The Quality of Surface Waters in the Suha Hydrographic Basin (Oriental Carpathian Mountains)

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Hydrographic basins located in mountain areas are affected by pollution only if there are mining operations that use antiquated technologies or due to poorly managed waste disposal programs. In the case of the Suha basin we may take into account both sources of pollution. The hydrologic monitoring of the Suha basin began in 1967 and physico-chemical monitoring began in 1986, after an increase in underground resources exploitations (the Lesu Ursului mine and the Tarnita complex ore processing plant in the upper basin of the Suha river). Along the river there is a series of towns that influence the surface and the underground waters. The average values of the physico-chemical parameters (temperature, pH, dissolved oxygen, CBO5, CCO-Mn, CCO-Cr, Cu, total Fe, total Mn and Zn) measured during the 1986-2011 period in the Stulpicani section (P1) and during the 2006-2011 period for the Ostra section (P2) place the water in the Suha river among first quality waters, which may be used for various economic purposes.

Keywords: hydrographic basin, mining operations, physico-chemical parameters, classes of quality

Small hydrographic basins that are not permanently monitored hydrologically often fail to make the object of chemical studies [1, 2]. The Suha hydrographic basin, located in the North of the Oriental Carpathian Mountains, is of high importance chemically, as it encompasses the Lesu Ursului mine and the Tarnita complex ores processing plant. That hydrographic basin is densely populated. The only studies on the Suha hydrographic basin, mainly hydrological in essence (with brief mentions of certain chemical characteristics), were performed by the Siret Water Basin Administration (2005, 2008, 2009, 2011).

Knowing the particularities of the Suha hydrographic basin is highly important in assessing the water resources and also in assessing their quality. The entire population gets its water supply from surface waters (household use) and from underground waters (drinking water). This is the first analysis of its kind that has been performed on the Suha hydrographic basin and it was necessary, because over the last years there has been a massive anthropic intervention on all component levels: household waste disposals directly into the river, improper location of toilets and of animal stables, poor maintenance of the sterile filters in the mining area, the deforestation of vast areas, the exploitation of gravel from the minor riverbed in constructions etc. [3]. There is an extremely large number of national and international studies on subjects pertaining to physical and chemical particularities of surface waters [4-26].

Geographical location

The Suha hydrographic basin is located within the Northern Group of the Oriental Carpatians. It spreads over the southern extremity of Obcina Feredeului, the south-eastern slope of the Rarău Massif, the western slope of the Ostra and Suha mountains, as well as the north-eastern part of Obcina Voronetului. Suha is a right side tributary to the Moldova river (fig. 1).

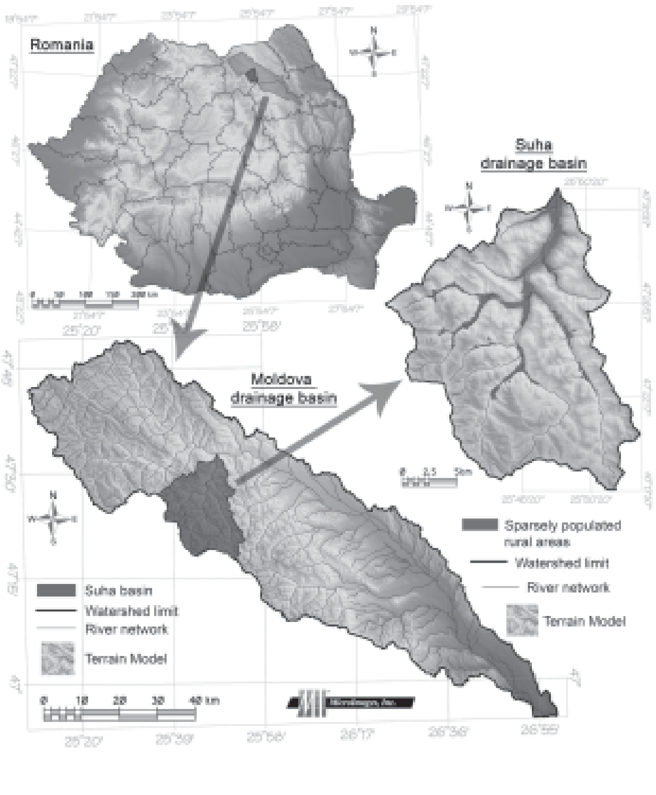

Fig. 1. Geographic position of the Suha hydrographic basin

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Fig. 2. The hydrographic network of the Suha basin the settlements in the area and the old mines

