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Optimal Measurements of Surface Water Pollution-Case Study on Southern Part of Romania

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In this research, some surface waters originating from southern of Romania (Arges, Olt and Jiu rivers) were studied in order to assess the effects of atrophic pollution, based on analyses performed in the springtime of 2010. Water quality indicators like pH, conductivity, turbidity and dissolved oxygen, chloride, calcium and fluorine ions, nitrates and ammonia ions, total organic carbon and heavy metals content have been analyzed in three different points/rivers thereby before, after and from a main city on the rivers. The measured parameters in analyzed water samples showed slight variations depending on location, the water quality for all the three investigated rivers being affected by both natural and anthropogenic factors.

Key Words: Surface water quality, Chemical analysis, Water parameters, Heavy metals.

INTRODUCTION

This study is part of a program managed by the Research Department of ICIT Rm. Valcea, that aim to assess and establish a baseline data on the water quality of southern part of Romanian 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.

The three investigated rivers, Arges, Olt and Jiu, has large importance for the development of Romania South-West area. Crossing areas with high potential for development, they are providing water for industry, agriculture and human use, but are also collecting treated and not treated wastewaters from different sources.

Arges river, with a length of 350 km, starts at the junction of headwaters Buda and Capra in the Fagaras Mountains, in the Southern Carpathians. It crosses by Arges, Dimbovita, Ilfov, Giurgiu and Calarasi counties and disgorge into the Danube river at Oltenita. Upstream, it is retained by the Vidraru Dam, which has created Lake Vidraru.

Olt river is one of the most important rivers[1-3] from Romania which length is 615 km. Its source is in the Hasmas mountains of the eastern Carpathian mountains. It crosses by Harghita, Covasna, Brasov, Sibiu, Valcea and Olt counties and disgorge into the Danube river at Turnu Magurele. Main pollutants in Olt river basin are: Cellulose and Paper factory Zarnesti, Colourom Codlea factory, Chemical plant, Fagaras, Chemical plant, Victoria, Chemical plant - OLTCHIM Rm. Valcea, Soda factory, Govora.

Jiu river flows southward through the Romanian counties Hunedoara, Gorj and Dolj before flowing into the Danube river, a few kilometers upstream from the Bulgarian city of Oryahovo, 331 kilometers from its sources. The upper Jiu Valley, around Petrosani and Lupeni, is Romania's principal coal mining region[1-3].

The water samples were collected in areas with high pollution potential, the main pollutants near the collecting samples sites being 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.

Twelve sample-places were selected, as follow: (1) Catanele, (2) Pitesti, (3) Bascov - on Arges river, near Pitesti city, (4) Goranu, (5) Riureni, (6) Tatarani - on Olt river, near Rm. Valcea city and (7) Braniste, (8) Craiova, (9) Isalnita - on Jiu river, near Craiova city.

EXPERIMENTAL

Characterization of seasonal changes in surface water quality is an important aspect in evaluating temporal variations of river pollution due to natural or anthropogenic inputs of point and non-point sources[1-3].

Surface water quality data for 12 physical and chemical parameters collected from three main sampling sites/river

