CHEMISTRY JOURNAL OF MOLDOVA. General, Industrial and Ecological Chemistry. 2022, 17(2), 7-18
ISSN (p) 1857-1727 ISSN (e) 2345-1688
http://cjm.ichem.md
http://dx.doi.org/10.19261/cjm.2022.1018

THE ROAD TO ENVIRONMENTAL CHEMISTRY IN REPUBLIC OF MOLDOVA PAVED BY THE ILLUSTRUOUS SCIENTIST AND RENOWNED ECOLOGIST VALERIU ROPOT

Tudor Lupascu [a*] and Maria Sandu [b]

[a]*Institute of Chemistry, 3, Academiei str., Chisinau MD-2028, Republic of Moldova*
[b]*Institute of Ecology and Geography, 1, Academiei str., Chisinau MD-2028, Republic of Moldova*
[*]*e-mail: tudor.lupascu@ichem.md; lupascut@gmail.com*

Abstract. In this paper, the main scientific and innovative results are presented, which were obtained by the talented chemist and renowned ecologist Valeriu Ropot throughout his scientific career. The results of scientific investigations are bestowed and analysed, focusing on the quality of the waters of the Dniester and the Prut Rivers, Dubasari reservoir on the Dniester River, as well as the main water bodies in the Republic of Moldova. Recommendations are also presented regarding the studies on the improvements of water purification technologies from the Dniester and Prut Rivers, including practical applications for the removal of fluoride, iron, ammonium, and sulphide ions from groundwater. Another aspect of the work is devoted to scientific studies related to the solving of problems concerning the treatment of wastewater from industrial enterprises in the agro-industrial complex and from economic units, and galvanic processes. The paper also presents some practical recommendations for reducing the negative impact on the environment, of the discharge of hundreds of thousands of tons of brine into the Dniester River as a result of the accident at the mineral fertilizer plant in the Stebnik town, Ukraine. Moreover, the paper brings into discussion the results of studies aimed at developing methods for determining organic and inorganic pollutants in natural waters.

Keywords: water, wastewater, chemical composition, treatment technology, pollutant.

Received: 26 October 2022

Introduction

In the beginning of the 70's (1972), the young doctor of chemistry Valeriu Ropot founded the Laboratory of Mineral Resources and Chemistry of Water within the Institute of Chemistry of the Academy of Sciences of Moldova. Later on, in 1992, at the initiative of the ecologist Valeriu Ropot the laboratory was re-profiled to the Laboratory of Ecological Chemistry due to the need to solve environmental problems that were escalating in the world, including in Bessarabia.

Environmental protection requires the implementation of a series of complex social, economic, scientific research and technical measures that will guarantee the preservation of the natural environment. These measures can have both a global character, impacting the vital interests of the entire population on earth, and a local character, by solving ecological problems.

Amongst the principal scientific objectives of the Laboratory of Ecological Chemistry within the Institute of Chemistry of the Academy of Sciences of Moldova, was the evaluation of natural minerals, research and establishment of laws regarding the formation of the quality of surface and underground waters, as well as highlighting the processes and mechanisms of transformation of natural and anthropogenic pollutants in aquatic systems. Scientist Valeriu Ropot paid special attention to the development of high-performance technologies for making surface water potable, as well as those for treating wastewaters resulted from the activity of various economic units in the Republic of Moldova.

Under the leadership of Dr. Valeriu Ropot, a vast body of scientific research was carried out, concerning the mechanism of pollutant immobilization through mineral absorbents, and description of the role of active centres in the processes of pollutant migration and transformation in the aquatic environment were highlighted. Thus, the initial field of research was the evaluation of natural minerals (clays) used for the purification of winery wastewaters. The results of the study were appreciated with the Silver Medal at the Exhibition of Achievements of the National Economy of the USSR in 1975 - for implementing the technology at the Brandy Plant in Balti municipality, Republic of Moldova.

Table 1

Dynamics of the annual average values of the mineralization and the concentration of the main mineral components in the Dniester River water, Vadul lui Voda section, in the years 1961-1990 [1].

Years	*Content, mg/L*							
	K^+	Na^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-	HCO_3^-	*Dry residue*
1961-1970	3-4	16-19	52-66	7-10	48-65	20-35	160-210	240-320
1971-1980	4-6	18-20	53-62	8-12	53-70	31-42	161-218	310-416
1981	5-6	19-24	56-63	10-13	67-84	41-52	160-270	318-338
1982	5-7	23-28	60-68	12-13	75-96	54-68	164-276	300-452
1983	9-70	22-230	59-90	14-84	87-280	65-502	185-330	316-1520
1984	16-21	68-75	86-92	24-40	128-160	115-145	214-290	497-670
1985	13-14	50-72	62-90	20-28	94-130	70-110	196-244	415-460
1986	12-13	36-58	62-69	16-18	92-102	62-72	164-300	410-488
1987	11-12	34-57	61-68	15-18	93-110	67-71	152-230	384-486
1988	9-11	33-58	54-70	12-17	76-108	50-68	168-220	338-490
1989	9-10	31-56	53-70	12-16	78-96	52-65	170-240	330-470
1990	5-6	20-25	52-68	10-12	72-84	35-52	160-210	320-406

Many scientific expeditions have been organized by the scientist Ropot Valeriu with the goal to study the quality of surface and underground waters, starting from the source and to the Black Sea, and respectively to the Danube along the Rivers of Dniester and Prut and many small rivers of the Republic of Moldova. The scientific research results obtained regarding the state of the surface and underground waters were reported in various scientific publications (1972-2002), presented at many national and international scientific conferences and used in the development of the National Strategic Action Program in the field of environmental protection, during the years 1995-2010-2020.

The scope of this paper is to put forward concisely the main achievements and contributions to the development of the field of environmental chemistry in the Republic of Moldova by the much-appreciated scientist and renowned ecologist Dr. Valeriu Ropot.

Background

Aspects regarding Dniester River water quality

A detailed study regarding the annual average values of the mineralization and concentration of the main mineral components in the Dniester River water, Vadul lui Voda section, was performed for the years 1961-1970, 1971-1980 and annually during 1981-1990 (Table 1) [1]. It was demonstrated that higher values of some indices (Na^+, K^+, SO_4^{2-}, Cl^- and mineralization) in the years 1983-1985 (Table 1) were the consequence of the serious accident at the mineral fertilizer complex in the Stebnic town (Ukraine) on 15 September 1983, when 1.35 million tons of salt (5 million m^3 of brine) were discharged into the Dniester River. The brine reached the Novodnestrovsk reservoir and continued its course in the Dniester River on the Republic of Moldova territory.

