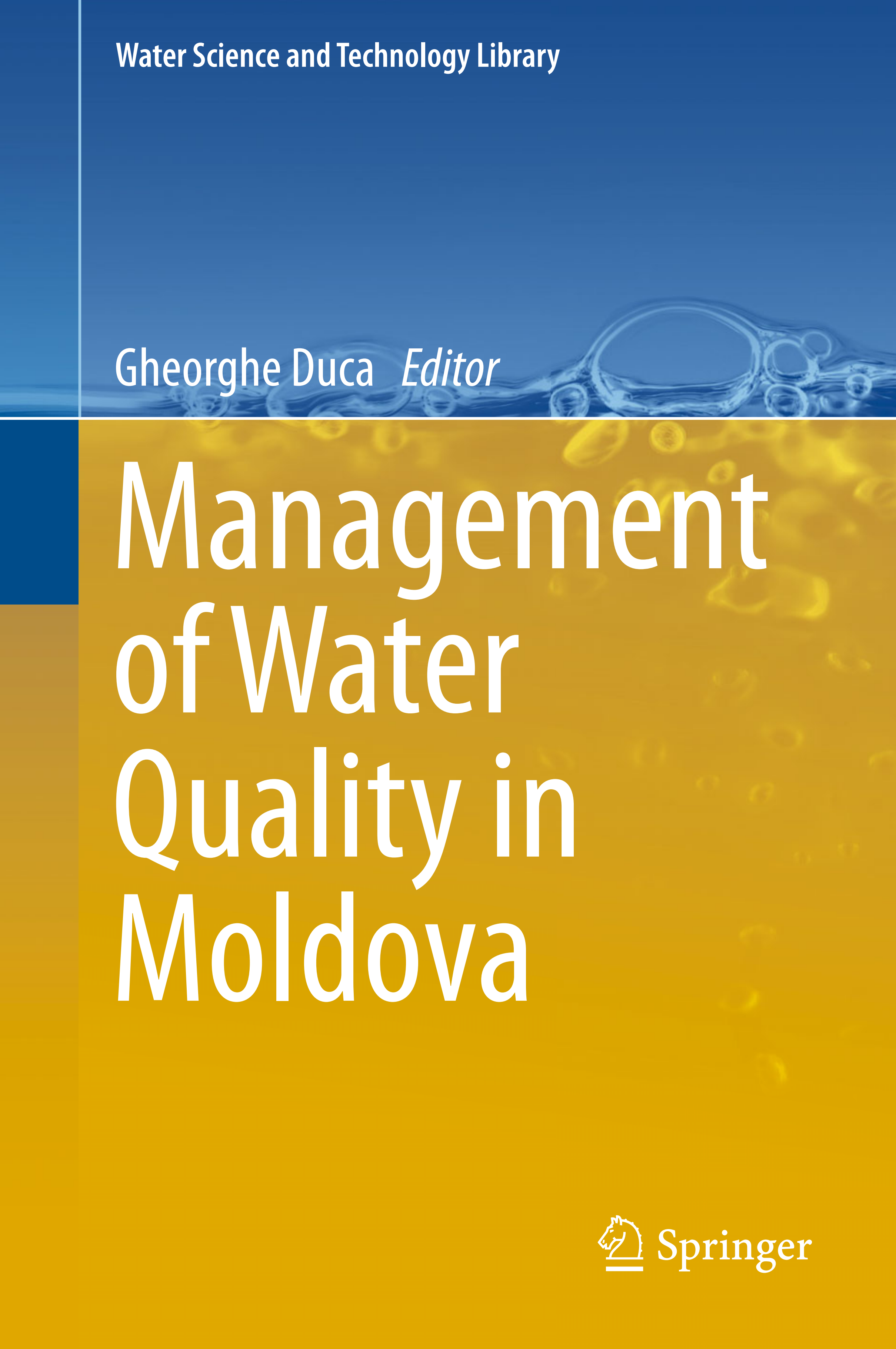

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Editor

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Preface

One of the most challenging issues of contemporary society is water. Particularly, the water management specifics prevail, when considering sustainable development of any country, in a market economy.