TABLE-1
WATER QUALITY PARAMETERS FOR STUDIED SITES

Quality indicators	Arges river						Olt river						Jiu river					
	Catanele		Pitesti		Bascov		Goranu		Riureni		Tatarani		Braniste		Craiova		Isalnita	
	Apr	May	Apr	May	Apr	May	Apr	May	Apr	May	Apr	May	Apr	May	Apr	May	Apr	May
Temp. [ºC]	19.2	23.5	19.0	23	20	23.2	21.0	24.0	20.5	24.5	19.5	24.7	20.0	23.3	20.9	23.5	22.0	23.0
pH [upH]	7.07	8.18	7.25	7.83	7.18	8.5	7.23	7.92	7.59	7.82	7.19	7.83	7.28	7.86	7.49	8.05	7.44	8.08
Conductivity [µS/cm]	372	237	362	290	400	289	457	324	499	342	960	783	497	277	556	295	602	315
Turbidity [NTU]	1.5	3.76	5.0	4.51	3.5	6.21	11.7	12.2	9.3	5.67	10.9	7.18	25.3	43.8	30.5	49.0	27.7	33.5
Particulate matter [mg/L]	119	98.0	90.5	77.4	62.2	39.9	40.0	25.0	323	454	41.5	58.8	75.0	60.1	94.0	72.6	585	383
DO [mg/L]	7.0	8.3	8.6	8.6	6.7	7.2	8.6	9.1	8.3	9.1	9.0	6.7	7.7	7.0	8.3	8.3	9.2	9.2
Cl^- [mg/L]	33.3	61.9	27.4	41.7	25.8	48.2	152	124	265	177	249	219	44.1	42.6	26.9	30.5	55.2	56.8
Ca^{2+} [mg/L]	72.1	54.5	37.7	48.9	39.2	55.3	170	52.9	94.4	54	109	83.4	23.3	60.2	15.9	46.4	25.6	56.1
NO_3^- mg/L]	17.5	21.7	15.4	17.8	15.3	18.02	13.9	17.1	19.27	16.8	11.9	14.53	16.0	19.2	12.4	10.2	20.9	19.2
NH_4^+ mg/L]	0.26	0.18	0.38	0.09	0.18	0.10	0.27	0.62	0.72	0.26	0.23	0.26	0.2	0.4	1.2	0.9	0.95	1.6
F^- [mg/L]	0.26	0.25	0.31	0.18	0.32	0.19	0.35	0.62	0.37	0.15	0.5	0.9	0.5	0.4	0.10	0.25	0.77	1.1
TOC [ppm]	3.34	2.41	3.0	2.02	3.0	2.43	1.9	2.40	1.7	2.69	1.9	2.48	1.1	0.9	2.2	1.72	2.9	1.6
Ni [µg/L]	0.4	4.3	0.4	4.2	0.4	4.4	1.6	4.1	0.96	4.5	4.1	8.3	0.4	4.1	0.4	5.1	0.4	4.2
Cd [µg/L]	0.04	0.23	0.04	0.26	0.04	0.22	0.04	0.2	0.04	0.21	0.04	0.18	0.04	0.22	0.04	0.22	0.04	0.24
Pb [µg/L]	1.64	1.64	2.3	1.8	1.94	1.95	1.97	1.79	1.02	1.84	3.62	2.08	1.67	2.04	2.59	2.72	3.58	3.2
Zn [µg/L]	15.3	12.15	4.61	5.15	4.83	6.37	5.07	6.92	7.34	7.8	11.36	11.0	8.8	8.6	14.6	10.46	14.5	11.7
Cu [µg/L]	49.6	113.6	13.2	27.3	25.01	22.8	40.1	18.1	12.2	33.8	32.3	105.3	19.8	104	18.4	157.6	35.6	113

Data collected in spring time of year 2010

(before, after and respectively, from a main pollution point along the rivers) during the springtime of years 2010 were analyzed.

General procedure: 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 ºC and the sky partly clear. At our arrival to Rm. Valcea, the next city from our sampling schedule, the temperature increased to 15 ºC, 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 and 25 ºC.

The samples were collected in polyethylene bottle at depth between 0.20 to 0.50 meters. tThe experimental part being made at Research Department Laboratories, ICIT Rm. Valcea. 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.

Detection method: The studied parameters were: temperature, pH, turbidity, particulate matters, electrical conductivity, dissolved oxygen, Cl^-, Ca^{2+}, NO_3^-, F^-, NH_4^+ and organic carbon. The main water quality parameters were determined by potentiometric methods and the particulate matter was determined by gravimetric method and the heavy metals by inductively coupled plasma mass spectrometry measurements.

RESULTS AND DISCUSSION

The water quality in Arges, Olt and Jiu rivers are most influenced by the specific anthropogenic factor through activities developed through the study area, such as extracting underground resources (minerals, salt), processes the resulting wastewater, wastewater discharges from households, chemicals, *etc.*, the most significant pollutant sources being from chemical industry and mining activities (Table-1).

