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DETERMINATION OF QUALITY INDICATORS OF PRUT RIVER WATER

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Abstract. This study presents an assessment of water quality of Prut River using the Water Quality Index (WQI), calculated according to the weighted arithmetic water quality index method. The following quality indicators were considered: pH, total dissolved solids, hardness, chemical oxygen demand, dissolved oxygen, sulphate, nitrate, and ammonium ions and heavy metals (Mn, Cd, Pb, Hg, Ni, Cu, and Zn) concentrations. The obtained results show that the water of Prut River may be classified according to WQI as good water quality of grade B for sampling points Sculeni and Cislita-Prut villages, and very poor water quality of grade D collected in the sampling point Criva village.

Keywords: Prut River, heavy metal, quality indicator, Water Quality Index.

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Introduction

River Prut is a transboundary basin shared by three countries: Republic of Moldova, Romania and Ukraine. Of the total basin area, 28% of the Prut River Basin is located in the territory of Republic of Moldova, 33% in the territory of Ukraine, and 39% in the territory of Romania. Prut River is one of the most important rivers that cross the territory of Republic of Moldova and constitutes an important source of water supply for the country; therefore its water quality must be continuously monitored.

Different teams of researchers from Republic of Moldova, Romania and Ukraine are actively involved in the assessment of the quality of water of Prut River based on various physicochemical parameters *e.g.* pH, total dissolved solids (TDS), hardness, dissolved oxygen (DO), sulphate, nitrate, and ammonium ions and heavy metals concentrations. Thus, Matache, M.L. *et al.* studied the concentration levels of Cu, Zn, Pb, and Cd by inductively coupled plasma – optical emission spectrometry in sediments and water samples from six locations situated along the inferior reach of the Prut River on the Romanian shore. Their investigation demonstrated that these trace elements were present in water samples at concentration levels below the maximum allowable concentration (MAC) imposed by the Romania regulations for freshwater bodies [1]. Another study performed by Ene, A. *et al.* on the detection of heavy metals concentration in water samples collected from different rivers, including Prut (Giurgulesti village, Romanian shore of the river) using atomic adsorption spectrometry also showed that the concentration was within the MAC limits imposed by the Romania regulations for freshwater bodies [2]. Hrytsku, V.S. and Hrytsku-Andriyesh, I.P. performed the quality monitoring of the Prut River water (Chernivtsi region, Ukraine) over the years 2006-2013. Using the Water Pollution Index (WPI) they showed that Prut River water was moderately polluted (class III) and proved that the water treatment technology used in Chernivtsi district is ineffective [3]. The water quality of Prut River in Republic of Moldova is monitored monthly by the State Hydrometeorological Service. Water quality is assessed as well, based on WPI that accounts for six physicochemical parameters including ammonium nitrogen, nitrite nitrogen, petroleum products, phenols, dissolved oxygen (DO), and biochemical oxygen demand at 5 days (BOD_5) [4]. According to the report of the State Hydrometeorological Service for the first semester of 2017, the quality of the Prut water was attributed to moderately polluted water (class III) [5]. Another concept of water quality estimation is by using the Water Quality Index (WQI) that summarizes a large spectrum of physicochemical parameters and translates them into simple terms *e.g.*, excellent, good, bad, *etc*., thus facilitating the reporting to management and the public in a consistent manner [6].

For the first time, the concept of WQI was introduced by Horton, R.K. [7], and later, in 1970 Brown, R.M. *et al.* developed a WQI based on the weights of individual parameters [8,9]. Currently many modifications for WQI are used by scientists according to particularities of the monitored regions [10-14]. For instance, Dascalescu, I.G. *et al.* proposed a modified version of the Canadian Council of Ministry of the Environment Water Quality Index (CCME-WQI) model that was developed using the data recorded by the on-line monitoring system of Prut River water quality. The CCME-WQI accounts for the following physicochemical parameters: pH, temperature, turbidity, conductivity, dissolved oxygen, nitrates, and total organic carbon [15].

Thus, the goal of this study was to evaluate the water quality of Prut River by WQI according to the weighted arithmetic water quality index method accounting for the physicochemical parameters such as pH, total dissolved solids (TDS), hardness, chemical oxygen demand (COD-Mn), dissolved oxygen (DO), sulphate, nitrate, and ammonium ions and heavy metals (Mn, Cd, Pb, Hg, Ni, Cu, and Zn) concentrations.