Analysing the dynamics of the chemical indicators of water, until the year 1987, the scientist Ropot Valeriu found that in the water of the Dniester River, the mineralization and most of the mineral components were increasing.

Table 2

The maximum values (mg/L) of specific parameters in the water of Dniester River, Vadul lui Voda section (years 1987 and 1988).

Parameters	*1987*	*1988*	*MAC**
Phenol	0.0008	0.0009	0.001
Anionic surfactants	0.26	0.27	0.5
Petroleum products	0.08	0.07	0.5
F^-	0.3	0.3	1.2
CN^-	-	-	0.05
AsO_2^-	traces	0.001	0.05
Se (SeO_3^{2-}+SeO_4^{2-})	0.0001	0.0001	0.001
Mn^{2+}	0.003	0.002	0.1
Al^{3+}	0.12	0.11	0.5
Hg^{2+}	0.0006	0.0007	0.001
Cd^{2+}	0.0017	0.0015	0.001
Fe (Fe^{3+}+Fe^{2+})	0.20	0.15	0.3
Cu^{2+}	0.12	0.12	1.0
Ni^{2+}	0.008	0.007	0.1
Cr^{3+}	0.003	0.003	0.01
Zn^{2+}	0.08	0.09	5.0
Ba^{2+}	0.016	0.018	0.1
Ag^+	0.0013	0.0014	0.05
Ti^{2+}	0.045	0.046	0.1
Co^{3+}	0.00016	0.00017	0.1
Sr^{2+}	1.08	1.08	7.0
Be^{2+}	0.00014	0.00014	0.0002
Mo^{3+}	0.0025	0.0026	0.5
Pb^{2+}	0.018	0.017	0.1

**MAC – maximum allowable concentration [2].*

For example, the potassium content tripled (from 3-4 mg/L to 11-12 mg/L), sodium content doubled (from 16-19 mg/L to 34-57 mg/L), chlorides content increased from 20 mg/L to 50 mg/L and that of sulphates from 48 mg/L to 76 mg/L. The comparison of the average values of water mineralization also demonstrated a permanent increase from 240 mg/L to 488 mg/L, reaching an increase of 50% during the years 1961-1987.

The evaluation of the content of organic substances (phenol, anionic surfactants, petroleum products), fluorine, cyanide, arsenic, selenium and heavy metals in the Dniester River water (Vadul lui Voda section) was performed during the years 1987-1988, to ensure that the water can be used for drinking purposes (Table 2).

Based on the main *conclusions and recommendations* drawn from the study regarding the prevention of water pollution and removal of pollutants from the Dniester River, and also for other water basins [1], the ecologist Valeriu Ropot proposed a set of recommendations in the following directions:

1. *Legislation:* elaboration of legislative and normative acts for the protection and rational use of water resources;
2. *Organizational:* development of basins and territories schemes for complex use and water resources protection;
3. *Environmental monitoring:* organization of permanent monitoring of the state of natural resources on the Dniester River;
4. *Technological:* development of technological schemes of production at economic units that are friendlier to the environment, based on the production of a small volume of wastes, technologies with no waste and wastewater, implementation of wastewater recycling systems after treatment, *etc*.;
5. *Economic:* the development of criteria and methods for evaluating the damage caused by the pollution of water resources and the efficiency of the protection of water resources;
6. *Scientific:* carrying out complex scientific research combining theoretical and experimental methods in the field of environmental protection, rational use of water resources and implementation of the scientific results into practice;
7. *Social:* creating optimal conditions for human life, health and rest.

Scientist Ropot Valeriu mentioned that compliance with these recommendations would lead to the regulation of water consumption from the Dniester River basin and would increase the responsibility of consumers of water resources, improving the ecological condition of the hydrographic basin on the territory of the republic.

Optimization of the potabilization technology for water from the Dniester River [3,4]

With the purpose of evaluating the efficiency of the water treatment technology applied for Dniester River water with the goal to obtain potable water, the chemical composition of the water was studied after each treatment step. The analysis of the results presented in Table 3 highlights the fact that the chemical consumption of oxygen, determined by the CCO_{Cr} method was ≈4 times higher than that of CCO_{Mn} method and exceeded the maximum allowable concentration (CCO_{Cr}= 3 mgO_2/L). The organic phosphorus and nitrogen detected in water imply the presence of organic micropollutants with complex structures, probably pesticides. Thus, it was concluded that the technology applied at the water treatment plant for Chisinau municipality did not allow obtaining qualitative drinking water.

Table 3

Chemical composition of the water from the Dniester River at different stages of treatment.

Parameters	*Initial water*	*Water after the stage of coagulation and sedimentation*	*Water after the stage of filtration through sand filters*	*Drinking water*
pH	7.97	7.67	7.67	7.8
CCO_{Cr}, mgO_2/L	18.96	13.8	11.4	9.8
Phenol total, mg/L	0.003	0.002	0.002	<0.001
Anionic surfactants, mg/L	0.54	0.04	0.026	0.024
NH_4^+, mg/L	0.47	0.45	0.42	0.31
N-organic, mg/L	2.30	1.01	0.29	0.10
NO_3^-, mg/L	12.86	13.36	11.68	13.8
P-organic, mg/L	0.031	0.024	0.024	0.005
PO_4^{3-}, mg/L	0.26	0.12	0.10	0.10
Humic substances, mg/L	0.38	0.10	0.08	0.08

For the improvement of the water purification technology, the quality of water from Dniester River was assessed using 4 technological schemes presented in Table 4; their efficiency in water treatment from Dniester River is illustrated in Table 5. The analysis of the results (Table 5) allowed to conclude that Scheme 4 (D) was the most suitable for obtaining high-quality drinking water.

Table 4

Treatment schemes of Dniester River water.

