THE STUDY OF REDOX CONDITIONS IN THE DNIESTER RIVER

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Abstract: The work presented in the paper discusses the contribution of the Novodnestrovsc water system to the formation of redox conditions in the lower Dniester. The conclusions were drawn on the basis of a long-term protocol of analyses that included the analysis of the oxygen regime, evaluation of the content of hydrogen peroxide, rH_2, biological oxygen demand as well as other additional parameters.

Keywords: kinetic indicators, hydrogen peroxide, redox state, free radicals, inhibition capacity

Introduction

The Dniester is a trans-boundary river crossing the countries of Moldova and Ukraine, discharging into the Black Sea. Its total length is 1352 km, with 636 km flowing through Moldova. The river is the largest one in Moldova and the chief source of drinking water for more than a million people. The Dniester River basin occupies 57% of the area of the Republic of Moldova, and run-off water, municipal effluents and industrial discharges contribute to the degradation in water quality [1-5].

In 1981 in the middle part of the river on the territory of Ukraine a barrage was constructed, creating the Hydropower Station. The newly formed storage pond is 194 km long; the capacity of the reservoir is 3.0 km^3. The main purpose of the reservoir construction was for power supply and flood control. In 1985 another dam was constructed downstream of the Novodnestrovsc barrage in order to create a 20-km buffer reservoir. The second barrage also serves as a frontier between Moldova and Ukraine. The main purpose of the second barrage construction was to regulate the water discharge from the first barrage and also to generate electric power.

The Dniester reservoir is a canyon-type, deep-water lake with a 54 m maximum depth near the dam. Low water temperature, a deficiency in dissolved oxygen, and the presence of hydrogen sulfide and ammonium are typical for the hypolimnion of such reservoirs [6]. Once the reservoir was filled with water, organic-rich sediments have accumulated, and the decomposition of this organic material creates low red-ox conditions. In other similar reservoirs, elevated phosphate and transition metal concentrations have been measured that can be attributed to the reductive-dissolution of iron- and manganese- oxides, and the release of adsorbed phosphate [7]. All these chemical species can have an adverse impact on down-stream aquatic life [8].

Since the beginning of full-capacity operation of the Hydroelectric Power Plant, dramatic changes in the water quality occurred in the river emerging from the buffer reservoir. The temperature regime of the river has been changed as follows: the mean temperature value decreased by 8-10^{0}C in summer time; when the average air temperature reached 30-32^{0}C, the water temperature in the lower reach was 16-18^{0}C. Severe changes in the aquatic ecosystem occurred: the diversity of hydrobiont species was decreased, fish stocks also decreased, and mass fish kills were often observed [9]. Ichthyologists have pointed out the negative effects of the dam on the ichthyo-fauna. Some fish species have stopped spawning, and fish stocks have been 18-fold reduced. Reproduction of some species has decreased 30-fold. Certain studies revealed that 80% of the sturgeon sampled showed signs of spawn reabsorption. The presence of reducing substances in the amounts exceeding quite often the contents in oxidizers (hydrogen peroxide), provoke the unbalance of these processes in water environment. It is known that the reductive, quasi-reducing and super oxidative conditions of natural waters are destructive for the development of hydro-bionts, including fish [10-12; 13-32]. Quasi-reducing conditions is toxic for certain bacteria, and fish larvae [13]. The red-ox state of surface natural waters is a parameter that characterizes the ecological state of the water body and its auto-purification capacity [8; 15-17; 30-32]. Biologically healthy fresh water is determined by the presence in it of hydrogen peroxide within the limits of 10^{-6} mol/l [15-16]. In sea water the amount of hydrogen peroxide is substantially lower then in fresh waters [7,11,12; 22-25]. In the biogeochemical cycle of oxygen in fresh water ecosystems the stationary concentrations of oxidative equivalents such as OH radicals constitute $3\text{-}5 \cdot 10^{-16}$ mol/l. The range of variation of their concentration should not vary by more than a factor of 10 [23]. Red-ox processes in surface natural waters containing dissolved oxygen occur with the formation of intermediate active forms, namely, hydrogen peroxide, and hydroxide - and super-oxide radicals. Chemical processes of oxidation, which change the red-ox state of metal ions, depend on the rates of free radical formation and destruction, and their steady-state concentrations.

In order to perform investigations of the river there were selected 6 permanent sites located as follows:Site 1 – v.

Naslavcea, below the Dniestrovsk dam, 200 m from the buffer reservoir; site 2 – v. Mereseuca, 18 km from the dam, site 3 – v. Cosauti, 87 km from the dam and buffer reservoir; site 4 – v. Bosernita located at the distance of 145 km from Naslavcea; site 5 – c. Dubasari, above the dam of the Dubsari water reservoir, 309 km from Naslavea; site 6 – 100 m below the dam of the Dubasari water reservoir (310 km from the site 1). During the summer of the year 2006 two more sites have been added between the first and second sites. One was located at the fourth km from Naslavcea and the other one was located at v.Verejeni, 6 km from Naslavcea. The sites located between Naslavcea and Cosauti were characteristic for the river-bed flow while the sites 4-6 were located very close to the Dubasari water reservoir.