Table 1
THE MEASUREMENT EQUIPMENT USED

No.	Analysis type	Instruments
1	pH	Ph- meter
2	Dissolved oxygen	Oxymeter
3	CCOCr	Mineralizer grading and UV spectrophotometer
4	CCOMn	Grade
5	Fe and Mn	Atomic absorption or UV-vis
6	Temperature	Thermometer
7	Cu and Zn	Atomic absorption

Table 2
PHYSICO-CHEMICAL QUALITY STANDARDS AND ELEMENTS FOR WATER

No.	QUALITY INDICATOR	U/M	QUALITY CLASS				
			I	II	III	IV	V
C.1. REMPERATURE RATE AND ACIDIFICATION							
1	Temperature	°C	Not normed				
2	pH		6.5–8.5				
C.2. Oxygen values							
1	Dissolved oxygen	mg O_2/L	9	7	5	4	<4
2	CBO_5	mg O_2/L	3	5	7	20	>20
3	CCO-Mn	mg O_2/L	5	10	20	50	>50
4	CCO-Cr	mg O_2/L	10	25	50	125	>125
C.3. Specific natural toxic pollutants							
1	Copper $(Cu^{2+})^5$	mg/L	0.02	0.03	0.05	0.10	>0.10
2	Zinc (Zn^{2+})	mg/L	0.10	0.20	0.50	1.00	>1.00
3	Total Iron $(Fe^{2+} + Fe^{3+})$	mg/L	0.30	0.50	1.00	2.00	>2.00
4	Total manganese $(Mn^{2+} + Mn^{7+})$	mg/L	0.05	0.10	0.30	1.00	>1.00

The microclimate in the forest area is auspicious for human settlements, especially at the medium altitudes of the Suha hydrographic basin. Frasin, declared a city by Law 83/2004; the Stulpicani commune; the Ostra commune (fig. 2). At the census in 2011, the Frasin city had a population of 5702 inhabitants (in 2002 it had a population of 6532 inhabitants). The Stulpicani commune had a population of 6201 inhabitants in 2009 and a density of 26.5 inhabitants/km^2 (in 2002 it had a population of 6223 inhabitants and a density of 26.6 inhabitants/km^2). The Ostra commune had a population of 3241 inhabitants in 2009 and a density of 28.0 inhabitants/km^2 (in 2002 it had a population of 3158 inhabitants and a density of 27.3 inhabitants/km^2). Within the hydrographic basin there are 15144 inhabitants and an average density of 42.5 inhabitants/km^2 (an extremely high value for a mountain area where the average density is 10-20 inhabitants/km^2).

Experimental part

We took water samples monthly from two sections: Stulpicani (P1) and Ostra (P2). Both sections were chosen downstream from the two settlements. At the same time, we chose the sampling points to be downstream from the Lesu Ursului mining site and from the Tarnita ore processing plant. The liquid flow was different in the two sections (fig. 2).

The water samples were taken from the surface. We used recipients of 3l (canisters). The sampling frequency was set by the department for Monitoring-Protection and Quality of Water, according to various criteria: the operational criterion (O), investigation (I), surveillance (S), drinkability (D), the program of monitoring vulnerable zones (VZ), the reference program (R), the best available zone (BAZ), inter-calibration (IC), the impact of hydrological alterations on the water (IHAW). The equipment used belonged to the Siret Water Basin Administration and complied with European standards (table 1). We complied with the European norms on quality, as listed in five classes (table 2).

