ASSESSMENT OF RIVER WATER QUALITY IN CENTRAL AND EASTERN PARTS OF ROMANIA USING ATOMIC AND OPTICAL METHODS

ANTOANETA ENE[1], ION V. POPESCU[2,3,4], CLAUDIA STIHI[2,3], ANCA GHEBOIANU[3], CRISTIANA RADULESCU[2], NICOLAE TIGAU[1], STELUTA GOSAV[1]

[1] *„Dunarea de Jos" University of Galati, Faculty of Sciences, 800201, Galati, Romania*

[2] *Valahia University of Targoviste, Faculty of Sciences and Arts, 130082, Targoviste, Romania*

[3] *Valahia University of Targoviste, Multidisciplinary Research Institute for Sciences and Technologies, 130082, Targoviste, Romania*

[4] *Academy of Romanian Scientists, 050094, Bucharest, Romania*

Abstract: *The main objective of this paper is to assess the water quality of some rivers from Brasov, Braila and Galati counties (Timis, Danube and Prut) using atomic and optical methods: Atomic Absorption Spectrometry (AAS), UV-VIS Spectrometry and Turbidimetry. The concentrations of Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn in the water samples were determined by AAS technique using the AVANTA GBC spectrometer from Valahia University of Targoviste, with flame and hollow cathode lamps (HCL). The UV-VIS spectrometric and turbidimetric determinations were carried out at Physics Department, "Dunarea de Jos" University of Galati, using WTW - TURB 430 IRIR/T portable turbidimeter and Perkin Elmer Lambda 35 UV-VIS Spectrometer. The river water turbidity and absorbencies are correlated with the concentrations of heavy elements detected in the analyzed water samples. This study is part of a partnership project funded by National Plan of Research, Developing and Innovation, of implementation of high precision and sensibility methods for the biomonitoring of the environmental pollution in South, South-East and Central regions of Romania (Project 72-172/2008).*

Keywords: *water pollution, AAS technique, UV-VIS Spectrometry, turbidimetry, heavy metals*

1. INTRODUCTION

At national and international level, the control of anthropogenic pollution with heavy metals of waters, air, soils and biota is a constant preoccupation [1-5]. The increasing of heavy metal pollution level imposes a careful analysis of the polluting agents of waters, which represent life support [6,7]. The study of the heavy metal emissions at international level has shown that the impact of anthropogenic action became decisive in the global cycle of many elements. The main source of atmospheric pollution with heavy metals is the industrial processes (iron and steelmaking, chemical and petrochemical, material processing, mining etc), power stations and vehicle motors. The ore extraction inevitably leads to the soil pollution and implicit to water pollution. All these pollution sources are frequently found in Romania and the concentration of many polluting objectives in certain geographical regions leads to the accumulation of polluting agents which can produce a real ecological stress. Because of the grave consequences the pollution of surface waters could have upon the ecosystems and population health, the problem of attentive monitoring all over the country is imposed, especially in urban communities and industrial zones, by the implementation of high precision and sensibility modern techniques.

In this paper are presented the results of the analysis of some surface waters from the rivers basin of Timis (Brasov County) and Danube-Prut (Galati and Braila Counties), which are zones affected by the industrial activities.

The analytical technique used in our studies of the pollution of waters with heavy metals is atomic absorption spectrometry, which have been carried out in the research laboratories of Valahia University of Targoviste [8-10]. The experimental results obtained for the heavy metals concentration in the water samples have been correlated with water turbidity and absorbance in UV-VIS spectra obtained at Physics Department of "Dunarea de Jos" University of Galati.

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2. EXPERIMENTAL

The water samples have been collected from Timis river (samples BV1, BV2, BV3 and BV4), Prut river (sample GL1) and Danube river near Galati and Braila towns (samples GL2-GL8 and BR1), from different locations (zones with harbor activity – shipbuilding yard, mineral port; zone with touristic interest; from the vicinity of an affluent discharging mouth, agreement places – cliffs, beaches, fishing places – and industrial units, etc).