Experimental

Water samples were collected from the Prut River in Criva, Sculeni, and Cislita-Prut villages (Figure 1) in the spring and summer of 2017, and winter of 2018.

Figure 1. The map of Prut River basin showing the sampling points.

Sampling and sample analyses for quality indicators were performed according to the procedures and technical measures provided by the Decision of Republic of Moldova Government no. 932 of 20.11.2013 [16].

The pH of the water was measured by the potentiometric method using the Consort C5010 pH meter [17]. The TDS and sulphate ions were determined by gravimetric measurement using national standards [18,19].

The hardness was estimated by titration with EDTA [20] whilst COD with potassium permanganate [21]; DO was determined by the Winkler method [22].

Nitrate and ammonium ions were ascertained using the UV-Vis spectrophotometric method involving sulphosalicylic acid [23] and Nessler reagent [24], respectively.

The concentrations of Mn, Cd, Pb, Hg, Ni, Cu, and Zn were monitored using inductively coupled plasma mass spectrometry (ICP-MS). For ICP-MS quantitative analyses, calibration was done using a 4 point calibration curve (10, 20, 50, 100 μg/L) prepared from a Perkin Elmer Elan Standard III multielement standard solution by appropriate dilutions, that were measured using a Perkin Elmer Elan DRC II ICP-MS instrument. The detection limits of metal determination by ICP-MS method were 0.8 μg/L for Cd and Ni; 1.0 μg/L for Hg; 1.1 μg/L for Mn; 1.2 μg/L for Pb and Cu and 2.0 μg/L for Zn.

Water Quality Index (WQI) was calculated using the value of determined parameters using the weighted arithmetic water quality index method. This indicator expresses the overall quality of water, based on several quality parameters. WQI was computed using Eq.(1).

$$WQI = \frac{\sum W_i \times q_i}{\sum W_i} \quad (1)$$

where, W_i- the weighting factor and it is calculated using Eq.(2);
q_i- the quality rating for the i^{th} water quality parameter (calculated using Eq.(4)).

$$W_i = \frac{K}{S_i} \quad (2)$$

where, K is a constant value calculated by Eq.(3).

$$K = \frac{1}{\sum \left({}^{1}/_{S_i} \right)} \quad (3)$$

where, S_i represents standard value of the water quality parameter i.

$$q_i = \frac{V_i - V_0}{S_i - V_0} \times 100 \quad (4)$$

where, V_i is the measured value of the i parameter; V_o is the ideal value of analyzed parameter. V_o for pH= 7, for OD is 14.6 mg/L, and for the other parameters is 0 [9-12].

In the present study, the S_i values used for WQI estimation were the maximum allowable concentrations (MAC) for drinking water (class I of water quality) regulated by the Moldovan standards (Table 3) [25]. The obtained WQI values were compared with the standard values presented in Table 1.

Table 1

Water quality rating according to WQI[*] [9,11,12].

WQI value	*Water quality*	*Grading*
0-25	excellent water quality	A
26-50	good water quality	B
51-75	poor water quality	C
76-100	very poor water quality	D
above 100	unsuitable for drinking purpose	E

[*] *WQI was calculated using the weighted arithmetic water quality index method.*

Results and discussion

The analyses of physicochemical parameters of Prut River water were performed on samples collected in the spring and summer of 2017, and winter of 2018. The obtained results showed that pH varied between 7.95 and 8.31 in water samples, corresponding to class I of water quality. During summer pH of the sample from Criva village was higher in comparison to the other sampling points (8.07 at Sculeni village, and 7.95 at Cislita-Prut village) (Figure 2). In the same sample was determined an increased concentration of hydrogenocarbonate ions, which influenced the pH value. According to the obtained data for all samples (Figure 3), water of the Prut River may be considered as freshwater with TDS of 217-363 mg/L where the hydrogenocarbonate ions predominate.

The values of hardness determined for collected samples allowed to categorize the water as medium hard. On the territory of the Republic of Moldova the hardness of Prut River water did not show significant variations (Figure 4). Maximum value (about 6 mmol/L) was recorded at the end of winter in conditions of advanced TDS. Minimum value (about 4 mmol/L) was observed during spring when the water level is elevated.