Table 3
AVERAGE VALUES OF THE PHYSICO-CHEMICAL PARAMETERS RECORDED AT THE STULPICANI SECTION

Year	Flow -rate m^3/s	T°C	pH	Dissolve d oxygen mgO_2/L	CBO5 mgO_2/L	CCO-Mn mgO_2/L	CCO-Cr mgO_2/L	Cu µg/L	Total Fe mg/L	Total Mn mg/L	Zn µg/L
1986	0.62	-	7.4	-	-	-	-	-	0.23	-	-
1987	0.69	-	7.4	9.93	2.95	6.18	-	-	0.31	-	-
1988	1.77	-	8.0	10.25	2.26	5.06	-	-	0.19	0.02	-
1989	1.44	-	7.9	10.24	2.86	6.94	-	-	0.25	0.0	-
1990	0.63	-	8.1	9.93	2.99	6.37	-	-	0.17	-	-
1991	1.20	-	8.0	10.74	2.73	5.4	-	-	0.24	0.18	-
1992	0.92	8.4	7.9	9.57	1.95	3.61	-	-	0.29	0.09	-
1993	1.42	9.0	8.0	9.56	3.43	6.95	-	-	0.32	0.0	-
1994	3.5	9.8	8.2	9.2	2.59	5.45	-	-	0.28	0.18	-
1995	0.98	9.0	8.2	10.78	6.28	0.34	-	-	0.27	-	-
1996	-	-	-	-	-	-	-	-	-	-	-
1997	2.37	7.0	7.9	10.49	2.35	5.56	-	-	0.43	0.19	-
1998	5.98	8.6	8.4	10.9	1.95	4.87	0.44	-	0.25	-	-
1999	2.92	9.5	7.9	10.48	2.51	4.55	-	-	0.91	0.32	-
2000	1.89	9.9	8.0	10.73	1.47	2.98	-	-	0.24	0.11	-
2001	3.31	10.0	7.6	10.52	1.3	2.65	-	-	0.39	0.18	-
2002	2.74	8.9	7.9	9.6	1.0	4.0	-	0.02	0.1	0.27	0.02
2003	1.37	8.1	7.7	11.27	1.7	3.3	-	20.00	0.05	0.23	9.1
2004	2.00	7.4	7.7	10.79	1.5	3.4	6.3	7.65	0.09	0.25	2.18
2005	2.47	12.4	8.1	9.51	1.96	3.97	5.09	12.36	0.05	-	31.14
2006	1.79	-	7.8	10.63	1.6	3.18	5.76	23.35	0.06	-	32.53
2007	2.31	9.9	8.2	10.17	1.67	3.76	7.85	-	0.18	-	-
2008	3.5	10.1	8.3	10.39	1.52	2.27	6.68	-	0.05	0.01	-
2009	2.27	9.3	8.2	10.47	2.08	4.35	8.47	-	0.03	0.07	-
2010	-	8.7	8.3	10.32	1.82	5.04	9.04	14.4	0.04	-	16.1
2011	-	8.6	7.8	10.02	1.88	-	8.46	-	0.14	-	-

Table 4
AVERAGE VALUES OF THE PHYSICO-CHEMICAL PARAMETERS RECORDED AT THE OSTRA SECTION

Year	Flow-rate m^3/s	T°C	pH	Dissolved oxygen mgO_2/L	CBO5 mgO_2/L	CCO-Mn mgO_2/L	CCO-Cr mgO_2/L	Cu µg/L	Total Fe mg/L	Total Mn mg/L	Zn µg/L
2006	0.13	7.5	8.0	10.48	1.49	2.69	4.84	45.1	0.03	0.39	64.21
2007	0.13	8.8	8.1	10.32	2.23	3.32	5.88	-	0.03	-	-
2008	5.97	8.5	8.3	10.47	1.35	2.26	5.7	-	0.04	0.01	-
2009	1.71	6.9	8.1	10.21	1.57	3.42	6.86	-	0.02	0.00	-
2010	-	8.0	8.4	10.16	1.54	2.59	6.36	3.72	0.05	0.01	8.91
2011	-	10.0	7.9	9.51	1.61	-	7.35	-	0.14	-	-

