GEOCHEMICAL STUDIES APPLIED TO THE EXPLORATION OF WATER QUALITY IN THE CRISURI BASIN

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Abstract The water samples collected from 28 water stations belong to Crisuri Basin monitoring network were analyzed to evaluate sewage pollution. An amount of 21 substances, including geochemical carriers, major and trace heavy metals, oil compounds and organic particulate materials, were determined by atomic absorption spectrophotometry and chemical methods. R-mode factor analysis was used to assess the diverse sources and mechanisms influencing the elements distribution in surface waters of the Crisuri Basin.

Keywords: major and trace metals, water, factor analysis, pollution sources, Crisuri Basin

INTRODUCTION

The Crisuri hydrographical Basin is a large complicated system with tremendous topographic, hydrologic and biologic variability. Topographically, the basin system contains different topographical types differentiated on the basis of their stream gradients and floodplain characteristics. Although the system can be divided into these different components on the basis of topography, it is an interactive system, and it needs to be viewed consequently when monitoring purposes are planed.

The upper basin streams display flow variations typical for mountain streams. High water flow events carry significant amounts of sediment that are derived from erodable materials in the riverbed, riverbanks, and floodplain. On the opposite, low flows carry the highest concentrations of dissolved contaminants.

The total length of this system is 1093 km among which 670 km in Romania, and the study boundary includes an area of approximately 3500 km^2.

Historically, the community's development over time in the Crisuri Basin was based on industry that has been closely linked to the natural resources of the region.

Consequently, there are important relationships between the socioeconomic attributes of the basin communities and potential risks from environmental contaminants.

PROBLEM IDENTIFICATION

The area covered by the proposed monitoring efforts being reviewed includes the Crisul Alb, Crisul Negru, Crisul Repede, Barcau and Ier River Basins, dealing mainly with the contaminated portions of the basin.

The Crisuri Basin is typical of a moderated temperate continental climate with substantial variations in temperature and precipitation both from season to season and from year to year. The average annual precipitation at Oradea was 595 l/m^2.

The most common wind patterns in the basin are typical of the Western Europe. The winds flow from the west to the east and are characterized by an atmospheric transport from the ocean environment that influences the air quality of the investigated area.

The basin is also subject to local flood and accidental pollution events.

The Barcau River has several times been subject to accidental oil and farm sludge pollution. However, on the Crisuri Basin area there are major oil fields and related industries, which produce extensive amounts of oil-contaminated wastewater.

Considering the dense river network, permeable sediments as well as the location of various settlements and roads at the riverbanks, the Crisuri Basin is regarded very sensitive to pollution accidents. The most environmental problems in the Crisuri Basin are caused by municipal wastewater discharges, agriculture, mining, smelting, chemical and power industries (Figure 1) [1].

Based on the Romanian Standard for Water Quality (STAS 4706/1998), around 86% of the waters in this basin are included in the 1st category, 6,2% lie in the 2nd category and other 7% are considered degraded waters [2].

SAMPLING AND ANALYSIS

According to the EUROWATERNET guidelines, the Crisuri Basin monitoring network comprises 36 control sections, having 1 surveillance water station for less than 1000 km^2 hydrographic basin (although a much higher density of sampling sites was performed in the contaminated floodplain) [3].

The Romanian Water Authority of Crisuri, Oradea, had collected some 2,600 samples in the Crisuri Basin between 2003 and 2004 years under different regulatory programs. These samples, obtained from surface waters, had been collected to support investigations with different objectives, from monitoring to remediation. Multiple methods of analysis of the water data were used to characterize source areas.

The pH and the temperature were also measured. Water samples were collected in one liter polyethylene bottles. All samples were filtered through 0.45 μm membranes *in situ* and acidified immediately with nitric acid to avoid growth of microorganisms and then stored frozen (at – 20 ^{0}C) prior to analysis.

The samples were analyzed by atomic absorption spectrophotometry (AAS) and chemical methods [4] for more than 21 substances, including heavy metals and organic toxic substances. For the metal analysis 100 ml was taken from each water sample and treated with 5 ml HNO_3. The mixture was evaporated at 250°C, 5 ml HNO_3 was added again and once more evaporated at 250°C. Then, the samples were cooled at room temperature and diluted with distilled water. Accuracy of the metal analysis was evaluated by using blank analysis in distilled water and working standard solutions and replicate samples were analyzed to obtain a good analytical precision.

Factor analysis, a well-known multivariate statistical technique, has been used in geochemical studies [5], researches of sediment data [6] and surface water data [7].