The water samples were collected from the upper horizons (0,5 – 0,6 m). The measured hydrochemical indicators included hardness, mineralization and the content of major ions (Ca^{2+}, Mg^{2+}, $Na^{+}+K^{+}$, HCO_3^-, SO_4^{2-}, Cl^-). The traditional hydrochemical parameters of the river waters has served as additional indicators of potential impact of the water reservoir on the river waters flowing from the barrage. Redox components measured included: the temperature, the dissolved oxygen, pH, Eh, rH_2, BOD, COD, NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}, Cu(II), Fe(III), H_2O_2, and OH radicals.

Results

Redox active components

The assessment of the components of the Dniester river waters determining the oxidation-reduction processes has identified a series of regularities in seasonal and spatial dynamics. The hydrogen indicator (pH) for the duration of the year cycle was varying within the investigated segment of the river from 7.3 till 9.1, its average values constituted respectively 7.8 at Naslavcea and 8.2 at Dubasari water reservoir (at the barrage). Practically at all the times the pH of the initial site was lower than in other investigation sites. The seasonal variations were manifested by the decrease of this indicator almost in all the sectional lines of the water flow.

The dissolved oxygen was present in the Dniester waters during the investigation continuously, however, in the water masses, coming into Naslavchea pool from Novodnestrovsc's water reservoir; its content was reaching normal saturation only in spring. In summer the saturation of water with oxygen constituted 70.5% and was decreasing in certain periods down to 52%; in autumn the average saturation was equal to 79.5%. The decrease of saturation of waters with oxygen by 83% was observed also in summer at the Bosernita site. The investigation of saturation with oxygen at Cosauti, Bosernita and Dubasari water reservoir has identified over saturation of Novodnestrovsc water with oxygen up to 158 – 177%.

Novodnestrovsc's waters have demonstrated during the investigation an instable oxidation – reduction state. According to the rH_2, at Naslavcea the ratio of reduction and oxidation processes was varying from the predominance of the reduction processes to neutral state and in average it can be characterized as close to neutral. In Mereseuca the waters most often was predominant the reduction processes. The domination of reduction processes over oxidation processes was observed in summer period at Dubasari water reservoir as well.

Table 1

The content of redox components in Dniester waters between 12.08.05 and 24.08.06 (Numerator- the average value of the period, denominator - the limits of variation of the indicators)

Site Parameter		Naslavcea	Mereseuca	Cosauti	Bosernita	Dubasari, above the barrage	Dubasari, below the barrage
pH		$\frac{7.8}{7.3-8.5}$	$\frac{8.11}{7.7-8.5}$	$\frac{8.24}{8.0-8.6}$	$\frac{8.0}{7.3-8.4}$	$\frac{8.2}{7.4-9.0}$	$\frac{8.15}{7.6-9.1}$
rH_2 rH_2		$\frac{27.7}{26.9-28.6}$	$\frac{27.2}{25.5-28.0}$	$\frac{28.0}{27.6-28.4}$	$\frac{28.4}{27.2-30.5}$	$\frac{27.5}{25.3-29.0}$	$\frac{27.1}{22.1-29.2}$
$[O_2]$	mg/l	$\frac{8.7}{4.8-12.0}$	$\frac{11.65}{8.2-14.7}$	$\frac{12.5}{8.9-17.0}$	$\frac{11.3}{7.5-14.6}$	$\frac{11.1}{7.8-14.7}$	$\frac{10.6}{8.1-15.2}$
	%	$\frac{80.6}{52-101}$	$\frac{109.9}{87.2-127.0}$	$\frac{118.8}{97-187}$	$\frac{107.2}{83-158}$	$\frac{113.3}{88-171}$	$\frac{107.6}{95-133}$
$[NO_3^-]$, mg/l		$\frac{5.84}{1.9-8.4}$	$\frac{7.42}{3.9-10.7}$	$\frac{5.68}{1.7-10.7}$	$\frac{6.6}{1.6-14.2}$	$\frac{5.5}{0.9-12.0}$	$\frac{6.94}{0.6-13.4}$
$[NO_2^-]$, mg/l		$\frac{0.027}{0.008-0.054}$	$\frac{0.037}{0.014-0.078}$	$\frac{0.027}{0.006-0.052}$	$\frac{0.027}{0.012-0.042}$	$\frac{0.058}{0.0-0.231}$	$\frac{0.03}{0.0-0.095}$
$[NH_4^+]$, mg/l		$\frac{0.021}{0.0-0.07}$	$\frac{0.015}{0.0-0.10}$	$\frac{0.044}{0.0-0.20}$	$\frac{0.06}{0.0-0.20}$	$\frac{0.071}{0.0-0.32}$	$\frac{0.136}{0.0-0.54}$
$[PO_4^{3-}]$, mg/l		$\frac{0.48}{0.21-0.77}$	$\frac{0.54}{0.16-0.92}$	$\frac{0.73}{0.11-3.22}$	$\frac{0.52}{0.21-1.37}$	$\frac{0.46}{0.12-0.67}$	$\frac{0.52}{0.22-0.82}$
CBO, mgO_2/l		$\frac{3.3}{1.2-4.45}$	$\frac{3.13}{0.6-5.6}$	$\frac{3.21}{1.0-5.83}$	$\frac{3.6}{1.5-6.1}$	$\frac{3.9}{1.4-6.7}$	$\frac{3.7}{1.9-5.0}$
$[H_2O_2]\cdot 10^6$ M		$\frac{1.02}{0.0-4.8}$	$\frac{1.22}{0.0-5.44}$	$\frac{0.95}{0.0-1.9}$	$\frac{0.32}{0.0-1.44}$	$\frac{1.76}{0.0-9.52}$	$\frac{1.4}{0.0-8.48}$