Considering this aspect, it is necessary to acknowledge that in a society which is in the process of transition to more complete forms of governing, knowledge, cultural values, natural resources, such as water, play a defining role. That being the case of the Republic of Moldova, in its course toward a knowledgeable society, European integration, regional, and sustainable development.

One of the paramount premises of a knowledge-based society is the study of nature, an infinite source of knowledge. Thus, human pursuit of knowledge and its necessity represents one of the cornerstones of human nature. It is due to this pursuit that researchers and scholars strive to learn about the environment, natural resources, create energy generation technologies, invent new materials and means of their processing, and study the solar system and the depths of the world's oceans. The paradigm of a knowledge society is applicable today and is the defining element for any state. Research and innovation must take upon the role of creation and generation of a new knowledge and challenge society toward real and meaningful change.

The aforementioned is viable for water and water management issues as well. In this context, research and innovation in the field of water management must address certain fundamental aspects. These aspects include: access to water, water quality, water treatment, transboundary effect of water, etc.

While trying to address these particular aspects of water management in Moldova, it was necessary to consolidate a critical mass of researchers, practitioners, experts, businessmen, policy makers, and civil society representatives, in order to perform a comprehensive analysis of the issue at hand. Striving to improve effectiveness of work as well as to ensure a complex and comprehensive answer to the proposed task, a platform was proposed, aimed at bringing together people from different areas relating to water. This platform was created in 2009, taking the form of a national research program, entitled "Research and Management of Water Quality." The main goal of the research program was to create and improve the legal, scientific and methodological, technological, and cadastral bases for the capitalization and sustainable development of water, and implementation of modern technologies in water supply, treatment, and reuse.

Other priorities include: expansion of access to water sources; improvement of environmental protection, especially water protection against pollution and depletion, efficient water use; establishing effective monitoring systems for disaster prevention. The national research program consists of 11 projects grouped into five clusters: research of water structure and quality; surface water; groundwater; water treatment; and irrigation technologies.

Moldova is a small landlocked country in the Southeastern part of Europe between Ukraine and Romania. Its population is estimated at 3.5 million people. Moldova's water resources are composed of 3,621 rivers and streams with a general length of 16,000 km; around 4,117 natural lakes and artificial reservoirs; around 7,000 artesian wells and around 166,000 wells. The main water sources are the largest rivers Dniester (83.6 %) and Prut (1 %) and 15.2 % groundwater.

Water pollution provoked by industrialization remains one of the main environmental problems of our time. The quality of surface and groundwater in Moldova, in most cases, does not meet European and international standards. The main sources of surface water pollution have an anthropogenic origin.

Natural water bodies are extensively polluted by industrial, specifically, agricultural wastes. Existing treatment facilities are mainly in poor condition and do not meet the modern standards. Cumulatively, due to inefficient use of wastewater treatment plants, the numbers of pollutants are higher than prescribed by national regulations. This leads to an increase in morbidity and mortality.

The intensive land use as well as improper utilization of water resources during the last decades, along with the large-scale livestock activity, provoked a threatening situation in regard to freshwater in Moldova.

In solving the water-related issues, one must ask himself to what extent he is committed to the cause and what the outcome of such endeavor might be. Moreover, on a country scale, when considering involvement in such activities, it is of utmost importance to analyze and envision societal demand as well as the regional dimension. The latter, can determine the outcome of future efforts.

It is common knowledge that the whole spectrum of water issues can only be considered and resolved based on the solid scientific approach, including the fundamental and applied aspects. The research on water makes it possible to reveal the water structure, to ensure innovation development in water treatment, intensive technology of water use and reuse, and to draft coherent water policies. The outcomes of these activities are focused on societal needs, which supply information for government, empower people to participate in decision-making, giving them access to new and improved rights and liberties, while ensuring their basic need for water of improved quality.

Chisinau, Moldova Gheorghe Duca

Contents

Part I Water Structure and Quality

Part II Surface Water

Part III Groundwater

Part IV Water Treatment

Part I
Water Structure and Quality

Chapter 1
Integrated Water Management in the Republic of Moldova

Gheorghe Duca, Oleg Bogdevich and Diana Porubin

Abstract Water management aspects in Republic of Moldova are discussed. The aim of the article is to review the institutional capacity for water monitoring and management of water resources in Moldova. The characteristics of water monitoring network is presented and some aspects for the improvement of existing monitoring capacity are examined. The complex character of actual water management in the Republic of Moldova is determined and the role of scientific support for the problem solving in this field is proposed.