The method used in this investigation to characterize the water data was R-mode factor analysis [8], having as objective the identification of original sources of different substances in surface waters from Crisuri Basin.

The R-mode factor analysis as applied to the chemical substance concentrations in water samples allowed us to reduce the geochemical matrices of the data in terms of a few factors. The factor loadings are related to the input provided by individual concentrations to each factor and the most highly of them form a cluster that can be used to assign the physical source of that factor.

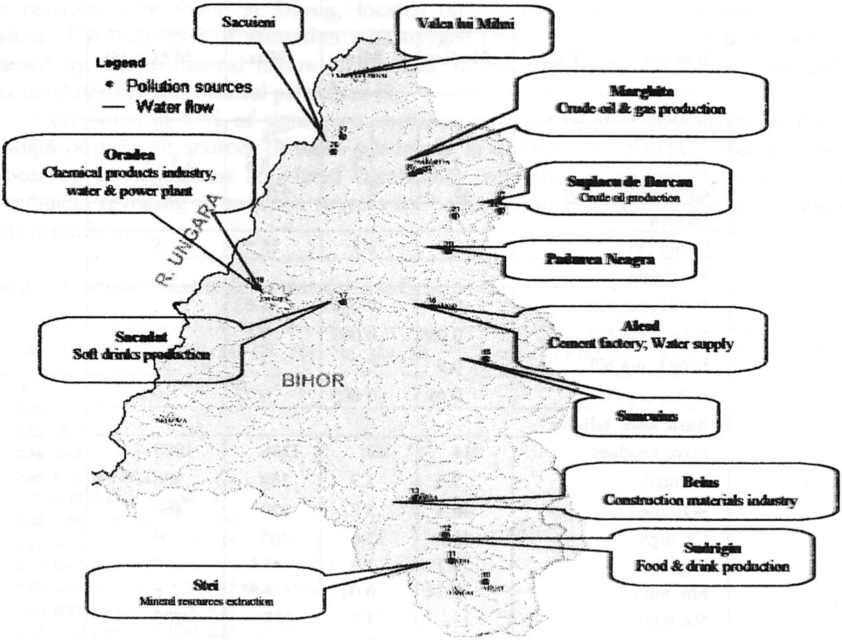

Figure 1. Location of potential sources causing the surface water pollution in Crisuri Basin

RESULTS AND DISCCUSION

The water temperature throughout the Crisuri Basin (Table 1) was characterized by an almost stable value in the winter and a little variation in the summer (1 - 5 ^{0}C and 20 - 28 ^{0}C, respectively).

The pH of the rivers water belong to Crisuri Basin (Table 1) was found to be close to neutral and showed rather smaller variations by seasons and network sections without significant trends.

The concentrations measured for the substances as As, Ca, Cd, Cl, Cu, Fe, Hg, Mg, Mn, Na, Ni, O, Pb, Zn, N-NH$_4$, N-NO$_2$, N-NO$_3$, P-PO$_4$, SO$_4$, phenols and oil compounds are listed in Table 1 by their median, minimum and maximum values. In order to estimate the level of toxicity, the maximum allowable concentrations (MAC) in Romania for different substances in the surface water are given in Table 1.

The metals in the water samples analyzed are contaminants of greatest concern, particularly compounds of arsenic, cadmium, zinc, oil hydrocarbons and fixed residues. The risk that these contaminants pose to human health and the environment depend not only on their concentration and the exposure to them but also on their chemical form or speciation. Some compounds are more biologically available and, therefore, pose higher risks than others.

Table 1. Summary statistics and allowed values for water data, in Crisuri Basin

Indexes / Value	Median	Min.	Max.	MAC^ [8]
Physical indexes				
Temperature, ^{0}C	18	1	28	30
pH	7.5	7.2	8.8	6.5 - 8.5
Suspensions, mg/l	28	2	478	1000
Oxigen				
O, mg O/l	10.7	1.7	15.5	5
Nutrients				
N-NH_4, mg N/l	0.02	0.005	1.63	3
N-NO_2, mg N/l	0.008	0.001	0.4	3
N-NO_3, mg N/l	0.9	0.2	3	30
P-PO_4, mg P/l	0.05	0.005	0.73	0.1
Basic ions, salinity				
Fixed residues	214	60	1296	1000
Cl, mg/l	9.5	1.7	359	300
SO_4, mg/l	46.5	5.2	520	400
Ca, mg/l	41.3	12.6	205	200
Mg, mg/l	14.2	1.9	43.3	100
Mn, mg/l	0.14	0.01	2.53	0.3
Na, mg/l	11	1.8	325	200
Fe, mg/l	0.24	0.02	2.7	1
Metals				
As, µg/l	17	0.8	124	10
Cd, µg/l	3	0.05	24	3
Cu, µg/l	1	0.05	35	50
Hg, µg/l	0.1	0.005	0.3	1
Ni, µg/l	1	0.6	13	100
Pb, µg/l	2	0.5	20.3	50
Zn, µg/l	7.1	1.6	35	30
Organic toxic substances				
Phenols, µg/l	5	0.05	40	20
Oil compounds, µg/l	30	10	140	100

