WATER QUALITY MONITORING AND MANAGEMENT IN MOLDOVA

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Abstract. The water resources of the Republic of Moldova are quite limited and can assure only 54% of the necessities of national economy. For the rational usage of these water resources the Academy of Sciences of Moldova initiated the development of the National Program on Water Management. The Program development was based on the results of the study of problems faced by all sectors of the national economy in regards to water supply and usage. The study also focused on the monitoring of the main water sources in order to assess their current state. This paper reflects the results of monitoring of river Dniester considered while developing the National Program on Water Management as well as the Program main components.

Keywords: water quality, monitoring, self-purification, redox-state, barrage influence, management.

1. Introduction

The main sources of surface water in the Republic of Moldova are constituted of Dniester and Prut rivers, a small part of Danube river and internal water network consisting of small rivers, lakes and artificial water bodies.

The Dniester is a trans-boundary river crossing the countries of Moldova and Ukraine, discharging into the Black Sea. From its total length of 1,352 km 636 km flow through Moldova and its basin occupies 57% of the area of the Republic of Moldova. This river is the largest one in Moldova and is the main source of water supply for about two million people. The run-off water as well as the municipal effluents, industrial discharges, and economical activity contribute to the degradation of the quality of this water source.

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In 1981, a barrage was constructed in the middle part of the river by Ukraine, creating the Dniestrovsk Hydroelectric Power Station (HPS). The newly formed storage pond is 194 km long; the capacity of the reservoir is 3.0 km^3. The main purpose of the barrage construction is power supply and flood control. In 1985, another barrage was constructed at the border between Moldova and Ukraine downstream of the Dniestrovsk HPS in order to create a 20 km buffer storage. The main purpose of the second barrage construction was to regulate the water discharge from the first barrage and also to generate electric power.

Since the beginning of full-capacity operation of the Dniestrovsk HPS, 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°C and reached an average of 16–18°C during summer time; while the average air temperature is usually 30–32°C. This led to the severe changes in the aquatic ecosystem: the diversity of hydrobilogical species and fish stocks decreased considerably and an increased rate of mass fish kills were observed periodically. Ichthyologists have pointed out the negative effects of the dam on the ichthyo-fauna. Some fish species have stopped spawning, thus, leading to a reduction in fish stocks by 18–30 times. Certain studies revealed that 80% of the sturgeon sampled showed signs of spawn reabsorption [1, 2].

Besides of the unfavorable temperature regime, dam construction had an impact on the water redox state [1, 3]. The presence of reducing substances in the amounts exceeding quite often the contents of oxidizers provokes a disbalance in the ecological state of water system [4, 5]. It is known that the reductive, quasi-reductive and super oxidative state of natural waters creates destructive conditions for the development of hydro-bionets, including fish. Quasi-reductive conditions are considered toxic for certain bacteria such as infusoria as well as fish larvae.

The redox state of surface natural waters is a parameter that characterizes the ecological state of the water and its capacity to self-purification [6]. Biologically favorable fresh water is determined by the presence of hydrogen peroxide within the limits of 10^{-6} mol/l. In sea water, the amount of hydrogen peroxide is substantially lower then in fresh waters. In the biogeochemical cycle of oxygen in fresh water ecosystems the stationary concentrations of oxidative equivalents such as OH radicals constitute $3–5\cdot10^{-16}$ mol/l. The range of variation of their concentration should not vary by more than 10 times.

In surface natural waters, redox processes occur in the presence of dissolved oxygen and lead to the formation of intermediate active forms such as hydrogen peroxide, hydroxide and super-oxide radicals [1, 7, 8]. Chemical and photochemical processes of oxidation occur with the involvement of transitional metal ions and depend on the rates of free radical formation and destruction, and their steady-state concentrations. Among transitional metal the copper, iron and manganese ions take the most essential part for redox transformation of dissolved oxygen and hydrogen peroxide in aquatic environment [9, 10].

The purpose of current investigation was to asses the impact of the Dniestrovsk HPS on the formation of redox conditions in the lower section of water reservoir in dependence of seasonal and spatial aspects.