The ammonia ions in the section line of Dniester were present in concentrations 0.015 – 0,136 ml NH_4^+/l. Starting from Cosauti towards the Dubasari hydroelectrical plant their content was steadily increasing. The maximal content was observed below the dam at Dubasari. The seasonal dynamics of ammonium nitrogen was manifested by the increase of its concentration in autumn. In spring the NH_4^+ ions were not identified in any site but Bosernita.

In average for the year, the content of NO_3^- in the section lines constituted 5.5 – 7.4 mg NO_3^-/l, and the lowest values were detected in autumn; the highest concentrations of NO_3^- were observed in spring in all the sites but Naslavcea.

The nitrites, during the investigation period, were a permanent component of Dniester waters. Their absence was registered only once in May 2006 above and below the Dubasari barrage. The average content of nitrites throughout the year constituted between 0.027 and 0.058 mg NO_2^-/l. In summer the content of nitrites in Dniester waters was increasing, while in spring it was decreasing. The permanent presence of nitrites in the background of low content or complete absence of ammonium nitrogen can occur due to unfavorable oxidation state and slow oxidation of NO_2^- to NO_3^-.

The phosphates were present in the river in quantities 0.11 – 3.22 mg PO_4^{3-}/l. Their average concentrations in the sections lines varied in the range 0.48-0.73 mg PO_4^{3-} /l. The maximal pollution with phosphates was observed in the summer of 2006 at Cosauti and Bosernita sites, and constituted respectively 3.22 and 1.37 mg PO_4^{3-} /l. The seasonal dynamics have shown an increase of the phosphates content in the segment Naslavcea – Mereseuca in spring, another increase being detected in summer between Cosauti and Dubasari.

The average content of organic compounds according to the BOD_5 in the section lines of the investigated sector of Dniester constituted 3.1 – 3.9 mg O_2/l. In summer this indicator was rising above the yearly average at Mereseuca and Cosauti sites and constituted respectively 4.6 and 3.7 mg O_2/l, in spring – at the Dubasari water reservoir (Bosernita – Dubasari, lower reach) and constituted respectively 6.1 – 5.0 mg O_2/l. At Naslavcea the maximal amount of organic compounds was 4.45 mg O_2/l that was detected in spring.

The hydrogen peroxide and the redox state of waters

The analyses of the waters of the sector under investigation have never detected an oxidant state throughout the period of research (table 2). The most favorable state, according to this parameter, was registered in September 2005 when hydrogen peroxide was detected in the samples collected from all the sites (the range of concentrations: $1.44 \cdot 10^{-6}$M – $9.52 \cdot 10^{-6}$M) except Naslavchea. At that site the waters were continuously in reducing state, the hydrogen peroxide was missing and only the organic substances of peroxidazic type that are easily titrated by hydrogen peroxide were present. The reducing state of water below the Naslavchea dam could be caused by a shift from the equilibrium state in the waters of the accumulation reservoir above the dam resulting from the inflow of substantial amounts of reducing peroxidazic substances. The negative impact of the resulted disequilibria has been attenuated along the investigation segment of the river, that was confirmed by the presence of hydrogen peroxide in the waters of the Mereseuca site, where its concentration was the lowest ($1.19 \cdot 10^{-6}$M) in the hole investigated part of the river. The detection of hydrogen peroxide can be related to the occurrence in the segment Naslavcea – Mereseuca (18 km) of self-purification processes that lead to the total oxidation of peroxidazic substances and to the low excess of hydrogen peroxide.