Keywords Water management and monitoring · Water resources · Institutional analysis · Quality indicators

1.1 Introduction

The groundwater management is very important for the countries with arid and semiarid climate. The climate change will impact on surface and groundwater balance. Periods with extremely high precipitation or strong drought will be more frequent and long. In this case, the respective Integrated Water Resource Management plays an important part in the economy development of every country. Water quality and quantity in any country is a critical factor affecting human health and welfare. Access to the water sources in Moldova is one of the important

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problems because our country ranks one of the last places in the Europe on number of sources of water per capita. Quality of surface and underground waters of the country in most cases mismatches state, European and international standards (UNESCO, the International Health Organization, etc.). The water resources are determined by the number of factors, including amount of water received from precipitation, inflow and outflow in rivers ant the amount lost by evaporation and transpiration. Republic of Moldova is located in South-East of Europe, in a region with insufficient precipitation, limited water resources, with tempered climate and relatively limited humidity [1]. The precipitation regime is very instable last time. Thus 2007 year is characterized by strong drought with average precipitation volume of 62–170 mm (35–85 % of yearly volume). Three years from every ten are drought-afflicted here. At the same time tremendous downfalls are took place with the precipitation more then 200 mm per day.

The management of a river basin requires that all movement of water, both natural and artificial, be monitored. The natural components include precipitation, river flow and groundwater levels, and the artificial components include abstractions and discharges. At many enterprises and in rural area there are no waste-water treatment facilities or they are in an unsatisfactory condition. Most wastewater discharges into surface waters in Moldova are municipal; enterprises usually discharge their wastewater into mixed municipal sewer systems.

In the Republic of Moldova there is no adequate legislative base for water management, maintenance of drinking water, implementation of modern technologies on water treatment. Moldova has taken a decision to align its legislation more closely with that of the European Union. Within this context Moldova has developed a Water Legislation for the implementation of the Directive 2000/60/EC establishing a framework for Community action in the field of water policy (the Water Framework Directive of EU). The EU Water Framework Directive (WFD) aims at a “good” status for surface waters. Good status implies good chemical as well as biological quality. For groundwater good status implies good chemical quality and sufficient quantity. To achieve the environmental objectives, the Directive makes it clear that an integrated approach to sustainable water management is necessary.

It also has taken on increased obligations in terms of River Basin Management (RBM). The main aim of the developed water legislation is to allow a coherent and harmonious implementation of this Directive. The focus of this article is on methodological questions related to a common understanding of the technical and scientific implications of the Water Framework Directive. These are reflected in the draft Water Law, which is currently being processed in the Moldovan Parliament. The current Water Code does not provide for RBM, while the draft Water law, once adopted, will create the legal framework for RBM implementation. Negotiations are ongoing between Moldova and the EU regarding an association agreement.

The quality and quantity of natural water resources is sufficient in the general for the sustainable development of Moldova. There are transboundary rivers Prut and Nistru, small rivers and lakes, shallow and deep groundwaters. However it is distributed irregular by country. South part of country is in semiarid zone with the deficiency of good water for different purposes: drinking, irrigation, industrial, etc. It should be noted that more than 30 % of groundwater sources, providing the city with drinking water, do not meet the quality requirements for chemical indicators that more than 70–80 % of wells, are not suitable, and often dangerous to use for drinking purposes. The shallow ground waters on a greater part of territory of the country are polluted by anthropogenous sources, in particular nitrates.

The Global Water Partnership defines Integrated River Basin Management (IRBM) as a "process of coordinating conservation, management and development of water, land and related resources across sectors within a given river basin, in order to maximize the economic and social benefits derived from water resources in an equitable manner while preserving and, where necessary, restoring freshwater ecosystems". The main objective of IRBM is to establish a balance between the existing natural functions of the river system and the developed aspects of the system. The management actions should fulfill the expectations of the society for industrial use, recreation, nature management, and agricultural purposes.