Temperature: Water temperature is a critical parameter for aquatic life and has an impact on other water quality parameters such as dissolved oxygen concentrations, pH, salts dissolubility in water and bacteria activity in water (Fig. 1).

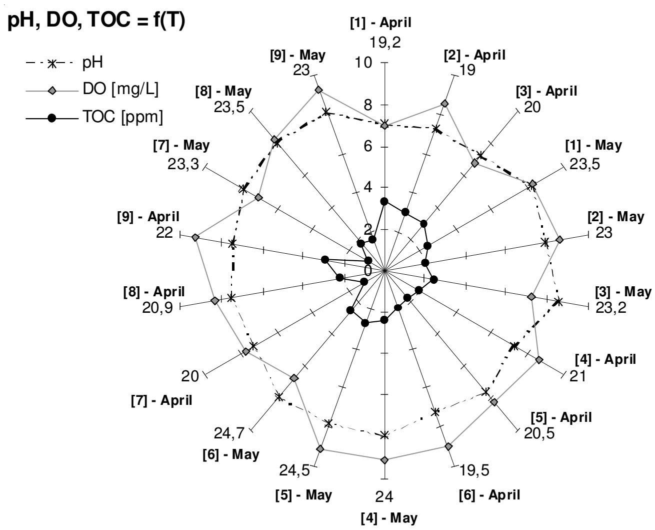

Fig. 1. pH, DO, TOC variation with temperature, on sample sites 1-9

Factors that can have an impact on water temperature could be the quantity and maturity of riparian vegetation, the rate of flow, the precipitations, thermal discharges, impoundments and groundwater.

pH: For the analyzed samples, the average pH values of water were in the range of 7.07 and 8.5, didn't exceeding the limits, according with the Romanian classification[4] (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 measured values for present 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: There is an increase of suspension particulate matter on Olt river (site 5 - Raureni) and Jiu river (site 9-Isalnita), at the interaction with the chemical industry and mining activity, in the studied area.

Dissolved oxygen- The measured value for dissolved oxygen, according with the water quality Romanian guideline[5], fit the water quality in the studied area in classes I and II.

Total organic carbon: Using total organic carbon measurements, the number of carbon-containing compounds in a source can be determined. Knowing the amount of carbon in a fresh water stream is an indicator of the organic character of that stream. The larger the carbon or organic content, the more oxygen is consumed (Fig. 2). A high organic content means an increase in the growth of microorganisms which contribute to the depletion of oxygen supplies. Industrial waste effluents may contain carbon-containing compounds with various toxicity levels. These situations can create unfavourable conditions for aquatic life, such as the depletion of oxygen and the presence of toxic substances.

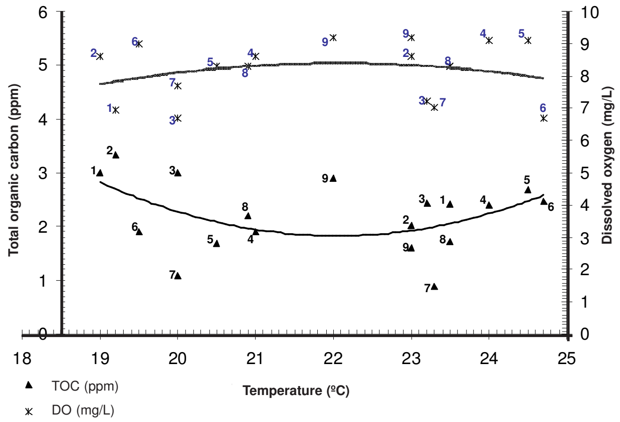

Fig. 2. Correlation between dissolved oxygen (DO) and total organic carbon (TOC), function on temperature

Hardness: The main reason for abundance of Ca^{2+} 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. In present study, an increase in calcium by the Olt river (Fig. 3) can be observed, as an influence of OLTCHIM activities.