No.	*Process diagram*	*Continuity of processes*
1	A	$O(O_3)$→CF→D→FN→FCA
2	B	CF→D→$O(O_3)$→ FN→FCA
3	C	$O(O_3 / H_2O_2)$→CF→D→FN→FCA
4	D	$PO(O_3 / H_2O_2)$→CF→D→FN→ IO→FCA

O- ozonation;
CF- coagulation-flocculation;
D-settlement; FN- sand filters;
FCA- filters with activated carbons;
PO- pre-ozonation;
IO- inter-ozonation.

Table 5

Efficiency of purification of water from the Dniester River by using different processes in treatment.

No.	*Parameters*	*Water treatment efficiency (%) with the use of different options*			
		A	*B*	*C*	*D*
1	CCO_{Cr}	66	19	77	94
2	N-organic	30	10	85	100
3	P-organic	70	20	89	96

Evaluation of the consequences of the accident at the mineral fertilizer plant in Stebnic town (Ukraine)

Unfortunately, on 15 September 1983, a serious accident occurred at the mineral fertilizer plant in Stebnic town (Ukraine). As a result of this accident, approximately 5 million m^3 of concentrated wastewaters (brine) with a concentration of 242.67 g/L were dumped into the Dniester River (on the Ukraine territory). The salty wastewaters contained fatty acids (0.01 g/L), potassium ions (20.06 g/L), sodium ions (36.19 g/L), magnesium ions (30.78 g/L), sulphates (60.58 g/L) and chlorides (97.09 g/L).

Brine, in the amount of about 1 million 350 thousand tons of salts, entered the reservoir of the Novodnestrovsk hydropower plant on the Dniester River. The height of the salt water layer was 10-12 m with a maximum salt concentration of 37 g/L. Although the salt content was decreasing during the water flow of the Dniester River, a high concentration still remained in the water, being dangerous for the river because it did not contain the oxygen necessary for the aquatic biota, and thus causing fish kills. The maximum concentration of chlorides and the mineralization value of the water of the Dniester River and the Novodnestrovsk reservoir after the discharge of wastewaters from the Stebnic plant are shown in Table 6 [5,6].

Resulting from the fact that the water from Lake Novodnestrovsk continues its course on the territory of the Republic of Moldova in the Dniester River, which is used to provide the population with drinking water, the Institute of Chemistry was actively involved in the scientific research of the composition of the water in the river. This theme was led by Dr. Valeriu Ropot, who contributed essentially to the evaluation of the composition of the water and the elaboration of special recommendations to solve the existing problem by using the Novodnestrovsk reservoir to avoid the disaster on the territory of the Republic of Moldova. The study demonstrated that the water in the reservoir needed to be discharged only from the surface and should not contain more than 2 g/L of salts (500-600 mg/L of chloride ions).

Table 6

Maximum concentration of chlorides and mineralization in Dniester River and Novodnestrovsk reservoir waters after the discharge of wastewaters from the Stebnic plant [5,6].

The supervision section	*Date of water sample collection*	*Chloride concentration, g/L*	*Mineralization, g/L*
Nikolaev town	16.09.1983	128.0	210.0
Galici town	18.09.1983	47.5	141.0
Zalescichi town	21.09.1983	36.0	114.0
Khotyn city	23.09.1983	34.0	105.0
Novodnestrovsk Lake	04.10.1983	12.0	37.0

The dynamics of ion content and water mineralization in Dniester River, Otaci city, upon entering the territory of the Republic of Moldova, demonstrates water pollution, especially with chlorine ions and total water mineralization (Table 7).

Dynamics of ion content and water mineralization in Dniester River, Vadul lui Voda town

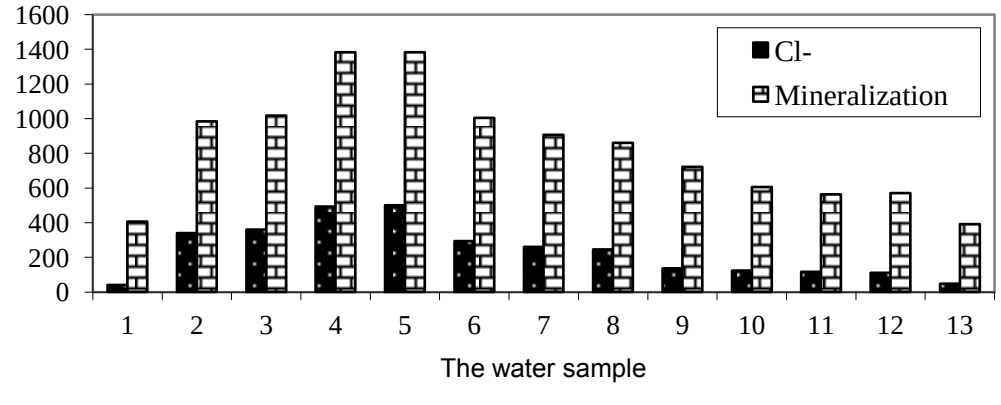
As a result of the scientific research carried out and the recommendations given by the devoted scientist, Dr. Valeriu Ropot, the Dniester River water at Vadul lui Voda town (Chisinau Municipal Supply Station) contained from 40.3 to 500 mg/L of chlorides in October-December of 1983, with a maximum mineralization of 1383.1 mg/L on November 15, 1983 confirming the importance of the conducted scientific research that was continued in the years 1984-1985. Only in September 1984, the chloride content has decreased to 115 mg/L and the mineralization to 561.7 mg/L, and in August 1985 was attested a content of 47.8 mg/L of chloride ions and 391.3 mg/L mineralization (Figure 1) [5].

Moreover, the conducted research demonstrated a negative influence of the salts from the river water on the sludge (bottom sediment) from the Dubasari reservoir, which contained montmorillonite having sodium and potassium ions replaced by calcium ions. As a result, the dispersion and compaction of montmorillonite particles took place with the elimination of marsh gases. Dr. Valeriu Ropot studied the bottom sediment from Dniester River in sections at Camenca city, the Oxentia village and Dubasari lake, with its granulometric change and chemical composition being demonstrated (Table 8) [5]. To inform the scientific society, the results of the study and the special recommendations for solving the problem of the accident at the mineral fertilizer plant in Stebnic town (Ukraine) were presented at the international conference in Bucharest, Romania, in 2001 [7].