^MAC = maximum admissible concentration

Mostly of the trace metals concentrations showed a general increased level in Crisul Alb River (km 32, 48, 90, 104, 161 and 234, respectively), in Crisul Negru River (km 22, 124 and 151, respectively), in Crisul Repede River (km 7, 133 and 168, respectively), in Barcau River (km 21, 66, 100, and 128, respectively) and in the Ier River (km 90), with a few highs and lows at closed sampling locations. Those trends may arise from a combination of either anthropogenic or natural causes, as the dissolved metals have a geological nature and/or were accumulated over the time, due to anthropogenic activities. The most representative locations in this respect are Stei and Baia de Cris, - known for the mineral resources extraction, municipal town Oradea - responsible for municipal waste discharges in river waters, Suplacu de Barcau and Parhida - oil and gas exploitation. The mostly higher levels of nutrients and fixed residues were found at Diosig, located on the Ier River and originate from farm activities. The high level of saturation with oxygen (Av. 135 %) in Crisuri Basin waters is explained by the geothermal nature of the area, in connection with mining activity and by redox conditions at near-neutral pH values [9].

Correlation at 5 % of significance between different pairs of substances certifies for the origin of different sources of those substances in surface river waters (Table 2). The oil hydrocarbon concentrations correlated significantly with the concentrations of nickel, lead and cadmium revealing as common sources for both substance categories the oil and gas ore and its manufacture.

Table 2. Correlation matrix for water data, in Crisuri Basin

	As	Ca	Cd	Cl	Cu	Fe	FR	Hg	Mg	Mn	Na	Ni	N-NH$_4$	N-NO$_2$	N-NO$_3$	O	OC	Pb	PE	P-PO$_4$	SO$_4$	Zn
As	1																					
Ca	**0.68**	1																				
Cd	**0.53**	-0.34	1																			
Cl	**0.58**	**0.62**	0.35	1																		
Cu	**0.40**	0.36	-0.11	0.23	1																	
Fe	0.37	0.22	**0.59**	-0.09	**0.86**	1																
FR*	**0.45**	**0.50**	0.32	**0.68**	-0.13	-0.07	1															
Hg	0.29	-0.15	0.26	-0.22	0.37	0.12	-0.06	1														
Mg	**0.72**	**0.64**	-0.17	0.39	-0.28	-0.12	-0.34	0.10	1													
Mn	0.09	0.32	0.15	0.38	-0.20	0.17	0.21	-0.05	**0.68**	1												
Na	-0.07	**0.59**	0.13	0.28	0.18	0.37	-0.04	-0.25	0.31	0.32	1											
Ni	0.19	-0.14	**0.85**	0.03	**0.59**	**0.52**	0.16	0.08	-0.32	-0.30	0.04	1										
N-NH$_4$	0.10	0.07	-0.36	-0.08	-0.21	-0.05	**0.58**	-0.04	0.06	0.23	-0.11	-0.08	1									
N-NO$_2$	0.08	0.09	-0.29	-0.06	-0.17	-0.09	**0.53**	-0.01	0.05	0.28	-0.04	-0.08	**0.91**	1								
N-NO$_3$	0.09	0.10	-0.30	-0.06	-0.17	-0.08	**0.56**	-0.01	0.05	0.27	-0.04	-0.08	**0.90**	**0.94**	1							
O	0.18	0.13	-0.07	-0.22	0.14	0.09	-0.13	-0.03	0.14	0.27	0.04	-0.02	-0.35	-0.29	-0.27	1						
OC*	0.13	0.16	**0.41**	-0.02	**0.49**	0.12	-0.18	0.05	-0.24	-0.31	-0.12	**0.68**	-0.02	-0.04	-0.04	-0.11	1					
Pb	0.25	-0.10	0.22	-0.02	**0.62**	**0.47**	0.08	0.13	0.17	0.10	0.15	**0.63**	-0.04	-0.01	-0.01	-0.07	**0.50**	1				
PE*	0.29	-0.08	0.16	0.24	0.10	-0.04	-0.11	0.17	-0.02	0.38	0.02	0.26	0.11	0.09	0.07	0.14	**0.59**	**0.40**	1			
P-PO$_4$	0.10	0.13	0.09	-0.02	-0.05	-0.05	**0.73**	-0.02	0.06	0.16	-0.01	-0.02	**0.86**	**0.80**	**0.80**	0.22	0.06	-0.04	0.08	1		
SO$_4$	**0.40**	**0.53**	0.19	**0.42**	0.04	0.01	0.28	-0.01	0.20	0.05	0.14	-0.02	0.12	0.17	0.17	0.16	0.13	-0.01	0.20	0.24	1	
Zn	0.17	0.12	**0.47**	-0.10	**0.60**	**0.52**	0.04	0.11	0.02	0.10	0.19	**0.45**	-0.01	-0.02	-0.02	-0.27	0.21	0.38	-0.01	-0.02	-0.01	1