Chlorides: The chloride ion (Cl^-) is found naturally in some surface waters and groundwater. Higher-than-normal chloride concentrations in freshwater is detrimental to water quality. 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

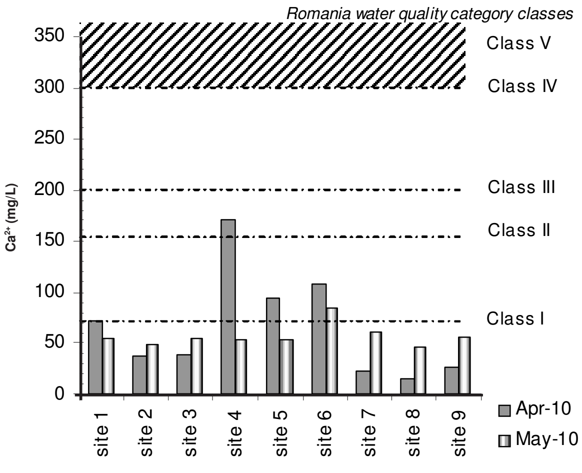

Fig. 3. Calcium ion concentration

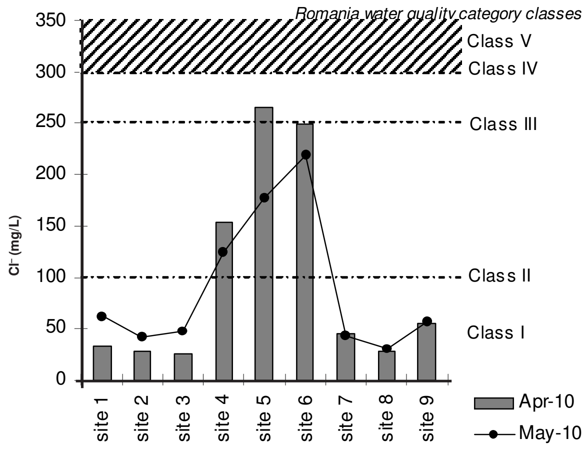

Fig. 4. Chloride ion concentrations

to the second class of quality. From Fig. 4, a higher amount of chloride ions can be observed on Olt river, as a consequence of OLTCHIM-chemical plant activities in the monitored area.

Fluoride: The amount of F^- concentrations in investigated area didn't exceed the Romanian maximum admissible value, of 5 mg/L, being in the range of 0.1 to 1.1 mg/L.

Nutrients: A high amount of nitrates in rivers water (Fig. 5) can be observed along the investigated route as a consequence of urban settlements, agricultural emissions and/or industry and traffic.

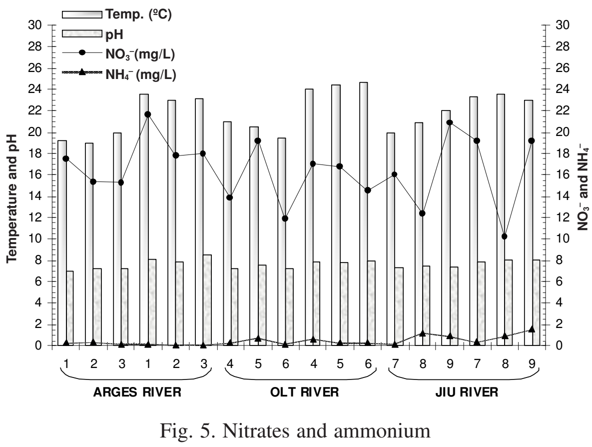

Fig. 5. Nitrates and ammonium

TABLE-2
ROMANIAN STANDARDIZED LIMITS BY WATER QUALITY CLASSES FOR THE INVESTIGATED HEAVY METALS CONCENTRATION IN RIVERS WATER

Metals [µg/L]	Values regulated by the Romanian standards				
	Class I (very good)	Class II (good)	Class III (moderate)	Class IV (satisfactory)	Class V (low)
Ni^{2+}	Natural background	1.0	2.0	5.0	> 5.0
Cd^{2+}	Natural background	0.1	0.2	0.5	> 0.5
Pb^{2+}	Natural background	1.0	2.0	5.0	> 5.0
Zn^{2+}	Natural background	5.0	10.0	25.0	> 25.0
Cu^{2+}	Natural background	20.0	40.0	100	> 100

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 NH_4^+ over 1.5 mg/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.