Table 7

Dynamics of ions content (mg/L) and water mineralization (mg/L) in Dniester River, Otaci city, the entrance on the Republic of Moldova territory [5,6].

Date of water sample collection	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	NO_3^-	*Mineralization*
29.09.1983	9.0	34.0	61.4	16.8	60.0	70.0	6.7	367.9
01.10.1983	78.6	190.0	61.2	96.4	486.4	254.0	6.2	1273.9
04.10.1983	108.4	365.9	62.0	116.8	780.4	350.4	8.0	1876.9
09.10.1983	112.4	385.9	62.8	112.9	745.0	380.0	7.8	1904.3
12.10.1983	100.4	262.8	73.8	99.8	560.4	340.4	6.7	1561.4
10.11.1983	32.5	110.8	83.0	50.8	270.8	162.0	8.2	832.3
23.12.1983	27.2	100.0	95.0	45.8	225.0	158.4	8.6	780.0
02.02.1984	20.8	72.0	102.0	35.2	135.8	150.2	9.4	670.4
06.05.1984	14.8	49.2	88.8	28.8	120.6	125.8	6.8	556.8
23.09.1984	18.0	42.3	84.8	30.0	119.8	113.0	6.9	527.3
21.12.1984	13.8	40.0	72.8	29.8	95.0	86.5	9.5	457.4
05.04.1985	11.8	38.8	68.8	24.0	75.8	72.8	9.6	414.1
22.08.1985	11.2	36.0	66.0	18.0	65.0	68.0	7.4	377.0



1 – 19.10.1983
2 – 25.10.1983
3 – 30.10.1983
4 – 09.11.1983
5 – 15.11.1983
6 – 30.11.1983
7 – 01.12.1983
8 – 10.12.1983
9 – 02.02.1984
10 – 24.07.1984
11 – 24.09.1984
12 – 05.04.1985
13 – 22.08.1985

Figure 1. Dynamics of chloride (mg/mL) and mineralization in Dniester River water, Vadul lui Voda town (Water supply station of the Chisinau municipality), years 1983-1985 [5].

Following the consequences of the 1983 accident at the mineral fertilizer plant in the Stebnic town (Ukraine), the famous scientist Valeriu Ropot developed detailed studies and practical communications regarding the management of water resources in the conditions of a vulnerable environment [8].

Table 8

Content of mineral components in the bottom sediment from the Dubasari reservoir [5].

City and date of sample collection	*$CaSO_4 \cdot 2H_2O$*	*$CaCO_3$*	*$MgCO_3$*
	% of the dry bottom sediment		
Camenca town			
13.10.1983	0.57	8.24	0.004
Oxentia village			
13.10.1983	0.60	8.45	0.011
10.06.1986	0.025	5.71	0.038

Aspects regarding the water quality of Prut River

Considered a border river, almost along its entire length the Prut was not subjected to the scientific research necessary for water protection for a long time. As a result, it was found that there were a limited number of publications on the problems of the Prut River in the specialized literature. Starting with 1985, the researchers of the Institute of Chemistry of the Academy of Sciences of Moldova carried out systematic research on the evaluation of the water quality of the Prut River and its tributaries. Since 1991, the research has been carried out jointly with collaborators of the Romanian Wastewater Treatment Research Institute, with joint publications [9,10].

The information presented in Table 9, regarding the content of heavy metals in the water and bottom sediments in the Prut River, Giurgiulesti village, proves that it was within the allowed limit for surface waters, being also accumulated in the silt of the river.

The average annual values of the water quality indicators of the Prut River on the Republic of Moldova territory in the years 1995 and 2000 are mentioned in Table 10 [11] and denote the increase in mineralization and the concentration of the main ions along the course of the river towards the Danube River.

Table 9

Content of heavy metals in water and bottom sediments in the Prut River, Giurgiulesti village.

Parameters	*Water, mg/L*	*Bottom sediments, mg/kg*
Iron (Fe^{2+} + Fe^{3+})	0.3	900
Cooper (Cu^{2+})	0.005	40
Manganese (Mn^{2+})	0.004	500
Lead (Pb^{2+})	0.01	30
Zinc (Zn^{2+})	0.002	16
Cadmium (Cd^{2+})	traces	0.09

Table 10

Annual values of water quality indicators of the Prut River on the Republic of Moldova territory, 1995 and 2000 years [11].

Parameters	*Sampling points*									
	Lipcani		*Costesti*		*Valea Mare*		*Cahul*		*Giurgiulesti*	
	1995	*2000*	*1995*	*2000*	*1995*	*2000*	*1995*	*2000*	*1995*	*2000*
Suspensions, mg/L	45	42	22	20	104	87	83	70	82	56
Mineralization, mg/L	354	356	338	334	466	473	476	475	476	473
O_2 dissolved, mg/L	9.8	10.3	11.2	11.2	6.3	7.2	9.3	9.5	7.8	8.1
Chloride, mg/L	42	45	34	35	41	41	35	32	34	32
Sulphates, mg/L	62	65	53	56	65	67	79	80	108	115
Hardness, mg eq./L	5.4	5.2	4.5	4.6	5.8	5.6	5.8	5.7	5.2	5.3
Fe_{total}, mg/L	0.2	0.2	0.2	0.2	0.3	0.3	0.4	0.4	0.4	0.4
Mn, mg/L	0.003	0.003	0.003	0.004	0.004	0.005	0.005	0.005	0.005	0.005
Zn, mg/L	0.0015	0.0015	0.002	0.002	0.009	0.009	0.008	0.008	0.006	0.006
Pb, mg/L	0.02	0.02	0.01	0.01	0.016	0.016	0.017	0.017	0.015	0.014
NH_4^+, mg/L	0.054	0.062	0.03	0.031	0.38	0.40	0.022	0.023	0.012	0.010
Cu, mg/L	0.002	0.002	0.001	0.001	0.003	0.003	0.003	0.003	0.003	0.003
Cd, mg/L	traces	traces	traces	traces	0.0001	0.0001	0.0001	0.0001	traces	traces
NO_2^-, mg/L	0.01	0.01	0.003	0.004	0.087	0.059	0.007	0.009	0.008	0.008
NO_3^- mg/L	4.94	1.73	4.02	2.25	6.45	1.97	6.85	3.92	6.72	3.74
P_{total}, mg/L	0.03	0.03	0.01	0.032	0.036	0.01	0.014	0.01	0.01	0.01
CBO_5, mgO_2/L	4.8	4.3	3.2	3.2	6.9	7.3	7.2	7.3	5.5	5.8
CCO_{Cr}, mgO_2/L	22.3	22.6	16.7	16.8	54.0	54.2	26.9	27.2	24.2	24.0
Volatile phenols, mg/L	0.002	0.002	0.001	0.001	0.007	0.008	0.005	0.005	0.003	0.003
Petroleum products, mg/L	0.04	0.04	0.04	0.03	0.1	0.2	0.12	0.2	0.04	0.03
Coli Index, mg/L	10^5	10^5	10^4	10^4	10^6	10^6	10^6	10^6	10^5	10^5

Petroleum products entered the river water, in a concentration of 0.04-0.2 mg/L. According to the study carried out at that time, the Prut River water corresponded to the quality class II-III (moderately polluted).