In order to determine the concentrations of heavy metals Cd, Cr, Co, Ni, Pb, Cu, Fe and Zn we used the atomic absorption spectrometry method. The calibration method for the determination of elemental concentration in sample has been performed: some sample solutions at known concentrations (three or more) are measured in order to draw the calibration curve of concentration as a function of absorbance. The absorbance of one unknown sample is determined by extrapolation of the calibration curve. The standard sample is prepared so its concentration should include the concentration value of the unknown sample. The samples have been analyzed with the atomic absorption spectrometer with flame AVANTA GBC from the Valahia University of Targoviste. This system is used for elemental analysis of a variety samples (solids, liquids) [9, 10]. It has the measurement limit at 1 ppm. The water samples have been kept in polypropylene bottle, filtrated by filter paper and the level of pH has been established at 4 – 5 with HNO_3. The obtained concentrations of Cd, Cr, Co, Ni, Cu, Fe and Zn are presented in Table 1. The concentration of Pb in all water samples was 0 mg/L. Standard error was less than 5%.

Turbidity is an important water quality variable, through its relation to light suppression, sediment-associated contaminant transport, and suspended sediment effects on organisms and habitats [11]. Precipitated particulate products suspended in the water specimen may be composed of clays, bacteria, algae or colloidal organic molecules and can be measured by the diffusion optical techniques turbidimetry or nephelometry. Turbidimetry determines the average concentration of these suspended particles by detecting a decrease in beam transmission from an optical probe (obscuration) and nephelometry by measuring the increase in scattered-light intensity.

The UV-VIS spectrometric and turbidimetric determinations were carried out at Physics Department, "Dunarea de Jos" University of Galati, using WTW - TURB 430 IRIR/T portable turbidimeter and Perkin Elmer Lambda 35 UV-VIS Spectrometer and the results are given in Table 1. In Fig. 1 are presented the absorbencies spectra in UV-VIS domain for the water samples labelled in Table 1. Fig.2 contains the correlation matrix for heavy metals (Cu, Fe, Zn) content (in mg/L), absorbencies obtained for wavelengths of 500 nm, 740 nm and 975 nm, respectively) and turbidity T (in NTU– Nephelometric Turbidity Units).

Table 1. Obtained values for heavy metal content (mg/L), absorbencies A1, A2, A3 (for wavelengths 500 nm, 740 nm and 975 nm, respectively) and turbidity T (NTU) of the investigated surface water samples

Sample no.	Cd	Co	Cr	Ni	Cu	Fe	Zn	A1, 500 nm	A2, 740 nm	A3, 975 nm	T (NTU)
BV1- Timis	0.0033	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.0003	0.187	0.68
BV2 - NE	0.0017	0.0000	0.0000	0.0000	0.0100	0.3867	0.0017	0.040	0.047	0.240	2.53
BV3 – Water sample 5	0.0050	0.0000	0.0000	0.0000	0.0000	0.3767	0.0100	0.078	0.067	0.251	2.52
BV4 – Treated water	0.0050	0.0000	0.0000	0.0000	0.0000	0.8867	0.0000	0.036	0.045	0.237	1.11
GL1-Prut Giurgiulesti	0.0000	0.0000	0.0800	0.0017	0.0000	0.0667	0.0000	0.257	0.073	0.081	59
GL2 –Danube Prut confluence	0.0000	0.0250	0.0000	0.0000	0.0000	0.2050	0.0000	0.258	0.071	0.072	46.3
GL3 –Danube inlet	0.0000	0.0217	1.5867	0.0800	0.0000	0.0050	0.0000	0.248	0.060	0.058	38.6
BR1- Danube ferryboat Braila	N.A	N.A	N.A	N.A	0.0167	2.6400	0.0583	0.301	0.114	0.115	12.8
GL4- Danube ferryboat Galati, sewerage	N.A	N.A	N.A	N.A	0.0283	7.0983	0.0300	0.278	0.089	0.087	15.4
GL5- Danube harbor	N.A	N.A	N.A	N.A	0.0250	2.6683	0.0333	0.267	0.078	0.076	7.67
GL6-Fluvial Station	N.A	N.A	N.A	N.A	0.0467	8.3350	0.0250	0.373	0.220	0.280	378
GL7- Danube Galati center cliff	N.A	N.A	N.A	N.A	0.0300	3.7550	0.0267	0.240	0.048	0.044	24.3
GL8 - Danube sewerage Malnas	N.A	N.A	N.A	N.A	0.0250	3.4017	0.0133	0.257	0.075	0.082	48.2

N.A.- not analyzed

3. RESULTS AND DISCUSSIONS

From the correlation matrix in Fig. 2 it can be seen that the river water turbidity and absorbencies are correlated with the concentrations of heavy elements detected in the analyzed water samples. Also, for the experimental data presented in Table 1 Principal Component Analysis (PCA) was applied and from Fig. 2 it is observed the formation of two clusters, each of them corresponding to one region: Brasov and Galati (the last one includes the Danube water sample from Braila). Only one exception exists: the sample GL6 collected in the vicinity of the fluvial station in Galati presents very high values of turbidity and of Fe content.