The maximal content of H_2O_2 in September 2005 was registered below and above the Dubasari dam ($8.48 \cdot 10^{-6}$M and $9.52 \cdot 10^{-6}$M), that can be explained by the existence of large quantities of microflora that eliminates metabolic H_2O_2 in the surrounding environment.

Table 2

The content of hydrogen peroxide and reducing substances ($H_2O_2 \cdot 10^{-6}$M/Red$\cdot 10^{-6}$M) in the waters of Dniester River).

Month, year	***Naslavcea***	***Mereseuca***	***Cosauti***	***Bosernita***	***Dubasari, above the dam***	***Dubasari, below the dam***
09.2005	- 1,10	1,19 -	1,77 -	1,44 -	9,52 -	8,48 -
10.2005	1,24 -	1,05 -	1,90 -	- -	1,52 -	- -
11.2005	0,32 -	0,35 -	0,70 -	- -	0,33 -	0,42 -
03.2006	- -	- -	- -	- -	- 0,90	- 0,92
05.2006	0,30 -	- 0,30	0,50 -	- -	0,50 -	0,40 -
06.2006	4,80 -	5,44 -	1,26 -	- 0,50	- 0,46	- 0,64
08.2006	0,50 -	0,49 -	0,48 -	0,49 -	0,49 -	0,48 -

In October 2005 the waters of the Dniester River collected from the Naslavecea- Cosauti segment and above the Dubasari dam were in oxidant state and hydrogen peroxide was present in quantities $1.05\cdot10^{-6}$M – $1.52\cdot10^{-6}$M. The maximal concentration values were registered, as well as in September 2005, above the Dubasari dam. At the sites located near Bosernica and below the Dubasari dam the state of the waters was characterized as instable since the samples did not contain either hydrogen peroxide or signs of organic substances that easily reacts with hydrogen peroxide.

In November 2005, March and May 2006 the quality of waters was characterized as being unfavorable for the occurrence of chemical self-purification with participation of hydrogen peroxide. In the other parts of the investigated segment the waters were in instable state as well, since the H_2O_2 content was very low ($3{,}2\cdot10^{-7}$M – $7{,}0\cdot10^{-6}$M) while at Bosernita H_2O_2 was not detected at all.

The obtained results have denoted that the worst situation was established in March 2006, when the instable state of the waters was extended throughout the total segment Naslavcea – Bosernita (neiter hydrogen peroxide nor reducing peroxiacids were present), while above and below the barrage there were detected reducing substances in quantities $9.0\cdot10^{-7}$M and $2\cdot10^{-7}$M respectively.

In May 2006 the instable state of waters was similar to the state detected in November 2005. Insignificant concentrations of H_2O_2 were registered at Naslavcea ($3.7\cdot10^{-7}$), Cosauti ($5{,}0\cdot10^{-7}$M), above ($5{,}0\cdot10^{-7}$M) and below ($4{,}0\cdot10^{-7}$M) the barrage at Dubasari. At the Mereseuca site the waters were in the reducing state (the content of reducers was $3.0\cdot10^{-7}$M), while at Cosauti and Bosernita neither H_2O_2 nor reducers were detected.

In June 2006 the redox state of waters was different in various segments of the river. Thus, in the segment Naslavcea – Cosauti (the part of the river with most intense flow) the waters were in oxidized state, and the content of hydrogen peroxide constituted $1{,}26\cdot10^{-6}$M – $5{,}44\cdot10^{-6}$M, that can assure the realization of the chemical self-purification processes with participation of effective oxidizers. The segment of the river Bosernita – upper side of Dubasari barrage did not contain H_2O_2 while in the content of peroxidazic reducers in the water samples constituted $4{,}6\cdot10^{-7}$M – $6{,}4\cdot10^{-7}$M. This variation of the redox state in this part of the river can be explained by the diminishing of the water flow, the accumulation of organic substances of reducing nature, mass development of microflora and related discharge of peroxidazic nature. Besides, it must be taken into account that in the warm part of the year, especially during summer, the hydrogen peroxide cycle in the natural water media is influenced both by the anthropogenic factors such as discharge of biologically treated residual waters, enriched with reducing substances and by the abundant development of blue-green algae that disseminate toxic metabolites that have reducing properties.

In August 2006 the state of water was again instable from the point of view of redox equivalents equilibrium. In the total segment under investigation there were identified insignificant quantities of H_2O_2 ($4{,}8\cdot10^{-7}$M – $5{,}0\cdot10^{-7}$M), a fact that impedes the occurrence of self-purification processes. This fact is related to the intense anthropogenic pollution of the river with organic substances.