The concentration of mineral components in the aquatic basins and lakes waters in the republic

An important scientific study was also carried out regarding the water quality of the aquatic basins (AB) and lakes in the republic, resulting from the fact that the water was used for different purposes, especially irrigation and fish farming, and some were on the course of the rivers. The renowned scientist, Dr. Valeriu Ropot, evaluated the information on the characteristics (surface, depth, length, width, the volume of water, silty part, *etc*.) of the aquatic basins of rivers including: Novodnestrovsk, Dubasari (Dniester River), Ghidighici (Bac River), Comrat, Congaz and Taraclia (Ialpug River), Costesti-Stanca (Prut River), Costesti-Ialoveni, Ulmu and Rezeni (Botna River), Ialoveni (Isnovat River) and Cuciurgan, Cahul, Ialpug and Cuhurlui lakes.

The chemical composition evaluation of the aquatic sources (Table 11) demonstrated high concentrations of Na^+ and SO_4^{2-} ions (AB Ghidighici, Bac River; AB Rezeni, Botna River; AB Comrat, Congaz, Taraclia, Ialpug River; Ialpug and Cuhurlui lakes), Cl^- (AB Comrat, Congaz, Taraclia, Ialpug River; Ialpug lake), dry residue and water hardness (AB Rezeni, Botna River; AB Comrat, Congaz, Taraclia, Ialpug River; Ialpug lake) [5]. The water from these aquatic basins and lakes according to the regulation regarding the environmental quality requirements for surface waters (Republic of Moldova) [12], was classified as polluted-very polluted (quality class IV-V). Moreover, it was determined that the chemical composition in the water basins and lakes water did not differ essentially from that of the rivers that feed them.

Table 11

The average values of the mineral components' concentrations (mg/L) in the Republic of Moldova aquatic basins and lakes, in the year 1987 [5].

Aquatic basins (AB) and lakes	K^+	Na^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-	HCO_3^-	Fe_{total}	NO_3^-	PO_4^{3-}	M^*	H^{**}	*pH*
AB Novodnestrovsc, Dniester River	8.6	39.4	65.7	13.2	102.6	65.8	132	0.07	2.4	0.08	439	4.7	-
AB Dubasari, Dniester River	11.2	46.3	62.7	16.2	98.6	69.4	197	0.14	2.9	0.11	519	5.0	8.2
AB Costesti-Stanca, Prut River	7.2	37.6	71.2	21.8	118.7	72.0	220	0.12	2.4	0.09	454	5.4	7.8
AB Ghidighici, Bac River	15.0	95.0	57.0	63.0	266.0	85.0	410	0.11	4.5	0.08	764	6.7	8.6
AB Rezeni, Botna River	28.3	138.3	122.4	91.3	426.2	108.7	496	0.07	18.5	0.12	1165	13.7	8.4
AB Ulmu, Botna River	4.8	21.5	63.4	32.5	54.6	36.7	316	0.06	1.3	0.04	320	6.0	7.6
AB Costesti, Botna Rriver	8.9	54.4	42.3	47.3	46.5	51.3	358	0.06	4.8	0.08	447	6.4	8.3
AB Ialoveni, Isnovat River	13.2	58.8	31.7	42.4	34.5	56.3	336	0.06	4.2	0.07	591	5.2	7.2
AB Cuciurgan, Cuciurgan River, alimentation from Turunciuc River	9.7	39.4	64.5	19.7	116.0	78.2	210	0.15	6.2	0.13	565	4.6	8.2
AB Comrat, Ialpug River	22.6	510	56.5	83.3	620.0	398.0	488	0.07	8.7	0.12	2183	9.6	8.6
AB Congaz, Ialpug River	28.4	560	58.4	94.5	580.0	412.0	473	0.08	9.4	0.12	2216	10.8	-
AB Taraclia, Ialpug River	15.3	520.5	64.2	89.8	750.0	463.0	390	0.08	7.5	0.10	2378	10.7	8.1
Lake Cahul	4.6	37.2	57.3	17.9	65.0	56.4	198	0.07	5.8	0.13	457	4.5	8.3
Lake Cuhurlui	7.2	98.7	59.4	31.7	262.0	69.4	210	0.08	6.4	0.16	740	5.7	8.4
Lake Ialpug	9.3	328.0	82.0	88.0	580.0	312.0	230	0.10	6.8	0.15	1650	11.5	8.3

** Mineralization*

*** Hardness, mg eq./L*

Methods developed for water quality control

For the evaluation of the composition of natural and used waters under the leadership of the scientist Ropot Valeriu, a series of methods were developed for determining chemical substances in water: phenol [13], aromatic hydrocarbons [14], nitrates, nitrites, sulphates [15-20], cationic surfactants, *etc*. The nitrate determination method has been patented (USSR Patent, 12.01.1990, No. SU 1638619 [18]). The methods of analysis of the chemical parameters of water were published [19] to ensure chemistry teachers and pupils of higher classes were able carry out hydrochemical assessments.

The main argument for the contribution to the development of the National Strategic Action Program in the field of environmental protection, Chisinau, 1995

The practice accumulated in the field of water quality assessment and protection in the republic laid down the base of the essential contribution granted to the elaboration of the National Strategic Action Program in the field of environmental protection, years 1995-2010-2020, approved by the decree of the President of the Republic of Moldova Mircea Snegur, no. 321 on 6 October 1995. The quality requirements for water use in different fields were specified, including for drinking purposes, agriculture, and animal husbandry, and with specific technical-industrial properties proposed for industry, energy, transport and construction. The Program also mentioned the sources of pollution of natural waters and industrial sources of wastewaters existing in 1995 [21].