In the water samples collected from sampling points Criva and Sculeni villages, the content of sulphate ions corresponded to class I of water quality (Figure 5). An insignificant increase in sulphate ions concentration, up to 150.71 mg/L (class II of quality), was recorded in the sampling point Cislita-Prut village, which can be explained by natural processes.

The maximum COD-Mn values were recorded in the spring, except for the sample collected in summer in the Sculeni region (Figure 6). The increased value of the parameter, as compared to the other samples, can be explained by pollution. The factors that caused the pollution are most likely to be natural because the COD increases by 1.8 mg/L and does not exceed the MAC for class I of water quality. Generally, on the territory of the republic between Sculeni and Cislita-Prut, this quality indicator increased slightly.

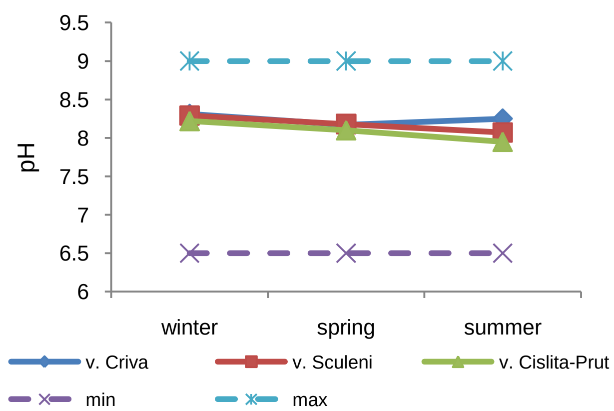

Figure 2. Dynamics of pH in water samples collected from the Prut River.

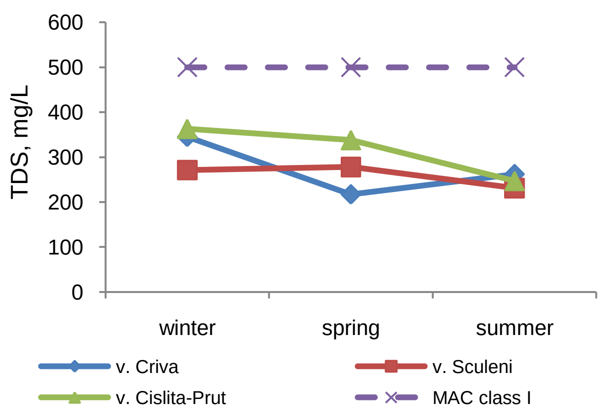

Figure 3. Dynamics of TDS in water samples collected from the Prut River.

The highest concentration of DO was observed during spring and summer (up to 10.5 mg/L) and the lowest in winter (8.3 mg/L), opposite to the expected effect when the low temperature of water favours higher amounts of DO (Figure 7). This effect is as a result of surface ice formation as the intake of oxygen in the atmosphere sets. This is confirmed by the obtained experimental data. Increased concentrations of DO recorded for summer are explained by weather conditions.

Generally, the nitrate content in Prut River water corresponded to class I of water quality. Only during winter the nitrate ions concentration was increased (about 1 mg/L) in samples collected in Cislita-Prut village. This could be explained by the seasonal NO_3^- dynamics where the concentration is minimal in the vegetation period when nitrate ions are used in plants nutrition, and increases in autumn, reaching the maximum in the winter when the organic substances are decomposed and organic nitrogen is transformed into the mineral form (Figure 8).

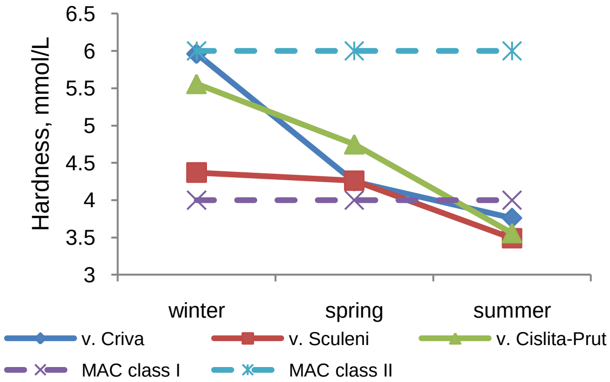

Figure 4. Dynamics of hardness in water samples collected from the Prut River.