During May – August 2006, when the solar irradiation was more intense, in the investigated segment there were evaluated kinetic parameters characterizing the self-purification processes occurring with participation of free radicals. The evaluated parameters included the capacity of inhibition of waters ($\Sigma k_i[S_i]$) and stationary concentration of OH free radicals. The value of the capacity of inhibition and its physical sense allows the consideration of this parameter as being the effective constant of rate of the reaction of OH free radicals "disappearance" in water medium, therefore it can be regarded as an indicator of the state of the water. The smaller the parameter $\Sigma K_i[S_i]$, the bigger is the contribution of the source of free radicals to the self-purification by radicals. When the $\Sigma K_i[S_i]$ is less than 10^4 s^{-1} the water is pure, at values of $\Sigma K_i[S_i]$ bigger than 10^6 s^{-1} the water is more polluted. For the majority of natural waters the typical values of $\Sigma K_i[S_i]$ equals 10^5 s^{-1}.

Table 3

Values of the capacity of inhibition of Dniester waters ($\Sigma k_i[S_i]$, s^{-1}) and the stationary concentration OH free radicals OH,M($[(\Sigma k_i[S_i]/[OH]]$) *during May – August 2006.*

Month, year	**Naslavcea**	**Mereseuca**	**Cosauti**	**Bosernita**	**Dubasari, above the barrage**	**Dubasari, below the barrage**
05.2006	$5{,}80\cdot10^5$ $1{,}72\cdot10^{-17}$	$7{,}60\cdot10^5$ $1{,}30\cdot10^{-17}$	$8{,}10\cdot10^5$ $1{,}23\cdot10^{-17}$		$3{,}0\cdot10^5$ $1{,}75\cdot10^{-17}$	$5{,}70\cdot10^5$ $3{,}4\cdot10^{-17}$
06.2006	$5{,}40\cdot10^4$ $7{,}60\cdot10^{-16}$	$6{,}70\cdot10^4$ $8{,}40\cdot10^{-16}$	$3{,}20\cdot10^4$ $6{,}70\cdot10^{-16}$	$5{,}60\cdot10^5$ $9{,}70\cdot10^{-17}$	$5{,}30\cdot10^5$ $8{,}30\cdot10^{-17}$	$4{,}20\cdot10^5$ $7{,}20\cdot10^{-17}$
08.2006	$1{,}85\cdot10^5$ $5{,}50\cdot10^{-17}$	$1{,}90\cdot10^5$ $5{,}20\cdot10^{-17}$	$1{,}50\cdot10^5$ $6{,}70\cdot10^{-17}$	$2{,}30\cdot10^5$ $4{,}40\cdot10^{-17}$	$1{,}90\cdot10^5$ $5{,}30\cdot10^{-17}$	$1{,}90\cdot10^5$ $5{,}30\cdot10^{-17}$

In May 2006 the Dniester water were in normal state from the point of view of chemical self-purification by free radicals (see table). The parameter $\Sigma K_i[S_i]$ had values of the order 10^5 s^{-1}, while the stationary content of OH free radicals was varying in the limits $1.30 \cdot 10^{-17}$ M – $3.40 \cdot 10^{-17}$M. More intensively the processes of self-purification by radicals were taking place below the Dubasari barrage ($\Sigma k_i[S_i] = 3{,}0 \cdot 10^5$ s^{-1}), and least intensively at Mereseuca and Cosauti ($\Sigma k_i[S_i] = 7.6 \cdot 10^5$ s^{-1} and $8.10 \cdot 10^5$ s^{-1}).

In June 2006 the waters of the segment Naslavcea – Cosauti were characterized by high purity since the values of the capacity of inhibition constituting $3.20 \cdot 10^4 – 6.70 \cdot 10^4$ s^{-1}. The sector Bosernita – upper side of the Dubasari barrage was also considered favorable for the occurrence of intense self-purification processes. The values of the capacity of inhibition were in the limits of the order 10^5 s^{-1}.

In August 2006 the values of the capacity of inhibition constituted $2.0 \cdot 10^5$ s^{-1} ($1.50 \cdot 10^5 – 1.90 \cdot 10^5$ s^{-1}) in all the sampling sites, except at Bosernita where $\Sigma k_i[S_i] = 2.3 \cdot 10^5$ s^{-1}. This fact denotes that in August the values of the capacity of inhibition of Dniester waters indicated a normal occurrence of self-purification process with participation of free radicals.

The self-purification processes of Dniester waters occur with participation of OH free radicals and during the seasons with high solar activity this process occur in normal conditions and the observations prove that the capacity of inhibition of waters indicate a normal state of waters. The investigated segment of the river have shown the following correlation between redox agents (Table 4).