Proposals to be introduced in the National Strategic Action Program in the field of environmental protection:

Sources of water pollution

- 3.3.49. In the Republic of Moldova, as in other countries, the hydrographic network is a receiver for the discharge and use of water in different branches of the national economy. In the year 1994, approx. 350 mln m^3 of wastewaters were released into the hydrographic network, including 182 mln m^3 treated at the treatment stations according to normative documents existing at that time, 160 mln m^3 insufficiently treated and 8 mln m^3 without being subjected to any treatment, with increased content of pollutants.
- 3.3.54. A particular danger for the environment is presented by the sludge resulting from biological urban wastewaters treatment systems. In the year 1995, the sludge was placed on special drying grounds. Thus, it is necessary to apply advanced methods - pressure filters, anaerobic fermentation with biogas production, *etc*.

Industrial wastewater sources

- 3.3.55. In the Republic of Moldova, industrial wastewaters, according to the chemical composition and degree of pollution, are very diverse. Waters with a predominant content of mineral salts of various metals, including heavy metals, come from the electronic and electro-technical industry, machines construction, equipment and materials production. The most dangerous for the environment are the waters used in the metal pickling and galvanizing processes; these contain heavy metals, have a strongly acidic or basic environment and cannot be discharged into sewage systems without being subjected to local purification. Non-ferrous metals can be recovered from these waters through various advanced methods, such as adsorption methods with ion exchangers, *etc*.
- 3.3.56. Wastewaters from the food industry, furniture, leather factories, textile industry, plastics' processing, *etc.*, contain many organic pollutants. Sometimes these contain substances that are quite toxic and "hard" biodegradable in the environment, such as polyphenols, organic acids, aldehydes, organic solvents, *etc*., which need to be removed at local treatment installations, by oxidation, adsorption, *etc*. Only after this stage, wastewaters can be discharged into the sewage system and subsequently treated/cleaned along with household water in the urban biological purification systems.
- 3.3.57. In the future, it is indispensable to introduce efficient local wastewater treatment systems in the industry, which, combined with the municipal treatment systems, allow the use of dangerous substances and the reuse of water after treatment in closed circuits.

The contribution of the scientist Dr. Valeriu Ropot to the development of the National Strategic Program of Actions in the Field of Environmental Protection (1995) laid the base of the environmental policy in the stage of transition to the market economy, which was laid down in the Conception of the Environmental Policy of the Republic of Moldova, compartment "Protection and use of natural resources". The need and objectives of the Environmental Policy Concept of the Republic of Moldova was approved by Parliament Decision no. 605 on 02.11.2001 [22].

Table 12

Dynamic of chemical parameters and their concentration values in the Dniester River water (Republic of Moldova territory) [5].

Parameters	*Sampling sections*									
	Otaci		*Vadul lui Voda*		*Bender*		*Slobozia*		*Olanesti*	
	I	*II*	*I*	*II*	*I*	*II*	*I*	*II*	*I*	*II*
Mineralization, mg/L	540	480	650	500	730	530	760	560	820	600
Oxidability, mgO_2/L	30	12	40	13	45	14	54	16	60	18
pH, un.	8.0	7.6	8.1	7.7	8.2	7.8	8.3	7.8	8.4	7.9
Hardness, mg eq. /L	7.8	4.4	8.2	4.5	8.9	4.7	9.8	5.3	10.1	5.8
Ca^{2+}, mg/L	80	66	86	68	92	74	97	78	100	82
Mg^{2+}, mg/L	45	12	48	15	53	16	60	18	63	20
Na^{+}, mg/L	70	46	78	50	84	55	86	60	88	64
K^{+}, mg/L	20	12	22	14	23.5	16	24.5	20	26	22
SO_4^{2-}, mg/L	130	75	136	80	141	84	157	90	164	94
Cl^{-}, mg/L	160	36	165	45	170	48	183	52	190	58
P_{total}, mg/L	0.5	0.5	0.6	0.6	0.7	0.7	0.8	0.8	0.8	0.8
NO_3^{-}, mg/L	10	10	12	12	15	15	18	18	20	20
Petroleum products, mg/L	0.04	0.04	0.05	0.03	0.05	0.04	0.05	0.05	0.06	0.06
Surfactants, mg/L	0.3	0.2	0.34	0.2	0.36	0.2	0.37	0.2	0.45	0.2

I – treatment of wastewaters and its discharge into natural aquifers;
II – implementation of efficient wastewaters treatment systems to ensure their reuse.

Evaluating the existing statistics regarding the hydrochemical and development information of the national economy, Dr. Ropot Valeriu conducted a study of the dynamics of chemical parameters in the Dniester River water on the Republic of Moldova territory in two versions:

I – treatment of wastewater and its discharge into natural aquifers;

II – implementation of efficient wastewater treatment systems to ensure their reuse.

As a result of the calculations, at the beginning of the 21st century, the composition of the water on different sections of the Dniester River has been predicted, the information is presented in Table 12 [5].

The concentration of biogenic elements (P_{total} and NO_3^{-}) and petroleum products was expected to be approximately the same in both versions due to their presence in the rainwater entering in the rivers. It has been demonstrated that through the implementation of efficient wastewater treatment systems to ensure their reuse, the content value of most hydrochemical indices decreases, according to the proposal 3.3.57 from the National Strategic Action Program in the field of environmental protection, 1995 (in the future it is absolutely indispensable the introduction of effective local treatment systems for wastewaters of industrial sources, which along with the treatment systems, allow the use of dangerous substances and the reuse of treated water in closed circuits).

Biography of doctor of chemistry Valeriu Ropot

Valeriu Ropot was born on 7 November 1934 in Viisoara village, Hotin County, Romania. After graduating from the Faculty of Chemistry at the Moldova State University in 1957, he engaged in scientific research at the Institute of Chemistry of the Academy of Sciences of Moldova. Between 1960 and 1963, he completed his doctoral studies in the Laboratory of Analytical Chemistry, under the guidance of academician of Academy of Sciences of Moldova, Iurie Lealikov. He brilliantly defended his doctoral thesis in chemistry, titled “Variation of current intensity as a function of time in polarography and analytical applications” in 1968.