2. Material and methods

The water monitoring was performed by selecting six permanent sites spread out on a distance of 310 km along the river bank between Naslavcea and Dubasari dams.

The water samples were collected from the upper horizons (0.5–0.6 m). The measured indicators hydrochemical 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 water served as additional indicators of potential impact of the water reservoir on the water flow from the Dniestrovsk barrage. The following parameters were measured: temperature, 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.

3. Results and discussions

The investigations carried out during 2005–2008 in the segment Naslavcea (below the barrage of the buffer reservoir) and Dubasari (below the barrage) led to figure out the following results.

It was identified that the water discharged in the buffer reservoir of the hydro-technical station at Dniestrovsk were characterized as hydrocarbonate, hydrocarbonate-sulphate types of calcium and magnesium group, in which the ratio of anions and cations most often could be presented as follows: $Cl^{-} > Na^{+} + Mg^{+}$. The mineralization determined throughout all the investigation period has varied between 257–417 mg/l, hardness from 3.5 to 4.8 mg·equiv./l, and the ion content was continuously unstable. The water discharged from the buffer reservoir in most cases determined the mineralization, hardness and instability of ion content of the investigated segment of the Dniester river. A strong correlation between the mineralization in samples collected at Naslavcea and all sites lower the barrage was observed.

The Dniester oxygen regime was characterized by the following peculiarities. The content of dissolved oxygen in the water samples at Naslavcea was always lower than in samples from other sections of the river. The normal saturation by oxygen of the Dniester water occurred only in spring. During summer and autumn the saturation of water by oxygen was permanently decreased, constituting an average of 70.5% in summer and 79.5% in autumn.

Lower Naslavcea, most part of the year the concentration of oxygen dissolved in water was close to normal saturation (95–110%), except in the cases of hyper-saturation of water (158–177%) observed at Cosauti and Dubasari. In the Dubasari water reservoir a decrease of oxygen content usually appears at the end of summer season.

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

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

The average content of nitrates throughout the year constituted 5.5–7.42 mg NO_3/l. The seasonal dynamics of the nitrates was opposite to the dynamics of nitrogen in the form of ammonium. The concentration of nitrates from Mereseuca to the lower part of Dubasari reservoir was increased in spring and decreased in autumn. At Naslavcea the maximum content of nitrates was observed in summer season. The content of nitrites was varying from 0.027–0.058 mg NO_2/l in the investigated segment of the Dniester river and was permanent in all the point of sample collection of the water. The absence of nitrites was observed only early in spring above and below the Dubasari barrage. The seasonal variation of nitrites content was manifested by the concentration increase in summer and decrease in spring. The continuous presence of nitrites in the Dniester waters and the low content or total absence of ammonium nitrogen allow concluding that the oxidation state of the waters is unfavorable, that causes a decrease of the rate of oxidation from NO_2^- to NO_3^-.

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, and 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 seasonal variation was manifested by the increase of the indicator in spring at Naslavcea and Dubasari water reservoir (Bosernita–lower section line), while at Mereseuca and Cosauti this increase occurred in summer.

The Dniester waters are characterized by seasonal variation of the redox state.

The general trend during autumn–spring was observed towards a decrease of the hydrogen peroxide concentration and the formation of an instable state close to a quasy-reducing state of waters.

During summer time the content of hydrogen peroxide was rising, so that in June 2006 the value of H_2O_2 was of the order 10^{-6} M. The increase, however, was registered only for the Naslavcea–Cosauti sector, while for the Bosernita–Dubasari (below the dam) the hydrogen peroxide was missing. The increase in June was followed by a decrease of one order in August 2006.

The diminishing of the hydrogen peroxide content in September and November, as well as from June to August, its absence in March can be explained on the one hand by the decrease of photosynthetic activity, when the dominant role in the formation of H_2O_2 in natural waters is determined by the solar radiation (influenced by solar light the superoxid O_2^{-}. anion radical is formed, which is precursor of H_2O_2). On the other hand, the water temperature is decreasing (in the case of autumn), therefore the influence of another important physical–chemical parameters that promotes the redox catalytic processes are diminished.

The values of H_2O_2 concentration were predominantly by order of 10^{-7}M which is insignificant for the occurrence of efficient chemical self-purification processes in water medium [6].