Table 4

The correlation equations and correlation coefficients of the redox parameters

Correlation parameters	***Correlation equations***	***Correlation coefficients***
Naslavcea		
$[H_2O_2] = f rH$	***$[H_2O_2] = 1.45 \cdot 10^{-6} \cdot rH - 3.94 \cdot 10^{-5}$***	***r = 0.7***
$[H_2O_2] = f(CBO)$	***$[H_2O_2] = 6{,}68 \cdot 10^{-7} \cdot CBO – 6.24 \cdot 10^{-7}$***	***r = 0.7***
$[H_2O_2] = f(\%O_2)$	$[H_2O_2] = 4.23 \cdot 10^{-8} \cdot (\%O_2) – 3.43 \cdot 10^{-6}$	r = 0.4
$rH = f[PO_4^{3-}]$	$rH = 1.20 \cdot [PO_4^{3-}] + 26.55$	r = 0.4
$rH = f(\%O_2)$	$rH = 0.01 \cdot (\%O_2) + 26.00$	r = 0.6
$[NO_2^-] = f[O_2]$	$[NO_2] = 0.002 \cdot [O_2] + 0.008$	r = 0.3
$CBO = f[O_2]$	$CBO = 0.259 \cdot [O_2] + 1.164$	r = 0.6
Mereseuca		
$CBO = f[O_2]$	***$CBO = 0{,}49 \cdot [O_2] – 2{,}345$***	***r = 0,7***
$[NO_2^-] = f[O_2]$	$[NO_2] = 0{,}003 \cdot [O_2] - 3{,}49 \cdot 10^{-6}$	r = 0,4
Bosernita		
$rH = f(\%O_2)$	$rH = 0{,}02 \cdot (\%O_2) + 26{,}09$	r = 0,5
$rH = f(pH)$	***$rH = 1{,}76 \cdot pH + 14{,}17$***	***r = 0,9***
$[H_2O_2] = f(\%O_2)$	***$[H_2O_2] = 1{,}73 \cdot 10^{-8} \cdot (\%O_2) – 1{,}54 \cdot 10^{-6}$***	***r = 0,8***
$[NO_2^-] = f[O_2]$	$[NO_2^-] = 0{,}002 \cdot [O_2] + 0{,}002$	r = 0,5
Cosauti		
$[H_2O_2] = f(CBO)$	$[H_2O_2] = 2{,}24 \cdot 10^{-7} \cdot CBO + 2{,}66 \cdot 10^{-7}$	r = 0,5
$[H_2O_2] = f(\%O_2)$	$[H_2O_2] = 9{,}13 \cdot 10^{-9} \cdot (\%O_2) – 1{,}39 \cdot 10^{-7}$	r = 0,4
$rH = f[NO_2^-]$	$rH = 9{,}99 \cdot [NO_2^-] + 27{,}75$	r = 0,6
$rH = f[O_2]$	$rH = 0{,}06 \cdot [O_2] + 27{,} 72$	r = 0,6
$CBO = f[O_2]$	$CBO = 0{,}16 \cdot [O_2] + 1{,}26$	r = 0,3
Dubasari, above the dam		
$CBO = f[O_2]$	***$CBO = 0{,}63 \cdot [O_2] – 2{,}303$***	***r = 0,7***
$[NO_2^-] = f[O_2]$	$[NO_2^-] = 0{,}003 \cdot [O_2] - 0{,}0008$	r = 0,3
Dubasari, below the dam		
$rH = f(pH)$	$rH = 2{,}16 \cdot pH + 9{,}13$	r = 0,5
$rH = f[O_2]$	$rH = 0{,}38 \cdot [O_2] + 22{,}75$	r = 0,4

Conclusions

The investigations carried out in the segment Naslavcea (below the barrage of the buffer reservoir) and Dubasari (below the barrage at) allowed the drawing of following conclusions.

The oxygen regime of Dniester was characterized by following peculiarities:

The content of dissolved oxygen in the waters of Naslavcea was always lower than in other sections of the river. The normal saturation of Dniester waters at this section line occurred only in spring, although in summer and in autumn the saturation of waters was permanently below the norms, constituting in average 70.5% in summer and 79.5% in autumn.

Lower at Naslavcea, most part of the year the concentrations of oxygen in water were close to normal saturation (95 – 110%), except in the cases when there was observed hypersaturation of waters of 158 -177% at Cosauti and Dubasari in 2005 and at the end of summer season of 2006 when there was observed a decrease of oxygen content at the Dubasari water reservoir.

According to the rH_2 indicator the Dniester waters were instable both in seasonal and spatial aspects. The ratio of oxidants and reducers of the waters can be characterized as neutral at Naslavcea, at Cosauti in summer and in spring, at Bosernita and Dubasari in autumn and in spring. At Mereseuca and in the deep waters of Dubasari water reservoir this indicator was shifted most often toward the reducing processes.

Mineral forms of nitrogen and phosphorous were constantly present in the waters of the river. The content of ammonium ions was increasing from Naslavcea toward the lower pool of the Dubasari barrage from 0.015 – 0.021 till 0.136 mg NH_4/l. The seasonal variation was manifested by the increase of NH_4 in autumn and its practical absence in spring.