Doctor of chemistry Valeriu Ropot (07.11.1934 - 05.03.2002)

Between 1964 and 1972 he worked as Scientific Secretary of the Institute of Chemistry of the Academy of Sciences of Moldova.

In 1972, doctor of chemistry Valeriu Ropot founded the Laboratory of Mineral Resources and Chemistry of Water within the Institute of Chemistry of the Academy of Sciences of Moldova. Later, in 1992, due to the need to solve environmental problems, which were intensifying in the world, including in Bessarabia, the laboratory was re-profiled as the Ecological Chemistry Laboratory. The main scientific objectives of the laboratory were aimed at researching and establishing the laws of formation of quality of surface and underground waters, highlighting the processes and mechanisms of transformation, immobilization of natural and anthropogenic pollutants in aquatic systems on carbonic and mineral adsorbents, the full utilization of secondary agricultural products to obtain new carbon catalysts and pharmaceutical products, *etc*. Dr. Valeriu Ropot paid special attention to the development of high-performance technologies for potabilization of surface and underground water, as well as technologies of treatment of wastewaters from various economic units in the Republic of Moldova.

Purification technologies of water from Dniester and Prut Rivers have been improved; many wastewater treatment processes from economic units of the agro-industrial complex, and units with galvanic processes, *etc*. have been implemented. The scientific research carried out by Dr. Valeriu Ropot allowed the application of methods to reduce the content of fluorine, iron, ammonium and sulphide ions in underground waters.

The scientific results are reflected in over 300 published works, including 3 monographs and 25 patents, *etc*. Under the leadership of Valeriu Ropot, a scientific school of hydrochemistry was formed in the Republic of Moldova, known far beyond its borders. He was an erudite supervisor for his disciples. In 1996, together with his 4 disciples, he was awarded the State Prize of the Republic of Moldova in the field of science, technology and production for a series of works in the field of natural water purification and wastewater purification technologies. For his outstanding scientific achievements, Dr. Valeriu Ropot was decorated with the "Civic Merit" medal and the "Glory of Work" Order; he was awarded the title "Emeritus Man and Emeritus Worker in the Protection of Nature".

Dr. Valeriu Ropot organized six expeditions to Dniester River from the source to the Black Sea, and to the Prut River starting from the Goverla Mountain to the Giurgiulesti commune. Moreover, he coordinated several international scientific events dedicated to water protection. The last international practical scientific seminar, held in the fall of 2001 with the title "Water resources management in the conditions of a vulnerable environment", which was organized by Dr. Valeriu Ropot with the financial support of the National Commission of the Republic of Moldova for UNESCO, is kept in our memory to date.

Conclusions

The results of the innovative, managerial and research activity of Valeriu Ropot, doctor of chemical sciences, talented chemist and renowned ecologist culminated into a great contribution to the environmental chemistry in Republic of Moldova and beyond its borders.

Under his guidance have been established the laws regarding the formation of surface and underground water quality, highlighting the processes and mechanisms of transformation, immobilization of natural and anthropogenic pollutants in aquatic systems on carbonic and mineral adsorbents.

The improvement of water purification technologies from the Dniester and Prut Rivers was achieved, as well as some practical recommendations were given regarding the removal of fluoride, iron, ammonium and sulphide ions from groundwaters.

Treatment procedures of wastewaters from economic units in the agro-industrial complex, units with galvanic processes, *etc*, were developed and implemented.

Argumentation of the practical recommendations helped to reduce the negative impact of the discharge of hundreds of thousands tons of brine into the Dniester River resulted from the accident at the mineral fertilizer plant in the city of Stebnik, Ukraine.

Methods for determining organic and inorganic pollutants in natural waters were developed.

Dr. Valeriu Ropot had essential contributions to the elaboration of the National Strategic Action Program in the field of environmental protection for the years 1995-2010-2020, approved by the decree of the President of Republic of Moldova Mircea Snegur no. 321 of October 6, 1995.

Acknowledgements

This work was prepared with the financial support of the national project "The reduction of the environmental and health impact of toxic chemicals through use of adsorbents and catalysts obtained from local raw material" DISTOX, No. 20.80009.7007.21.

