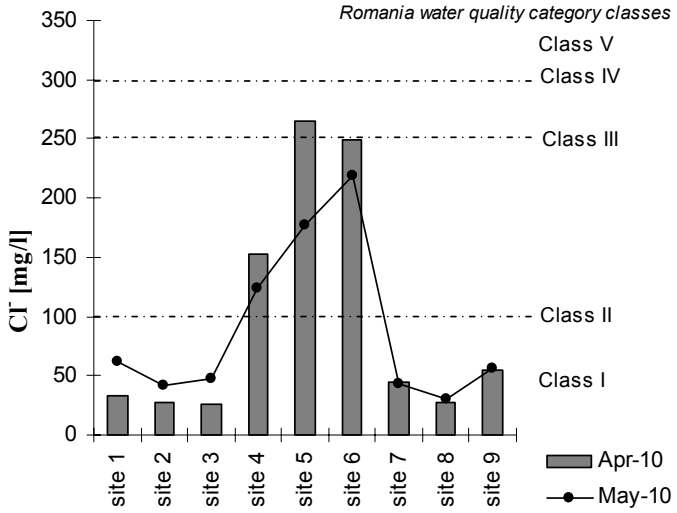

Fig. 5 – Chlorides concentrations.

Depending upon the end-user, there are maximum concentration limits recommended. 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. According to the results, a higher amount of chloride ions can be observed on Olt River (Figure 5), as a consequence of OLTCHIM – chemical plant activities in the monitored area.

Fluoride - exists naturally in water, the sources of most fluoride in natural fresh-water resources being various rocks and mineral bedrock and sediments. Although fluoride has a beneficial effect with a range of low concentration, at hither concentration has adverse effects. The amount of fluoride ions concentrations in investigated area didn't exceed the Romanian maximum admissible value, of 5 mg/l, being in the range of 0.1 ÷ 1.1 mg/l.

Nutrients – for water quality evaluation**,** a presence pre-confirmation of matters created by decomposition of wastes animal origin is important. In polluted water, varied products can appear: C and S compounds, a special importance being accorded to N compounds. Nitrogen may be in the form of nitrate, nitrite, ammonia or ammonium salts or what is termed albuminoid nitrogen together with an organic proteinoid molecule. The differing forms of nitrogen are relatively stable in most river systems with nitrite transforming into nitrate in well oxygenated rivers and ammonia transforming into nitrite/nitrate. However, the process is slow in cool rivers and reduction in concentration may more often be attributed to simple dilution. All forms of nitrogen are taken up by algae and elevated levels of nitrogen are often associated with overgrowths of plants. The more significant effect is on dissolved oxygen concentrations which may become saturated during daylight due to plant photosynthesis but then drop to very low levels during darkness as plant

respiration uses up the dissolved oxygen. Thus high levels of nitrogenous compounds tend to lead at extreme variations in parameters which in turn can degrade the ecological worth of the watercourse.

A high amount of ***nitrates*** in rivers water (Figure 6) can be observed along the investigated route as a consequence of urban settlements, agricultural emissions and/or industry and traffic.

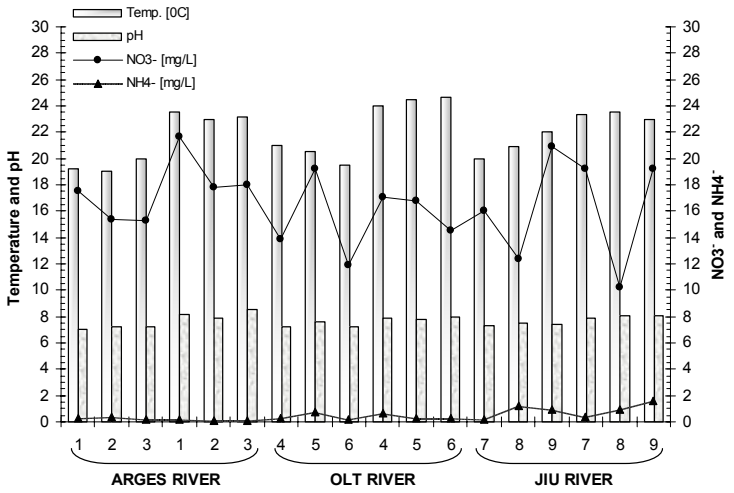

Fig. 6 – Nitrates and Ammonium.

Ammonium is a nutrient for plants, but can also have toxic effect, especially on fish, when its concentration is higher than 0.2 mg/l. The toxicity of ammonia is dependent on pH and temperature and added the buffering effect which masks any additional toxicity over pH = 8. To avoid ecological damage we have to consider the pH fluctuation caused by photosynthesis which is difficult in the case of ammonia as a wide range of parameters such as concentration, pH and temperature.

The surface water with a concentration of NH4- over 1.5 mg N/l belongs to the 5th class quality. In all the determinations, especially on Jiu River, a high level of ammonium can be observed, probably due to the organic matter dissolved in water. The consequence of high ammonium concentrations may be an increasing amount of algae.

3. CONCLUSIONS

There is a fact that water quality for all three investigated rivers is affected by both natural and anthropogenic factors. The measured parameters in analysed water samples showed slight variations depending on location.

River pollution indicators, such as ammonium, nitrates, organic carbon, dissolved oxygen, exceed the admissible limits for various classes of quality if in environmental area is evolved communal economy activities, chemical industry and agriculture activities followed by the economic units within the ore mining and metal processing.

The presence in water of nutrients, like nitrogen and ammonium ions, can be associated with the biogeochemical cycles, but also with the industrial (chemical industry and mining) and agricultural activities. The concentration of ammonium ions in water can be also correlated with the water temperature, concentration of dissolved oxygen and pH.

REFERENCES

1. V. Nistreanu, L. Vuta, G. Dumitran, *Water pollution in Olt River and Buzau River*, The 1th Conference Engineers, Bucharest, Romania, 2000.
2. A. Preda, F. Vasut, C. Pearsica, *Olt River pollution with heavy metals in Ramnicu Valcea Area*, The fourth Conference Isotopic and Molecular Processes, Cluj-Napoca, 2005.
3. * * * * * US Council on Environmental Quality, Contamination of Ground Water by Toxic Organic Chemicals, 1981.