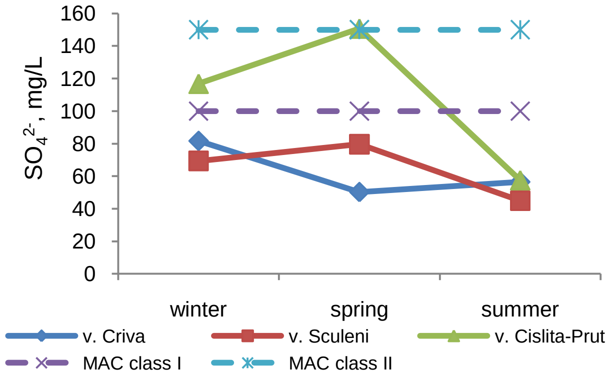

Figure 5. Dynamics of sulphate ions concentration in water samples collected from the Prut River.

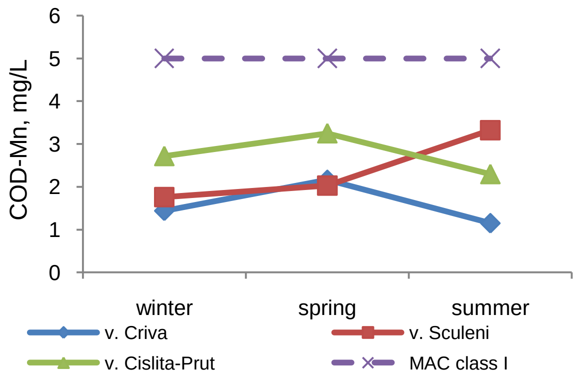

Figure 6. Dynamics of COD-Mn in water samples collected from the Prut River.

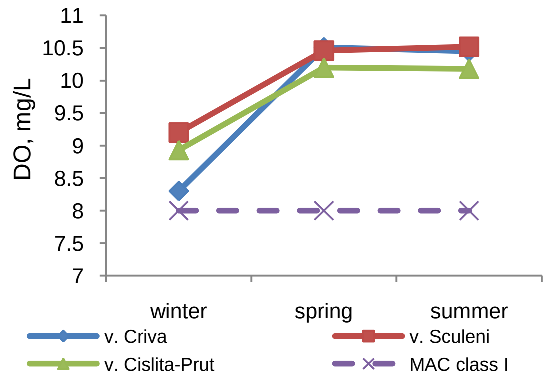

Figure 7. Dynamics of DO in water samples collected from the Prut River.

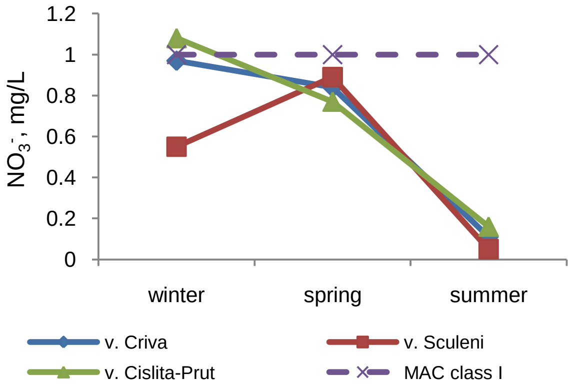

Figure 8. Dynamics of nitrate ions concentration in water samples collected from the Prut River.

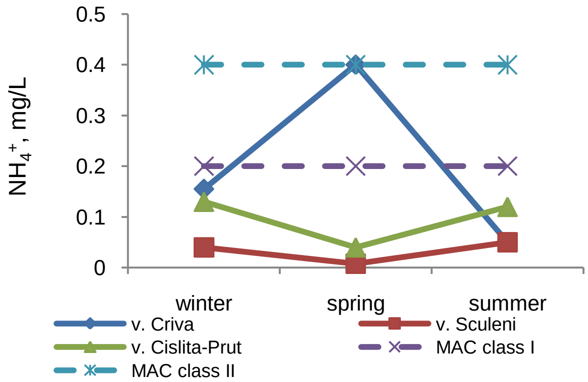

Figure 9. Dynamics of ammonium ions concentration in water samples collected from the Prut River.