Integrated Water Resources Management (IWRM) is conceptually similar to, but not completely synonymous with IRBM. In the case of River Basin Management, the focus is on the hydrological basin: in the case of Water Resources Management the focus is on the water resources. However, since IWRM recognizes the importance of management at the level of river basins, the outcomes would be the same. The aim of the proposed article is an analysis of the state with IWRM in Republic of Moldova and proposal development for the scientific support of legislative and technical improvement of water management issues.

1.2 Institutional Analysis

The different key water management institutions in Moldova include a range of public authorities such as: Ministry of Environment and its subordinated institutions (i.e. *Apele Moldovei* Agency, Agency for Geology and Mineral Resources, State Ecological Inspectorate, State Hydrometeorological Service, Fishery Service, Hydrogeological Expedition "EHGeoM", Institute of Ecology and Geography), Ministry of Health and Agency of Land Relations and Cadastre. Other public institutions with water-related functions include the Ministry of Agriculture and Food Industry, the Ministry of Regional Development and Constructions, and the Ministry of Internal Affairs, among others. And, the local public administration is vested with several water resources management-related responsibilities such as: management of surface water and water supply and sanitation at local level. The new Water Law (adopted in 2011) will create the legal framework for the river basin management implementation in Moldova harmonized with EU water Acts. It will have a series of implications on the future institutional framework and on water resources management practices.

The cooperation between Moldavian institutions is weak and there are no formal agreements for water-related data exchange. Three institutions are jointly responsible for elaboration and editing of the State Water Cadastre on an annual basis: Apele Moldovei Agency (Water Basin Management Department); State Hydrometeorological Service; and State Agency for Geology and Mineral Resources.

New divisions have been set up within the Ministry of Environment (ME) and Apele Moldovei Agency with the specific aim of enhancing the country's management of river basins. However, these new divisions, as they are presently constituted, are not likely to be able to fulfill all the tasks required in the development of a comprehensive river basin management plan. It is likely that additional specialists will need to be recruited with qualifications in specific disciplines: IT and database specialist, GIS specialist, hydrology and hydrogeology modeler, risk assessors, etc.

The aspect of water management was presented in different technical reports and publications by international projects in Moldova [2–11]. The technical and financial support to State Hydrometeorological Service was made for the installation of some hydrometric stations with remote data transmission on the Prut, Nistru and Raut rivers for the monitoring of surface water and protection against flood. But actually the remote data transfer is not working by technical problems.

The published reports indicated [2] that there are a number of gaps in the present institutional framework, which refer, in particular, to the following [2]:

- Identification and delimitation of water bodies;
- Establishing objectives for water resources (river basin) management;
- River basin planning;
- Flood risk management;
- Interaction with stakeholders.

There are a few proposals for the delimitation of the two river basin districts—the Danube/Prut and the Nistru—but pending the adoption of the draft Water Law, an official decision on the subject may not be taken, since none of the existing institutions carries this function under the present legal framework. The same applies to the identification and delimitation of water bodies and to the setting of objectives. The flood risk management is presented actually only by the provision of warnings and response measures. Prevention measures, including the assessment of flood risks, the identification of flood-risk areas, and flood management planning, are not envisioned in the near future.

The process of authorization obtaining for water and groundwater users is cumbersome because it is in the hands of several institutions, including institutions of the ME and others, such as the Ministry of Health. Water users should to visit several institutions in order to obtain their endorsement of an application. The responsibility for obtaining the approvals lies on the applicant, who first has to put together the documents needed in support of the application, and then to visit each institution before filing the application with the Inspectorate, together with the approvals and/or recommendations of the institutions. This procedure should to be simplified in the mode of the "single window".

Often both resource management and development functions are in the hands of one and the same institution, there is no way to assess performance, because the institution is at the same time a poacher and a gamekeeper (i.e., the controlled and the controller, responsible for supervising its own activities). Thus, there is no transparency and, in principle, it is difficult to ascertain whether water resources are developed and used in a sustainable manner, and whether the water services rendered to the end users are satisfactory.