Results and discussions

In 1844, on the superior course of the Suha river, it was opened the Lesu Ursului mine for copper ores and barite. That industrial exploitation was revitalized in 1953. It was opened a complex ores processing plant in Tarnita. Then, in 1980, it was closed the sterile decanting lake in Târnicioara. That lake contains 15.5 tones of industrial sterile material. All economic activities ceased in 2006. That is when the problem with stabilizing the decanting lake came up, which may cause a catastrophe anytime. Any dam collapse or any leak caused by any means may affect the water supply of the settlements downstream: Ostra, Stulpicani and Frasin. The Suha river is a tributary to the Moldova river, which supplied water to the cities Gura Humorului, Suceava, Fălticeni and Roman.

The surveillance of the Stulpicani section was performed between 1986 and 2011, with a one year pause in 1996. The surveillance in the Ostra section started in 2006. There were longer pauses in measurements made for certain characteristics (CCO-Cr, Cu,Zn).

The average annual flow of the Suha river between 1986 and 2001 was 1.92 m^3/s. The highest annual average flow was recorded in 2008 and it was 5.7 m^3/s (table 3). 2008 was one of the rainiest years in the history of Romania, especially in the Northern Group of the Oriental Carpathians. The average annual temperature varies according to the temperature of the atmosphere. In the summer, the temperature values may usually be 2-4°C lower in sections where the flow-speed is lower.

In all cases above, the *p*H values registered within the average limits of 6.5-8.5 (a minimum 7.4 and a maximum of 8.4). The dissolved oxygen registered within the limits of class I quality, because mountain waters flow fast and have low temperatures. That is why water alteration is prevented. CBO5 values are within the limits of class I quality, with one exception (in 1995, with 6.28 mg O_2/L). The CCO-Mn and CCO-Cr values were always within quality I limits. Measurement for Cu and Zn only started in 2002, but we had no values registered for the years 2007, 2008, 2009 and 2011.

The total iron and total manganese values sometimes registered within class II limits. That happened because of the existence of those old Cu an Zn mining spots from Lesu Ursului and of the ore processing plant in Tarnita. The measurements made in the Ostra section only started in 2006 (table 4). All values were always within quality I limits, with some minor exceptions.

The waters in both measurement sections (Stulpicani and Ostra) comply with quality I standards. Thus, the water of the Suha river qualify to be used in all domains of activity. The extremely low pollution degree owes much to the pullution-prevention measures, but also to the lack of any mining activities. The sterile decanters were stabilized.

Conclusions

The Suha hydrographic basin has the qualities of a mountain river. In the upper sector there was a mining operation which ceased its activity in 2006: Lesu Ursului. The density of human settlements is high. In such cases, the potential for water pollution is high. The largest source of pollution is the industrial sterile decanting lake from Tărnicioara.

The physico-chemical analyses that we performed in two sections (Stulpicani and Ostra) revealed that the water quality of the Suha river was good. The main elements (*p*H, dissolved oxygen, CBO_5, CCO-Mn, CCO-Cr,Cu, total Fe, total Mn and Zn) registered within quality I limits as a result of the removal of any pollution sources: by closing the mines, stabilizing the sterile decanters, collecting household wastes in special containers, providing a centralized water supply etc.