*FR = fixed residues, OC = oil compounds, PE = phenols

R-mode factor analysis extracted four factors (eigenvalue >1). To obtain the complete independence of factors, a varimax rotation with Kaiser normalization was applied and then the four factors accounted for 62 % of the total variance in the data set. The factors are assigned to physical sources as urban sewage, industry, and farm wastewater discharges and to geological structure, respectively.

The first factor (Figure 2), which described 25.8 % of the variance, was mostly loaded with As, Ca, Mg, fixed residues, Cl and SO$_4$, and was assigned to municipal waste leachate in running waters. The highest score of the first factor was found on the Crisul Repede River course - km 133 (in aval of Oradea city). Another higher scores were found on the Crisul Alb River – km 48 (in aval of Baia de Cris) and in the adjacent sampling locations. They introduce an industrial source (ore mining and/or accompanied by oxidation of sulphide minerals) having an important additional impact in mobilization of the arsenic according to the composition of the surface recharge. Another contribution may derive from the geothermal sources [10].

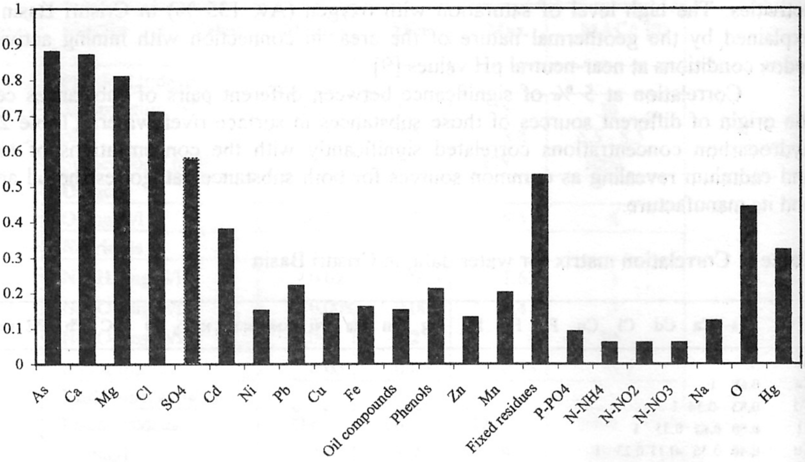

Figure 2. The first factor loadings by individual variables

The second factor (Figure 3) accounting for 22.6% of the variance has high loadings for Cd, Ni, Pb, Zn, Cu, Fe, oil compounds, phenols, and Mn and originates in local industry discharges. The highest score values of second factor were accounted on Crisul Repede River, – kms 133 and 94 and on Barcau River - kms 21, 66, 100, and 128, corresponding to the regions where the industry becomes dense (Oradea's varied plants and oil and gas manufacturing in Barcau area, respectively).

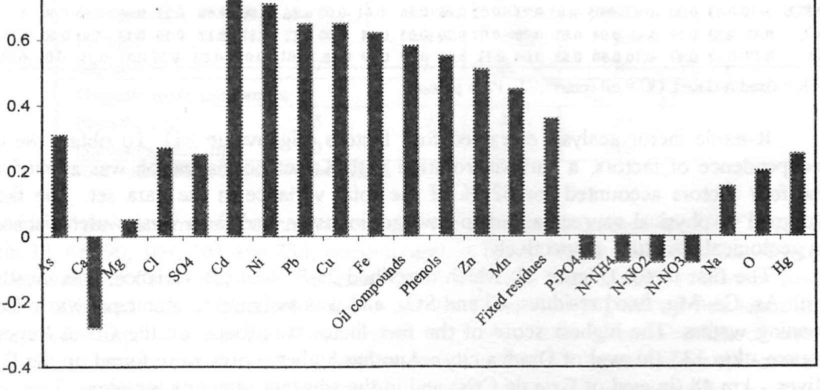

Figure 3. The second factor loadings by individual variables

The third factor, describing 8.2 % of the variance presented high loadings of nutrients ($P\text{-}PO_4$, $N\text{-}NH_4$, $N\text{-}NO_2$, $N\text{-}NO_3$), fixed residues, and Zn and assigns for agriculture as pollution source. This factor has the higher scores on Ier River at km 90 and in its surroundings and indicates the influence of wastewater discharge from farms.