To manage a river basin in an integrated way requires a wide variety of specialized skills. Many of these skills have been practiced in Moldova for years: monitoring of river flows, aquifer yields, taking samples of water for laboratory analysis, GIS elaboration and others. With the introduction of new equipment or more stringent water quality requirements some of these skills will need to upgraded; this is perfectly normal and many professional associations in Europe place emphasis on continuing professional development. Other skills, related to ecology or hydro-morphology, for example, will have to be developed. Developing these skills is likely to involve a cooperative approach between the Governmental authorities, universities and other academic institutions possibly involving training outside of Moldova.

1.3 Water Monitoring and Data Management

The water management on the river basin level requires than all waters should to be monitored: surface and ground water, natural, technological, waste water, etc. The summary of water abstraction from both surface water and groundwater is provided in Table 1.1. Table 1.2 summaries the discharge to rivers. While it does indeed suggest that there has been a decline in the percentage of waste treated, it is possible that the real situation might be more severe than the table suggests.

Table 1.1 Water consumption in Moldova during 2001–2008 (million m^3)*

Year	2001	2002	2003	2004	2005	2006	2007	2008
Number of water consumers, units	2535	2533	2549	2554	2547	2555	2507	2519
Water abstracted—total	874	866	864	852	852	854	885	861
• of which, water abstracted from groundwater	138	132	135	136	136	136	129	127
Water consumption (use)—total	797	792	795	786	785	787	809	794
• for production needs	587	587	586	585	583	583	581	581
○ of which, drinking water	19	20	20	20	18	17	17	17
• water supply for agriculture	36	36	35	36	35	36	36	37
• water supply for households needs and for drinking	130	120	116	115	120	120	125	124
Losses during transportation	71	68	64	62	61	61	69	64
Quantity of water in circulation and re-used	367	368	338	360	350	358	365	359

**Source*: Statistical Yearbook of the Republic of Moldova (2009)

Table 1.2 Summary of wastewater discharges in Moldova during 2001–2008 (million m^3)*

Year	2001	2002	2003	2004	2005	2006	2007	2008
Total, of which:	708	696	685	688	690	695	687	686
Conventionally pure waters (without purification)	557	560	558	561	556	562	551	550
Polluted waters	13	19	48	42	9	7	10	14
Without purification	0.3	0.5	0.8	0.5	0.6	0.5	0.7	0.8
Insufficiently purified	12.6	18.9	47.5	41.4	8.3	6.7	9.2	13.3
Conventionally purified waters	138	116	79	85	124	119	119	115
Conventionally purified sewage waters, in % of the total volume of water liable for purification	91 %	86 %	62 %	67 %	93 %	89 %	88 %	85 %

**Source*: Statistical Yearbook of the Republic of Moldova, 2009

Most wastewater discharges into surface waters in Moldova are municipal. Enterprises usually discharge their wastewater into mixed municipal sewer systems. Other discharges of wastewater directly into surface waters mainly concern wineries and food industry. In 2010, 69 290 000 m^3 of municipal wastewater was treated, out of which 6 % (4 151 000 m^3) was treated insufficiently. However, the overall statistics are dominated by the wastewater treatment of the city of Chisinau, which accounts for 81 % of the total municipal wastewater volume. When excluding “Apa-Canal Chisinau”, then 30 % of the remaining volume of 13 379 000 m^3 is treated insufficiently. Actually, in 20 of the 33 settlements mentioned in Table 1.3, all (100 %) of the wastewater is insufficiently treated; in 7 settlements there is no wastewater treatment at all.

In 2008, the regulation on conditions for urban wastewater discharge into natural receiving waters was adopted. This regulation has been largely based on the EU Directive 91/271/EEC concerning urban wastewater treatment. The regulation prescribes emission limit values for biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), and total suspended solids. In line with the EU Directive 91/271/EEC, also emission limit values for total phosphorus and total nitrogen are included for discharges from urban wastewater treatment plants into sensitive areas; however, the regulation does not provide with criteria for sensitive areas. The regulation on conditions for urban wastewater discharge into natural receiving waters has been adopted more than 2 years ago, sensitive areas have been not yet designated.