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 characterized repeatedly as well by instable state of the waters, since out of seven measurements of the redox state three have demonstrated an unfavorable state according to the content of hydrogen peroxide.

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

The degradation of the water quality of the 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.

4. Water management in Moldova

The results of the investigation presented above proves again that the anthropogenic impact on the water resources are manifested through radical changes of the water quality and biodiversity in aquatic ecosystems so that the management of quality of water resources and their sustainable use becomes one of the most stringent contemporary challenges. Thus, the National Program on Water Management initiated by the Academy of Sciences of Moldova has as major goal the development of the monitoring system of aquatic resources as well as all the other components related to water supply and treatment.

The realization of the program requires an active involvement of teams of specialists of high qualification and vast technical and scientific experience in the field from academia, ministries, educational institutions, industry, non-governmental organizations as well as other stakeholders. The program timeframe is set between the years 2009–2012 and has the following objectives:

1. Improvement of the legislative, normative and cadastre bases related to application of water resources, implementation of European standards of the indices of natural water quality
2. Development of the "Center of Scientific Control of Water Quality"
3. Development of a GIS database for water quality, complex monitoring of the state of the quality of water resources (based on investigation of the surface and ground water quality, identification of the sources of pollution, purification systems and evaluations of the possibilities to reuse of treated waters) in the context of provisions of the European Directive
4. Realization of fundamental investigations in the field of molecular structure and physical chemical properties of water
5. Elaboration of recommendations for conservation of river and lake ecosystems, for consolidation of concepts of integrated management and utilization of aquatic resources
6. Elaboration and implementation of new technologies of water treatment, supply and reuse, as well as rational utilization of water in the industrial, agricultural and fisheries sectors of the national economy, application of information software in the field of automation and monitoring of technological processes
7. Elaboration and construction of pilot-scale equipment and auxiliary devices for purification and reuse of wastewater in irrigation systems
8. Training of highly qualified specialists in hydrochemistry, hydrogeology, hydrology, environmental hygiene, environmental legislation, management of aquatic resources and other
9. Rising consciousness of population and involvement of the community in the decision-making processes related to implementing of the integrated management of water resources and, consequently, the improvement of the living conditions of the population

Originality of the Program consists of the development of complex investigations (hydrochemistry, hydrogeology, hydrology, ecotoxicology, etc.) that will allow the continuous estimation of the state of water resources and will contribute to the development of a geoinformation system satisfying modern requirements. On its basis, the implementation of the integrated management of water resources will be assured.

The realization of the Program will facilitate the development of fundamental and applied investigations and will contribute to improve the scientific and technological infrastructure of R&D institutions, including the development of a modern scientific Center for Water Quality Control.

The fields of application of the results of investigation include: ecology, environmental protection, drinking water supply, treatment, reuse of wastewaters, fish industry, irrigation, and other branches of economy. The Program will contribute to the development of bilateral and multilateral collaboration with other countries.

The implementation of the Program will facilitate the enforcement of the scientific recommendations that have the purpose to reorient the ecological state of the hydrographic basins of the rivers Dnister, Prut, and Danube and the Black Sea, elaboration and implementation of new standards and norms harmonized with ISO standards, modern technologies of water supply and treatment, and reuse of wastewaters. There will be proposed science-based criteria of construction and exploitation of hydro-technical systems, improvement of techniques of irrigation and optimization of water resources administration.

A system of continuous qualification of specialists from diverse fields will be developed, that will include study and utilization of surface and ground water resources. Involvement of undergraduate and graduate students, young researchers in the realization of the program as well as the implementation of the scientific results in educational process will contribute to train specialists in the field of monitoring and management of aquatic resources.

The Program will contribute to the sustainable development of the society and life quality, the amelioration of the analytical and material infrastructure of institutions and the establishment of collaborations with partners from Ukraine and Romania due to the transboundary character of the Dnister, Danube and Prut rivers and their aquifers.

The Program will assure the improvement of the technologies and sustainable supply of water to the population and the economic sectors. It will also improve the technology of irrigation, a fact that has important social, economic and environmental value as more than 60% of fresh water is used in agriculture.

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