The obtained results for the concentrations of heavy metals in surface water samples by the atomic absorption spectrometry were compared with the Romanian admissible values for water samples. Standard values of surface water for classes 1, 2 and 3 are presented in Table 2.

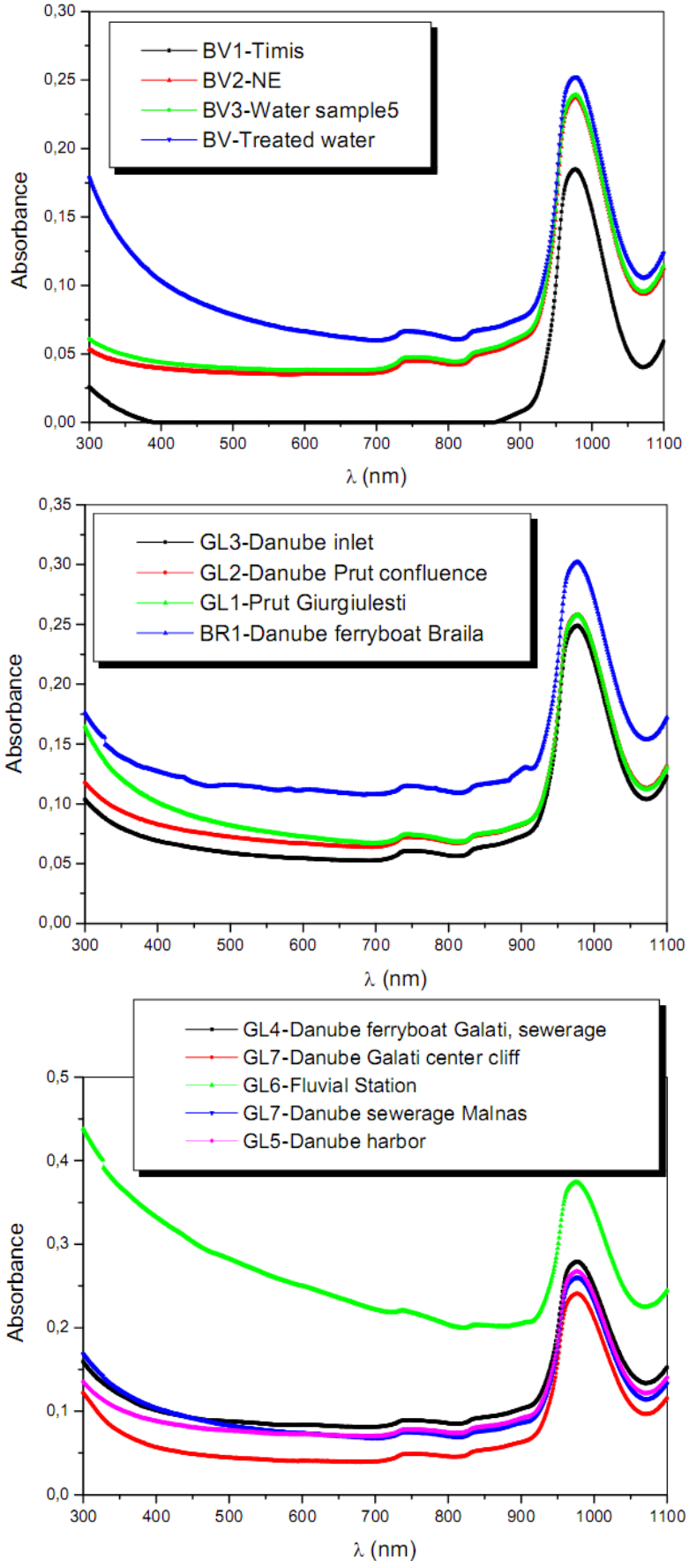

Fig. 1. UV-VIS absorbance spectra for investigated water samples

Variable	Cu	Fe	Zn	A1	A2	A3	T
Cu	1.000000	0.927251	0.638553	0.629140	0.690594	-0.010463	0.606172
Fe	0.927251	1.000000	0.590843	0.620841	0.737134	0.058537	0.632552
Zn	0.638553	0.590843	1.000000	0.557549	0.483001	-0.190333	0.113748
A1	0.629140	0.620841	0.557549	1.000000	0.732041	-0.486282	0.534209
A2	0.690594	0.737134	0.483001	0.732041	1.000000	0.238596	0.864428
A3	-0.010463	0.058537	-0.190333	-0.486282	0.238596	1.000000	0.361025
T	0.606172	0.632552	0.113748	0.534209	0.864428	0.361025	1.000000