According to the regulation on conditions for urban wastewater discharge into natural receiving waters requirements for the wastewater quality apply only to municipal wastewater discharges into receiving surface waters that are not used for drinking and recreation purposes. All other operators shall calculate emission limit values for a long range of parameters, based on the maximum allowable concentrations (MAC) for fishery that were established in the Soviet Union [2].

The Regulation on conditions for urban wastewater discharge into natural receiving waters has prescribed the requirements for the monitoring of discharges from treatment plants to be conducted by the operator, including self-monitoring.

Table 1.3 Overview of municipal wastewater discharges per river district in Moldova in 2010 [2]

Nr	Wastewater source (town)	Population in 2010 (ths)	Biologically treated (thousand m^3)			Discharged into			
			Total	Conventionally treated	Including insuficient treated	Watercourse 2	Watercourse 1	Watercourse 0	River bazin district
1	Basarabeasca	12.5	254.5	0.0	254.5			Cogilnic	Danube - Prut - Black Sea
2	Briceni	9.8	74.4	0.0	74.4		Lopatnic	Prut	
3	Cantemir	6.0	55.5	0.0	55.5		Tigheci	Prut	
4	Ciadir Lunga	22.7	116.6	0.0	116.6			Ialpug	
5	Cimislia	16.1	0.0	0.0	0.0			Cogilnic	
6	Comrat	23.3	479.3	0.0	479.3			Ialpug	
7	Edinet	20.2	341.9	205.5	136.4		Ciuhur	Prut	
8	Falesti	17.6	130.1	0.0	130.1		Isnovet	Prut	
9	Hincesti	16.8	188.2	188.2	0.0			Cogilnic	
10	leova	10.9	88.3	0.0	88.3			Prut	
11	Nisporeni	14.7	88.6	88.6	0.0		Nirnova	Prut	
12	Stefan Voda	8.7	83.9	0.0	83.9			Sarata	
13	Taraclia	15.0	78.2	0.0	78.2		Lunga	Ialpug	
14	Ungheni	38.0	863.9	0.0	863.9			Prut	
15	Vulcanesti	16.9	39.2	39.2	0.0			Cahul	
16	Cahul	40.7	715.8	715.8	0.0			Prut	
17	Ocnita	9.3	0.0	0.0	0.0	 Cubolta	Ciuhur Raut	Prut Nistru	Nistru
18	Anenii Noi	11.7	110.0	0.0	110.0		Bic	Nistru	
19	Balti	143.3	7683.0	7683.0	0.0		Raut	Nistru	
20	Calarasi	16.1	136.5	0.0	136.5		Bic	Nistru	
21	Causeni	19.9	140.2	0.0	140.2		Botna	Nistru	
22	Chisinau	663.4	55910.9	55814.5	96.4		Bic	Nistru	
23	Ciorescu	5.5	81.7	0.0	81.7		Ichel	Nistru	
24	Cojusna	0.0	0.0	0.0	0.0		Bic	Nistru	
25	Cricova	8.4	161.3	0.0	161.3		Ichel	Nistru	
26	Criuleni	9.5	0.0	0.0	0.0			Nistru	
27	Dondiuseni	10.7	81.0	0.0	81.0		Raut	Nistru	
28	Drochia	20.3	173.0	173.0	0.0		Raut	Nistru	
29	Floresti	15.3	231.2	231.2	0.0		Raut	Nistru	
30	Orhei	33.3	719.1	0.0	719.1		Raut	Nistru	

(continued)

Table 1.3 (continued)

Nr	Wastewater source (town)	Population in 2010 (ths)	Biologically treated (thousand m^3)			Discharged into			
			Total	Conventionally treated	Including insuficient treated	Watercourse 2	Watercourse 1	Watercourse 0	River bazin district
31	Rezina	15.9	0.0	0.0	0.0			Nistru	
32	Riscani	14.4	86.7	0.0	86.7	Copaceanca	Raut	Nistru	
33	Singerei	15.3	93.4	0.0	93.4	CiuluculMare	Raut	Nistru	
34	Soldanesti	7.6	0.0	0.0	0.0		Ciorna	Nistru	
35	Soroca	37.2	0.0	0.0	0.0			Nistru	
36	Straseni	21.1	0.0	0.0	0.0		Bic	Nistru	
37	Telenesti	9.8	83.1	0.0	83.1	CiuluculMic	Reut	Nistru	

Source Association “Moldova Apa-Canal” for columns No. 4-8, 2011

However, only the wastewater treatment plants from major towns (e.g. Chisinau and Balti) have their own laboratory to conduct the monitoring of wastewater quality. Other wastewater treatment plants conduct investigations on a contractual basis at the laboratories of the district centers of public health and investigation centers of the State Ecological inspectorate.