The content of nitrites was varying in the investigated segment of the Dniester in average from 0.027 – 0.058 mg NO_2/l. Its presence was permanent in all the section lines of the river. The absence of nitrites was observed only early in spring (March 2006) above and below the Dubasari barrage of the water reservoir.

The average content of phosphates was varying in the section lines in the range 0.11 – 3.22 mg PO_4^{3-}/l. The maximal content of phosphates was observed in the summer of 2006 at Cosauti and Bosernita sites and constituted 3.22 and 1.37 mg PO_4^{3-}/l respectively. The increase in the content of phosphates occurred in spring in the segment of the river Naslavcea – Mereseuca, in summer - from Cosauti to Dubasari.

The amount of organic substances according to the BOD indicator constituted in average 3.1 – 3.3 mg O_2/l in the segment Naslavcea – Cosauti, and 3.6 -3.9 mg O_2/l at Dubasari water reservoir.

The Dniester waters are characterized by seasonal variation of the redox state. The general trend for the part of the year autumn – spring was toward the decrease of the concentration of hydrogen peroxide and the formation of an instable state or even of a quasy-reducing state of waters from the point of view of equilibrium of redox equivalents – of hydrogen peroxide and of reducers of peroxidazic type. The values of H_2O_2 concentration were predominantly by order of 10^{-7}M, a value that is insignificant for the occurrence of efficient chemical self-purification processes in water medium. The point characterized by continuous instable reducing state was the Bosernita site that is located in the proximity of the accumulation segment of the river above the Dubasari barrage. The last one was as well characterized repeatedly by instable state of the waters, since out of seven measurements of the redox state three have demonstrated an unfavorable sate according to the content of hydrogen peroxide.

During the summer season, in the Dniester waters the chemical self-purification processes occur very effectively, that is why the negative impact of pollutants is partially diminished.

The degradation of the quality of water of Dniester river is influenced both by the elevated content of pollutants in tributary waters and discharges of wastewaters from municipalities located along the river above the Dubasari barrage.

References:

[1] Goreaceva, N. In Water resources in The state of the environment in the Republic of Moldova: Water Resources, 1999. p. 28-45.

[2] Goreaceva, N.; Gladchi, V. In Intellectus: The ecological state of surface waters in the Republic of Moldova, 1999. p. 68-71.

[3] Goreaceva, N.; Duca, Gh. Гидрохимия малых рек Республики Молдова: CE USM, 2004. 288 p.

[4] Goreaceva, N. In Proceedings of the Symposium on Ecological Chemistry, Chişinău, 1- 4 october, 1995: Small rivers in the conditions of antropogenic stress. 1995, p. 15.

[5] Bespalov, I.; Goreaceva N. In The International Scientific and Applied Conference on Dniester problems: Днестровское водохранилище – один из факторов деградации экосистем ижнего Днестра */The Dniestrovsc water reserve as a factor of Lower Dniester Ecosystem degradation/*. 2000. p. 52.

[6] Rusev, I., Ruseva T., Ternova P., Ternovaia Iu. Внедрение экологических правил эксплуатации Днестровского гидроузла – важнейший инструмент устойчивого функционирования экосистемы дельты Днестра */The introduction of ecologicaly sound rules for exploitation of Dniestrovsk hydropower complex/* .In: Integrated management of natural resources in the transboundatry Dnister river basin. Chisinau. Eco-TIRAS. 2004.p. 61.

[7] Rusev, I.; Ruseva, T.; Ternova, P.; Ternovaia, Iu. In: Integrated management of natural resources in the transboundatry Dnister river basin: Внедрение экологических правил эксплуатации Днестровского гидроузла – важнейший инструмент устойчивого функционирования экосистемы дельты Днестра */The introduction of ecologicaly sound rules for exploitation of Dniestrovsk hydropower complex/*. 2004. p. 82.

[8] Duca, Gh.; Scurlatov, Iu.; Misiti, A.; Macoveanu, M.; Surpățeanu, M. Chimie ecologică Matrix Rom: Bucureşti, 1999. 305 p.

[9] Duca, Gh.; Scurlatov, Yu.; Sychev, A. Redox Catalysis and Ecological Chemistry. CE USM: Chişinău, 2002. p. 291-316.

[10] Biodiversity Conservation of the Dniester River Basin. Kishinev, 1999. p. 89.

[11] Gladchi, V.; Goreaceva, N.; Bunduci, E.; Borodaev, R. In ECWATEC –2004: The problems of the trans-boundary Dniester River. Moscow, 2004. p. 125.