In spring, the sample collected in the Criva village had an ammonium quantity exceeding the MAC for the class I of water quality. Since the same trend was not observed throughout the river flow, this might suggest the influence of anthropogenic factors. Water quality returns to normal until the next sampling point. This can be explained by diluting the river water with the water of Vilia, Lopatnic, Racovat, Ciuhur, and Camenca Rivers.

Figures 10-12 show the variation of the heavy metals concentration in the Prut River water. Thus, the most significant pollution was recorded for Cd (class III-IV), especially in the spring, and insignificant overruns for Mn and Cu (class II). The concentration of Zn and Ni corresponds to surface waters without alterations. The concentration of Pb and Hg was below the detection limit during all seasons. The obtained results in this study are in agreement with the low level of metal pollution of the Prut River observed earlier by Matache, M.L. *et al.* [2] and Ene, A. *et al.* [3].

The WQI was calculated using afore mentioned parameters and the average of the experimental value determined for 3 sampling points over three seasons (Table 2). The concentration of heavy metals usually is not introduced in WQI computing, but it helps to assess water quality. In the present work, only the concentration of Pb and Hg was not used in WQI computing because these were under the detection limit in all analyzed samples.

The WQI values indicated good water quality (grade B) in sampling points Sculeni and Cislita-Prut villages, and very poor water quality (grade D) in village Criva (Table 3). Criva is situated in the northern part of the Prut River at the border with Ukraine. Thus, the water pollution may be caused by anthropogenic activities carried out on Ukraine territory. The WQI decreases on Moldovan territory, reaching the minimum value in Sculeni village. Further, water quality slightly worsens reaching a value close to grade C in Cislita-Prut village (49.77). The obtained results for water samples collected in Cislita-Prut village keep the trend described by Iticescu, C. *et al.* over the years 2011-2013 [11].

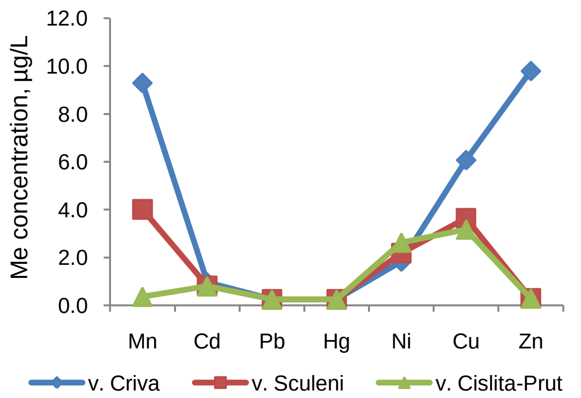

Figure 10. Dynamics of metals concentration in water samples collected from the Prut River in spring.

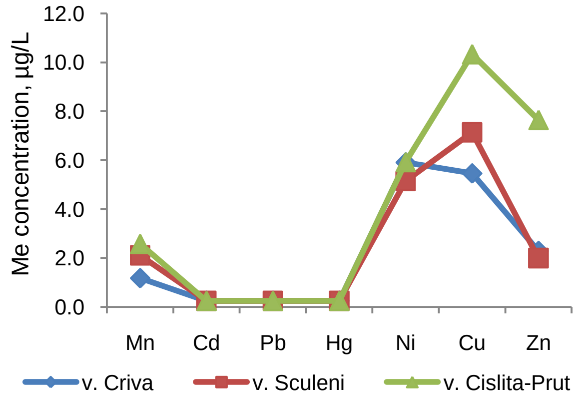

Figure 11. Dynamics of metals concentration in water samples collected from the Prut River in summer.

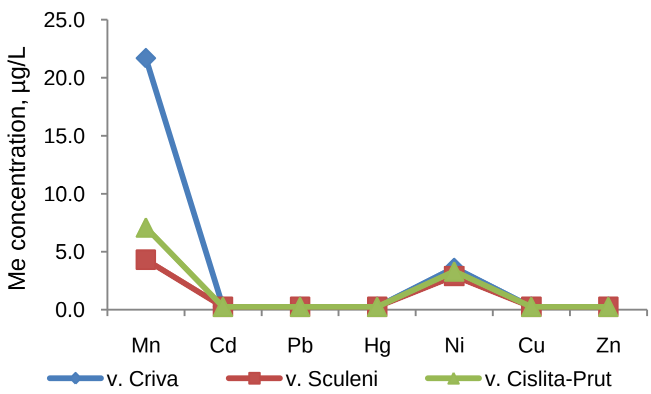

Figure 12. Dynamics of metals concentration in water samples collected from the Prut River in winter.