The State Ecological Inspectorate is in charge of checking the compliance with the requirements for wastewater discharges set up in the authorization for the special use of water. The laboratory analysis of both discharges from treatment plants and the receiving waters are conducted by the environmental investigation centers of the State Ecological inspectorate placed in Balti, Chisinau and Cahul. For that purpose, the investigation centers establish annual sampling programs for wastewater quality for the monitoring of biochemical oxygen demand, suspended solids and ammonium (NH4) at 29 wastewater treatment plants.

1.4 Surface Water Monitoring

The following map (Fig. 1.1) shows the location and type of surface water level and flow measuring stations. The present network consists of 39 stations. Seven stations are on the River Prut, eight are on the River Dniester, one is on the Danube, and the others are on basins lying wholly within Moldova (including two within the area of Transnistria). All stations record water level, water temperature, and flow rate. Most stations also record the thickness of the ice. The Moldovan stations on the River Prut are maintained by the Moldovan Hydrometeorological Service, but the flow is gauged jointly with Romania. There is regular exchange of data. In the case of the Nistru, although some of the measuring sites are on the Transnistrian side of the river, the exchange of data is on a regular basis based on unofficial agreements with the Transnistrian Hydrometeorological Service. The earliest level data from Moldovan stations starts in 1920, and the earliest flow data are from 1949.

Five stations have been fitted with automatic level measurement and transmitting equipment. These use pressure transducers to measure water level and transmit level values by cable to a data logger. The data logger is able to store data for several months and, if so equipped, can transmit data in real-time. The sensor also measures water temperature. The logger is fitted with a SIM card and the data are transmitted via the mobile phone network. In addition to hydrological data the battery voltage is also transmitted. Data before 1993 are available on paper only. From 1993 to 2009, data were entered in digital format in a DOS program. Since 2009 data are in Excel format.

SHS made a monitoring of benthic invertebrate fauna and phytoplankton, but is now in the process of harmonizing sampling and assessments methods with the WFD requirements. Zooplankton has also been monitored for a long period, but this is not included among the WFD hydrobiological quality elements.