[12] Duca, Gh. Goreaceva, N.; Romanchuk, L. In Water resources: Исследование самоочищающей способности природной воды в модельных условиях /*The Assessment of self-purification capacity of natural waters on model systems/,*1996, t 23, Nr 6, pp 668-671.

[13] Semeniak, L.; Scurlatov, Yu.; Shtamm, E. Сезонные изменения направленности внутриводоемных окислительно-восстановительных процессов и проблемы воспроизводства осетровых в Волго-Каспийском регионе /*The seasonal changes of the direction of aquatic oxidation and reduction processes and the problems of regeneration of sturgeon fisheries in Volga and Kaspik Region/,* 1996. p. 28-35.

[14] Shtamm, E.; Purmal, A.; Scurlatov, Y. In The realizations in Chemistry: The role of hydrogen peroxide in the aquatic environment, Russia, 1991.

[15] Romanciuc, L.; Goreaceva, N.; Duca, Gh. In Water Pollution-95, III-rd Int. Conf., 25-28 Apr., Porto-Carras: Modelysing of self-purification processes of aquatic medium, 1995, pp 98.

[16] Duca, Gh.; Romanciuc, L.; Goreacev, N.; Borodaev, R. In Metal Compounds in Environment and Life, VII-th Int., Hans Wolfgang Nurnberg Memorial Symp., 4-7 June 1997, Modena (Italy): Model of self-purification processing in natural water, 1997. pp 51.

[17] Goreaceva, N; Gladchi, V. Методика определения кинетических показателей качества поверхностных (пресных) вод /A method of determination of kinetic indicators of the quality of fresh waters/; Guidance document. Hydrometeoizdat publisher: Moscow, 1990.

[18] Duca, Gh.; Bunduchi, E. In Abstracts of The Second Int. Conf. on Ecological Chemistry, 11-12 Oct., 2002: Radical self-purification of Prut river waters in the period of summer 2002 mean water, Chişinău, 2002. pp 40-41.

[19] Cutter, G. Ph.D. Dissertation, Old Dominion University. 1991.

[20] Rue, E.; Smith, G.; Cutter, G.; Bruland, K. The response of trace element redox couples to subox conditions in the water column; Deep-See Res., 1997, Vol 44, pp113-134.

[21] Bielski, H.; Cabelli, D.; Arud, R.L. Journal of Physical Chemistry.1985.

[22] Petasne, R.; Zika, R. Nature, 1987, Vol 325.

[23] Borodaev, R. In The collection of Scien. Papers of MSU: Редокс условия нижнего Днестра и состояние растворенных форм железа и меди /*The redox conditions of Lover Dniester and of the state of dissolved forms of iron and copper/*, 2002. p. 165-168.

[24] Duca, Gh. In Free Radicals in Biology and Environment: Free radicals in natural water; Dordrecht, 1997; pp 475-489.

[25] Gladchi, V. Starea redox a apelor naturale şi influenţa ei asupra proceselor naturale /*The redox state of natural waters and its influence on natural processes*/. J. Intellectus, 2000. p. 21-26.

[26] Sichev, A.; Duca, Gh. Aspecte fundamentale şi aplicate ale catalizei omogene cu metalocompuşi: Sisteme oxidice şi peroxidice. CE USM: Chisinau, 2002; p. 42.

[27] Sichev, A. *Aspecte fundamentale şi aplicate ale catalizei omogene cu metalocompuşi: Sisteme oxidice şi peroxidice.* CE USM: Chişinău, 2002, p. 332.

[28] Gladchi, V. In The Scientific Proceedings of Moldova State University: Chemical and Biological Sciences Series Procese de transformare chimică a poluanţilor şi rolul substanţelor tiolice în mediul acvatic /*Processes of pollutants chemical transformation and the role of thiolic substances /*. Chişinău, 2000.

[29] Gladchi, V. In The Proceedings of the didactic and scientific staff conference "Balance of scientific activity of the Moldova State University for 1998/1999 years: Transformările chimice ale unor substanţe tiolice în mediul acvatic /*Chemical transformation of thiolic substances in aquatic medium*/. Chişinău, 2000.

[30] Duca, Gh.; Gladchi, V.; Goreacev, N. Chimia apelor naturale; CEP USM: Chişinău, 2007. 107 p.

[31] [30] Klokov, D.; Jacob, P. Chemistry of Multiphases Atmospheric Systems. Springer: Berlin – Verlag, 1986. p. 125.

[32] Skurlatov, Yu.; Shtamm, E. In "Self-Purification Processes in Natural Waters. Proceedings of the International Symposium on Ecological Chemistry: Aquatic cycling of hydrogen peroxide as a principal way of natural waters self-purification, Chisinau, Moldova. 1995. p. 135.

[33] Duca, Gh.; Zanoagă, C.; Duca, M.; Gladchi V. Procese redox în mediul ambiant, CEP USM: Chişinău, 2001. 386 p.