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References

1 FARNSWORTH, K.L., MILLIMAN, J.D., Global Planet. Change, **39**, 2003, p. 53.
2. LÓCZY, D., Central European Journal of Geosciences, **2,** no.4, 2010, p. 537.
3. ROMANESCU, G., DINU, C., RADU A., TOROK, L., Carpath. J. Earth Env., **5**, no. 2, 2010, p. 25.
4. ARDUINO, G., REGGIANI, P., TODINI, E., Hydrol. Earth Syst. Sc., **9**, no. 4, 2005, p. 280.
5. BADALUTA-MINDA, C., CRETU, G., Environ. Eng. Manag. J., **9**, no. 4, 2010, p. 535.
6. BARBULESCU, A., BARBES, L., Rev. Chim. (Bucharest), **64**, no. 8, 2013, p. 868.
7. BARREDO, J.I., Nat. Hazards, **42**, no. 1, 2007, p. 125.
8. BRANDIMARTE, L., WOLDEYES, M.K., Hydrol. Process., **27**, no. 9, 2012, p. 1292.
9. BRONSTERT, A., BARDOSSY, A., BISMUTH, C., BUITERELD, H., DISSE, M., ENGEL, H., FRISCH, U., HUNDECHA, Y., LAMMERSEN, R., NIEHOFF, D., RITTER, N., River Res. Appl., **23**, no. 10, 2007, p. 1102.
10. CAMERON, D., Hydrol. Process., **21**, no. 11, 2007, p. 1460.
11. ČECH, M., ČECH, P., Hydrobiologia, **717**, no. 1, 2013, p. 203.
12. CRIVINEANU, M.F., PERJU, D., DUMITREL, G.A., PERJU, D.S., Rev Rev. Chim. (Bucharest), **63**, no. 4, 2012, p. 435.
13. ERNST, J., DEWALS, B.J., DETREMBLEUR, S., ARCHAMBEAU, P., ERPICUM, S., PIROTTON, M., Nat. Hazards, **55**, no. 2, 2010, p. 181.
14. GURZAU, A.E., POPOVICI, E., PINTEA, A., POPA, O., POP, C., DUMITRASCU, I., Carpath. J. Earth Env., **5**, no. 2, 2010, p. 119.
15. HOHENSINNER, S., JUNGWIRTH, M., MUHR, S., SCHMUTZ, S., River Res. Appl., **27**, no. 8, 2011, p. 939.
16. MENDIZABAL, M., SEPULVEDA, J., TORP, P., Int. J. Environ. Res., **8,** no. 1, 2014, p. 221.
17. NEGOITESCU, A., TOKAR, A., Rev. Chim. (Bucharest), **63**, no. 10, 2012, p. 1079.
18. OLANG, L.O., FÜRST, J., Hydrol. Process., **25,** no. 1, 2010, p. 80.
19. POP, A.I., MIHĂIESCU, R., MIHĂIESCU, T., OPREA, M.G., TĂNĂSELIA, C., OZUNU, A., Carpath. J. Earth Env., **8**, no. 4, 2013, p.5.
20. RASI NEZAMI, S., NAZARIHA, M., MORIDI, A., BAGHVAND, A., Int. J. Environ. Res., **7,** no. 3, 2013, p. 569.
21. ROMANESCU, G., COJOCARU, I., Environ. Eng. Manag. J., **9**, no 6, 2010, p. 795.
22. ROMANESCU, G., DINU, C., RADU, A., STOLERIU, C., ROMANESCU, A.M., PURICE, C., International Journal of Conservation Science, **4**, no. 2, 2013, p. 223.
23. VASILACHE, V., FILOTE, C., CRETU, M.A., SANDU, I., COISIN, V., VASILACHE, T., MAXIM, C., Environ. Eng. Manag. J., **11**, no. 2, 2012, p. 471.
24. ROMANESCU, G., CRETU, M.A., SANDU, I.G., PAUN, E., SANDU, I., Rev. chim. (Bucharest), **64**, no.12, 2013, p. 1416.
25.ROMANESCU, G., SANDU, I., STOLERIU, C., SANDU, I.G., Rev. Chim. (Bucharest), **65**, no. 3, 2014, p. 344
26. ROMANESCU, G., PAUN, E., SANDU, I., JORA, I., PANAITESCU, E., MACHIDON, O., STOLERIU, C., Rev. Chim. (Bucharest), **65**, no.4, 2014, p. 401

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