The negative component moderately loaded with phenols, sodium and chlorine can be influenced by discharges of chemical plants in Oradea city.

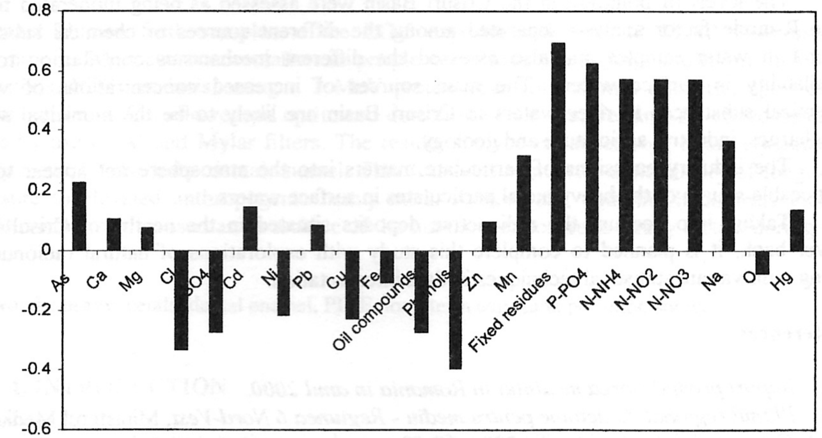

Figure 4. The third factor loadings by individual variables

The fourth factor, accounts for 5.4 % of the total variance and includes Ca, Na and Fe. These components are coming from eroding rocks by the running waters. The higher scores were counted on the upper basin of Crisul Repede River at kms 7, and 37.

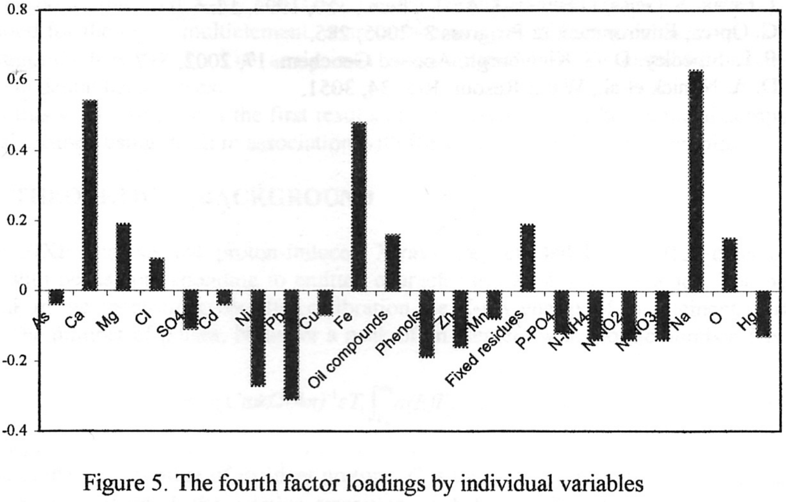

Figure 5. The fourth factor loadings by individual variables

CONCLUSIONS

This paper presents the analyzed concentrations of 21 substances in surface water of the Crisuri Basin. The investigations conducted on the basis of a monitoring network composed from 36 stations resulted in: the distribution of major and trace heavy metals in surface water, the contamination degree and the pollution sources were determined.

The levels of pollution in the Crisuri Basin were assessed as being moderated to low. The R-mode factor analysis separated among the different sources of chemical substances found in water samples and also assessed the different mechanisms contribution to their availability in surface waters. The main sources of increased concentrations of various chemical substances in river waters in Crisuri Basin are likely to be the municipal sewage discharges, industry, agriculture and geology.

The industry emissions of particulate matters into the atmosphere not appear to be a noticeable source of the heavy metal particulates in surface waters.

Taking into account the radioactive deposits situated in the nearby of Crisul Negru River bank, it is planned to complete this study with explorations of natural radionuclides, using multivariate statistical techniques in data interpretation.

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