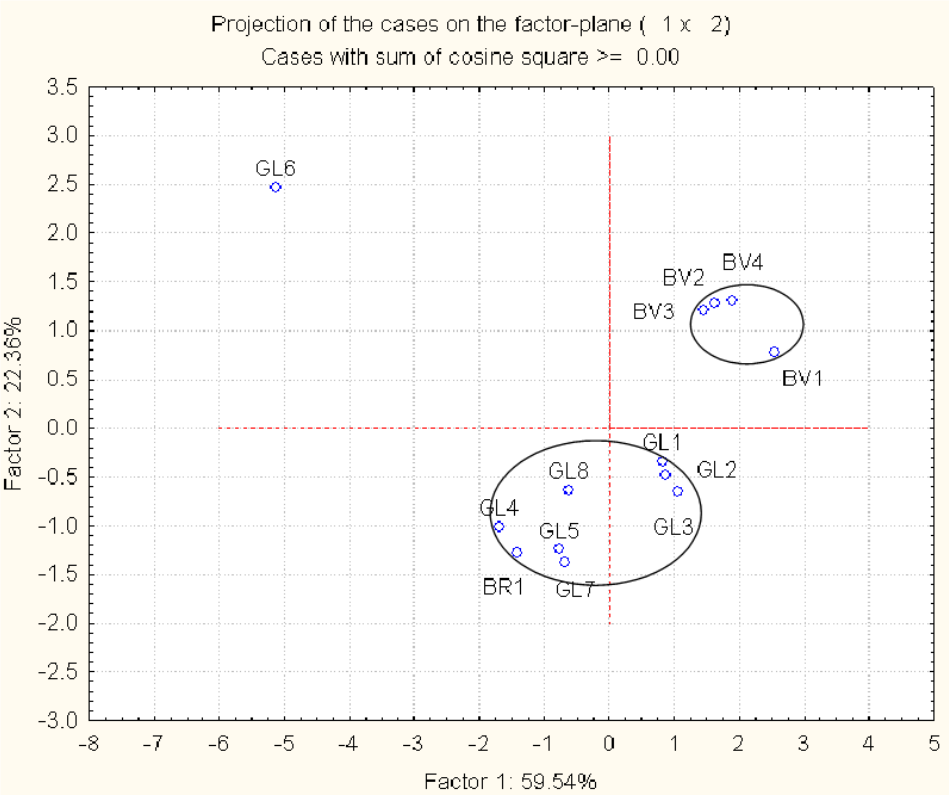

Fig. 2. Correlation matrix and Principal Component Analysis (PCA) of the experimental data from Table 1

Table 2. Standard values of surface water for Class 1, 2 and 3 (National standards STAS 4706 for surface waters, quality categories and conditions)

Element	Class 1 (mg/L)	Class 2 (mg/L)	Class 3 (mg/L)
Fe	0.3	1	1
Cu	0.05	0.05	0.05
Zn	0.03	0.03	0.03
Ni	0.1	0.1	0.1
Cd	0.003	0.003	0.003
Co	1	1	1
Cr	0.5	0.5	0.5

From Table 1 we can see that the rivers from the zones where are present industrial activities are affected by a pollution with heavy metals. We observe that the values of some heavy metal concentrations are over the maximum admissible values (Table 2): Fe in six Danube samples (class 2 and 3), Zn in three Danube samples (all classes), Cd in three Timis samples (all classes) and Cr in one Danube sample (all classes).

Acknowledgement: This study is part of a partnership project funded by National Plan of Research, Deveoping and Innovation, of implementation of high precision and sensibility methods for the biomonitoring of the environmental pollution in South, South-East and Central regions of Romania (*Project PN2 No. 72-172/1.10.2008*).

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Manuscript received: 29.04.2010
Accepted paper: 01.06.2010
Published online: 22.06.2010