References

1. Ropot, V.M. Problems of quality, use and protection of the Dniester River water resources. Chisinau, 1992, 49 p. (in Russian).
2. USSR State Standard, GOST 2874-82, Drinking Water. Moscow, 1984, 239 p. (in Russian). https://standartgost.ru/0/299-pitevaya_voda
3. Lupascu, T.; Sandu, M.; Nicolau, M.; Rusu, V.; Ropot, V.; Kerdivarenko, M. The current state of the Dniester River water quality and improvement of the technology of its purification for drinking needs. Collection of scientific articles "Water and health", Odessa, 2001, pp. 136-139. (in Russian).
4. Lupascu, T.; Ropot, V.; Nicolau, M.; Ballo, A.; Cosma, C. Studies of processes of the Dniester River water treatment for its utilization for drinking. The International Ecological Seminar Lviv – Vadul lui Voda "Tiras-96", 9-23 september, Chisinau, 1996, pp. 19-27. (in Romanian).
5. Ropot, V.; Stratulat, G.; Sandu, M.; Lupascu, T.; Rusu V.; Ciobanu M.; Dranca I.; Lozan, R.; Rusu, V. C.; Botan, V.; Shafranschii, V.; Vavelischii, M. Problems of quality, use and protection of water resources in the SSRM. Chisinau: Stiinta, 1991, 285 p. ISBN 5-376-01191-7. (in Russian).
6. Ropot, V. Dniester River pollution with toxically waste as a result of the accident at potassium fertilizers factory. The materials of the international ecological seminar "Tiras-96", Chisinau, 9-23 septembrie, 1996, pp. 3-12.
7. Ropot, V.; Sandu, M.; Lozan, R. The impact of Novodnesrtovsc (Ukraine) hydro energetic complex concerning Dniester River water quality downstream the Republic of Moldova. 12-th Romanian International Conference on Chemistry and Chemical Engineering RICCE-12, Romania, Bucharest, September, 13-15, 2001, pp. 148-152.
8. Ropot, V.; Lozan, R.; Sandu, M.; Dumbraveanu, A. Studies and practical communications regarding the management of water resources under the conditions of a vulnerable environment. Chisinau, Universul, 2002, 205 p. (in Romanian).
9. Ropot, V.; Nicolau, M.; Curcaneanu, N.; Lozan, R.; Iliescu Ş.; Lupaşcu, T.; Drancă, I.; Negru, M. Study on the Prut River water quality. Bulletin of the Academy of Sciences of Moldova, Biological and Chemical Sciences, 1994, 6, pp. 41-46. (in Romanian). http://www.bsl.asm.md/archive
10. Lupascu, T.; Sandu, M.; Rusu, V.; Ropot, V.; Revenco, M.; Kerdivarenco, M. The current state of water quality in the Prut River. Collection of scientific articles "Water and health", Odessa, 2001, pp. 132-136. (in Russian).
11. Ropot, V.; Sandu, M.; Revenco, M.; Mereanu, V.; Lupascu, T.; Rusu, V. Aspects regarding the current water quality of the Prut River. Hydrotechnic Journal, 2002, 47(2), pp. 34-38. (in Romanian). https://rowater.ro/documente-de-interes-public/revista-hidrotehnica/
12. Decision of Republic of Moldova Government no. 890 of 12.11.2013 for approving the Regulation regarding the environmental quality requirements for surface waters. Official Monitor no. 262-267 of 22.11.2013, art. no. 1006. (in Romanian). https://www.legis.md/cautare/getResults?doc_id=114535&lang=ro
13. Ropot, V.; Pinkas, M.; Lozan, R. Spectrophotometer determination of phenol in natural and wastewaters. The Republican Conference „Application of advanced methods and equipment for water treatment and drainless technology in the production of VPTIEMP", Chisinau, 5-6 October, 1982, pp. 373. (in Russian).
14. Ropot, V.; Pinkas, M.; Lozan, R. Spectrophotometer determination of some aromatic hydrocarbons using DMAA. Bulletin of the Academy of Sciences of Moldova, Biological and Chemical Sciences, 1984, 6, pp. 74. (in Russian). http://www.bsl.asm.md/archive?language=en-gb
15. Lozan, R.; Ropot, V.; Sandu, M. Determination of nitrates and nitrites in natural waters. Chemistry and water technology, 1989, 11(2), pp. 120-122. (in Russian). https://link.springer.com/journal/11962/volumes-and-issues
16. Ropot, V.; Sandu, M.; Lozan, R. Determination of nitrate ions in natural waters. The XI National Conference of Analytical Chemistry, 24-25 September, 1992, Cluj-Napoca, pp. 78. (in Romanian).
17. Sandu, M.; Lozan, R.; Ropot, V. Determination of sulfates, nitrates and nitrites in galvanic wastewater. Republican Conference Waste-free technology, Chisinau, 1990, pp. 108-109. (in Russian).
18. Lozan, R.; Sandu, M.; Ropot, V. A method for determining nitrates. USSR Patent, 1990, No. SU 1638619 A1. (in Russian). https://patents.su/3-1638619-sposob-opredeleniya-nitrat-ionov.html
19. Sandu, M.; Lozan, R.; Ropot, V. Methods and instructions for water quality control. Chisinau, 1992, 160 p. ISBN 5-376-01636-1. (in Romanian).
20. Ropot, V.; Lozan, R.; Sandu, M. On the issue of the nitrates determining in natural waters. Materials of the XV Mendeleev Congress on General and Applied Chemistry, Minsk, 1993, pp. 156-157. (in Russian).
21. Ropot, V.; Sandu, M. Water quality. National Strategic Action Program in the field of environmental protection. Chisinau, 1995, pp. 18-24. (in Romanian).
22. Decision of the Parliament of the Republic of Moldova, no. 605 of 02.11.2001 regarding the approval of the Environmental Policy Concept of

the Republic of Moldova. Official Monitor no. 9-10 of 15.01.2002, art. 20. (in Romanian). https://www.legis.md/cautare/getResults?doc_id=58192&lang=ro

Short biography of the authors

Maria Sandu, *doctor of chemistry, is the associate researcher of the Laboratory of Natural and Anthropogenic Ecosystems of the Institute of Ecology and Geography, Republic of Moldova. She detains expertise in the fields of analytical chemistry, natural water quality and chemistry. Dr. Maria Sandu has a scientific activity of over 50 years, devoted to the assessment of the state of surface waters in the Republic of Moldova. She developed technologies for water purification and potabilization in Republic of Moldova, possessing invention patents and 465 scientific publications dedicated to natural water problems. In 2013 she was awarded the "Order of Work Glory" and in 2021 the "Order of the Republic" by the decree of the Republic of Moldova President.*

Tudor Lupascu, *academician, professor, doctor habilitate, head of the scientific Center of Ecological Chemistry and Environmental Protection, at the Institute of Chemistry (Republic of Moldova) is a remarkable personality and notorious scientist, and former director of the Institute of Chemistry (2001-2018), founder of the scientific school of chemistry of adsorbents. Acad. Tudor Lupascu is known to the scientific world due to complex scientific investigations, among which: synthesis of carbonaceous adsorbents with scheduled properties from local raw materials, useful for detoxification of the human body and protection of the environment; elaboration of biologically active substance Enoxil (from tannins) useful for medicine, veterinary and agriculture; new plastering materials for buildings surfaces from local raw materials. The prosperous scientific activity of academician Tudor Lupascu is eloquently described by the great number of scientific works that have exceeded 800. The scientific, innovational and managerial contribution of academician Tudor Lupascu was appreciated at home as well as abroad, being awarded many honorific titles, such as: Emeritus of the Republic of Moldova (2000); State Prize in Science and Technology(1996); Medals "Dimitrie Cantemir" (2010) and "Nicolae Testimitanu" (2010; Knight of the Orders "Labour Glory" (2010); "of the Republic"(2019); "Leonardo da Vinci" (2009); "Aurel Vlaicu" (2011) and "Pro Scientia et innovatio" with the rank of Officer (2019); Award of the Government of the Republic of Moldova "The most gifted inventor of the year" (2019); Gold Medal of OMPI (2009) and many, many others.*