Table 2

Values of weighting factor, W_i.

Parameter	Measured value, V_i			Standard value, S_i	$1/S_i$	Weighting factor, W_i
	Criva	*Sculeni*	*Cislita-Prut*			
pH	8.24	8.18	8.09	8.5	0.1176	0.0145
TDS, mg/L	274.67	260.0	316.0	500	0.0020	0.0002
Hardness, mmol/L	4.66	4.04	4.62	4	0.2500	0.0309
Sulphate, mg/L	62.82	64.63	108.34	100	0.0100	0.0012
COD-Mn, mg/L	1.58	2.37	2.76	5	0.2000	0.0247
DO, mg/L	9.75	10.06	9.77	8	0.1250	0.0155
Nitrate, mgN/L	0.64	0.50	0.67	1	1.0000	0.1236
Ammonia, mgN/L	0.20	0.03	0.09	0.2	5.0000	0.6181
Mn, µg/L	10.72	3.47	3.35	100	0.0100	0.0012
Cd, µg/L	0.33	0.27	0.27	1	1.0000	0.1236
Ni, µg/L	3.78	3.41	3.95	8	0.1250	0.0155
Cu, µg/L	3.87	3.57	4.50	5	0.2000	0.0247
Zn, µg/L	4.03	0.67	2.53	20	0.0500	0.0062

Table 3

Calculation of WQI.

Parameter*	Quality rating, q_i			Sub index, $W_i \cdot q_i$			Water quality index		
	Criva	*Sculeni*	*Cislita-Prut*	*Criva*	*Sculeni*	*Cislita-Prut*	*Criva*	*Sculeni*	*Cislita-Prut*
pH	82.6667	78.6667	72.6667	1.2022	1.1440	1.0568			
TDS	54.9340	52.0	63.20	0.0136	0.0129	0.0156			
Hardness	116.50	101.0	115.50	3.6003	3.1213	3.5694			
Sulphate	62.82	64.63	108.34	0.0777	0.0799	0.1339			
COD-Mn	31.60	47.40	55.20	0.7812	1.1719	1.3647			
DO	73.4848	68.78788	73.18182	1.1355	1.0629	1.1308			
Nitrate	64.0	50.0	67.0	7.9113	6.1807	8.2822	83.39	27.83	49.77
Ammonia	100.0	15.0	45.0	61.8074	9.2711	27.8133			
Mn	10.7200	3.4700	3.3500	0.0133	0.0043	0.0041			
Cd	33.0	27.0	27.0	4.0793	3.3376	3.3376			
Ni	47.2500	42.6250	49.3750	0.7301	0.6586	0.7629			
Cu	77.40	71.40	90.0	1.9136	1.7652	2.2251			
Zn	20.1500	3.3500	12.6500	0.1245	0.0207	0.0782			

The measurement units are the same as in Table 2.

The most significant influence on WQI assessing was attested by the ammonium, copper, and cadmium concentrations. In some cases, the concentrations of sulphate and nitrate ions exceed MAC for drinking water (class I of water quality) regulated by the Moldovan standards. The main sources of pollution with both heavy metals and other pollutants are considered: agriculture, municipal waste and industry (characteristic of the Iasi area, Romania).

Conclusions

This study presents an assessment of water quality of Prut River using Water Quality Index (WQI) that was calculated using the weighted arithmetic water quality index method accounting for pH, total dissolved solids, hardness, chemical oxygen demand, dissolved oxygen, sulphate, nitrate, and ammonium ions and heavy metals (Mn, Cd, Pb, Hg, Ni, Cu, and Zn) concentrations.

The results presented in this work showed that the most significant influence on WQI assessing was attested by the ammonium, copper, and cadmium concentration. In some cases the concentrations of sulphate and nitrate ions exceed maximum allowed concentration.

The obtained results show that the water of Prut River monitored in the spring and summer of 2017, and winter of 2018 could be classified according to WQI as good water quality of grade B for the sampling points Sculeni and Cislita-Prut villages, and very poor water quality of grade D in sampling point Criva village.

Acknowledgments

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