Metals: The heavy metals analysis has been performed with an ICP-MS, the amounts of micro-contaminants in investigated river waters being in normal limits, with few exceptions (Fig. 6).

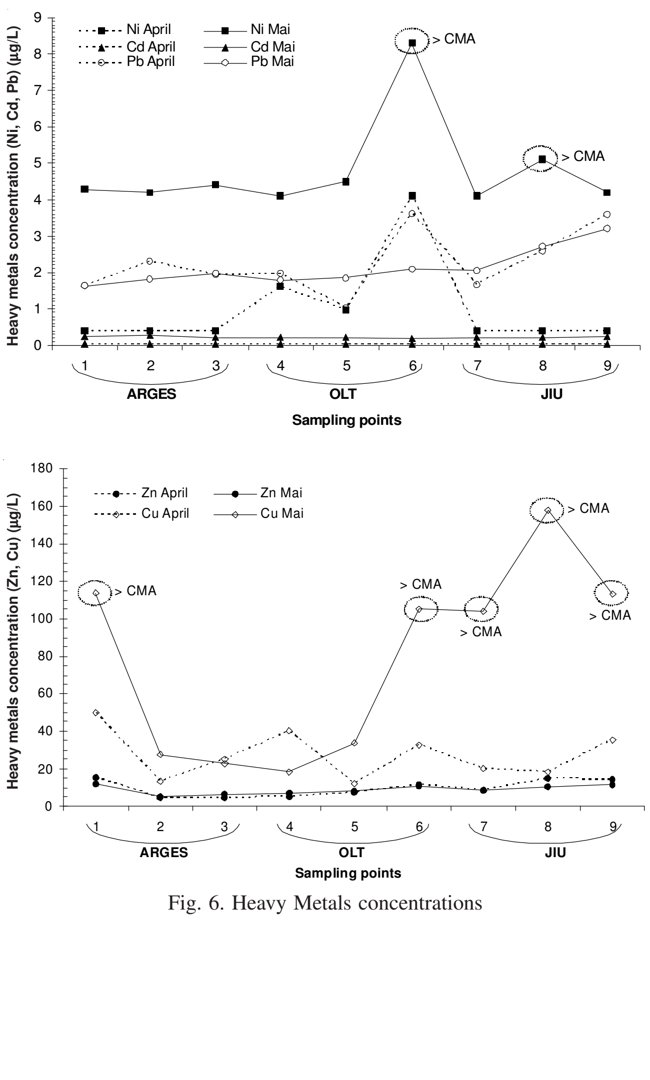

Fig. 6. Heavy Metals concentrations

In terms of water quality, the Romanian river waters are classified by classes. For the investigated elements, the limits/ classes are given in Table-2.

An increase of Ni and Cu can be observed on Jiu river, as a concequence of mining activities in the area. Also, on Arges river - site (2) and Olt river - site (4), there is a much higher Ni concentration than the permissible limit of the Romanian Standards, possible as a part of wastewater streams.

Water can also be polluted with zinc, due to the presence of large quantities of zinc in the wastewater of industrial plants. This wastewater is not purified satisfactory, one of the consequences being that rivers are depositing zinc-polluted sludge on their banks. There is a high concentration of Zn on Arges river - site 1, Olt river - site 6 and Jiu river - site 8 and 9.

As regard of Cd and Pb concentrations, the investigated waters rivers are almost all included in class II and III, according with the Romanian standards.

Conclusion

The water quality for all three rivers is affected by both natural and anthropogenic factors. The river pollution indicators, such as ammonium, nitrogen, organic carbon, dissolved oxygen and heavy metals exceed the admissible limits for various classes of quality if in environmental area is evolve communal economy activities, chemical industry and agriculture activities followed by the economic units within the ore mining and metal processing.

The presence of nutrients in water, 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 NH_4^+ in water can also be correlated with the water temperature, concentration of dissolved oxygen and pH.

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