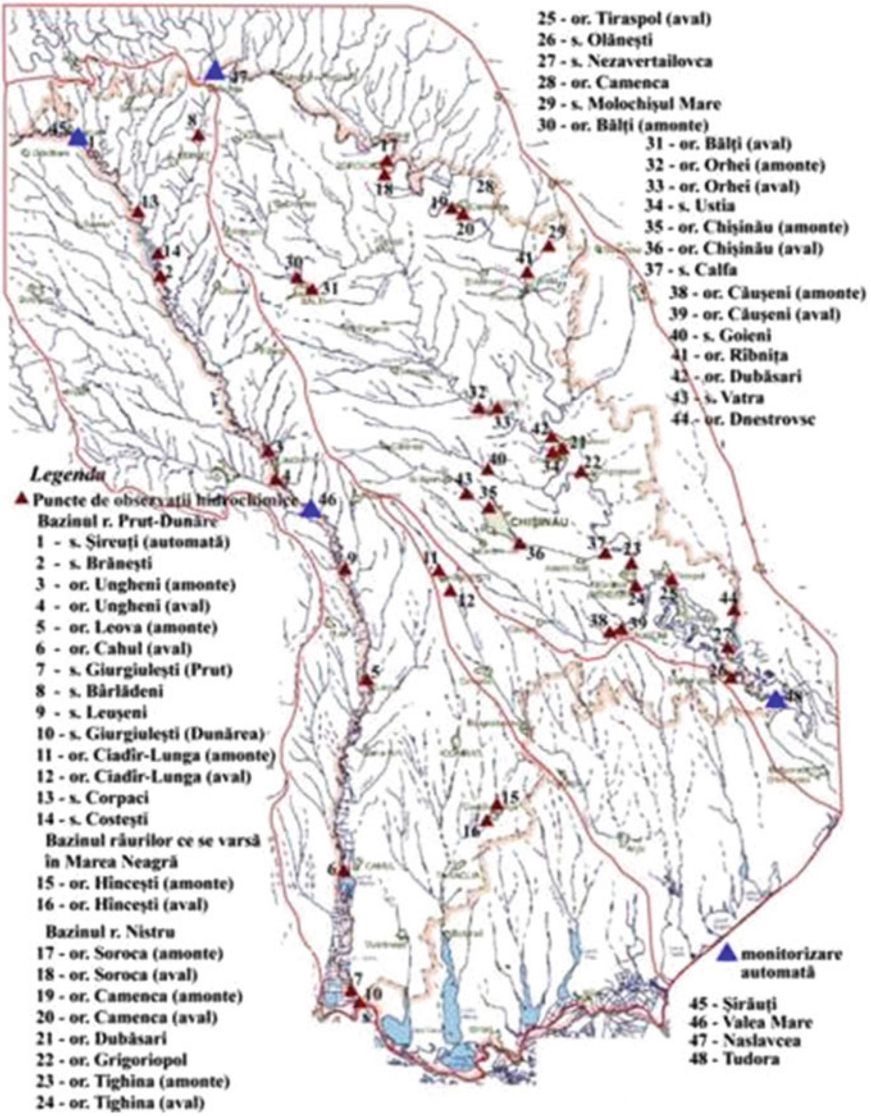

Fig. 1.1 Location and types of hydrologic station in Moldova (State Hydrometeorological Service)

Monitoring of phytobenthos is scheduled to substitute the traditional monitoring of periphyton; introduction of methods for sampling and assessment of phytobenthos, in line with the WFD requirements, is under development. Monitoring of macrophytes is envisaged but also not yet operational.

Special points of attention with monitoring and assessment of hydrobiological quality elements are “reference conditions” and the “ecological quality ratio”.

Both terms originate from the WFD, but expected to become relevant for Moldova as well.

- *Reference conditions* are closely linked with WFD's 'high status', defined as the biological, chemical and morphological conditions associated with no or very low human pressure. This is also called the 'reference condition' as it is the best status achievable. Reference conditions are type-specific and region-specific, so they are different for different types of rivers, lakes or coastal waters so as to take into account the broad diversity of ecological regions in Europe.
- The *ecological quality ratio* is an expression of the relationship between the values of the biological parameters observed for a given body of surface water and the values for those parameters in the reference conditions. The ratio is expressed as a numerical value between zero and one, with high ecological status represented by values close to one and bad ecological status by values close to zero.

Moldavian institutions are merely in the preliminary stages of starting to define reference conditions and ecological quality ratios for Moldovan surface waters.

1.5 Groundwater Monitoring

Groundwater status refers to both the quantity and chemical quality of groundwater. Groundwater levels are used as the main measure of quantitative status. To achieve good groundwater quantitative status, the available groundwater resource should not show signs of depletion and the ecological quality objectives for groundwater-dependent surface waters should be met. For this to occur, the long-term average rate of groundwater recharge should not be exceeded by long-term average rate of abstraction and maintenance of surface minimum flows. Groundwater abstraction must not also cause failure of good ecological status in dependent surface water bodies, such as damage of groundwater dependent terrestrial ecosystems, saline intrusion in coastal aquifers or upward migration of deep-seated brackish water.

Groundwater chemical status can be measured by determining the principal chemical composition and the concentration of pollutants in the groundwater body. This is usually done by reference to threshold concentrations and EU water quality standards, and the environmental objectives in associated surface waters or terrestrial ecosystems.

Moldova has multiple aquifer layers, composed predominantly of limestones and sandstones in the north and sands to the south, each with discretely different characteristics and different sources of recharge:

- A_3 Alluvial floodplain and terrace deposits
- N_2 p Pontian sands
- N_1S_3m Upper Sarmatian-Meotian aquifer group

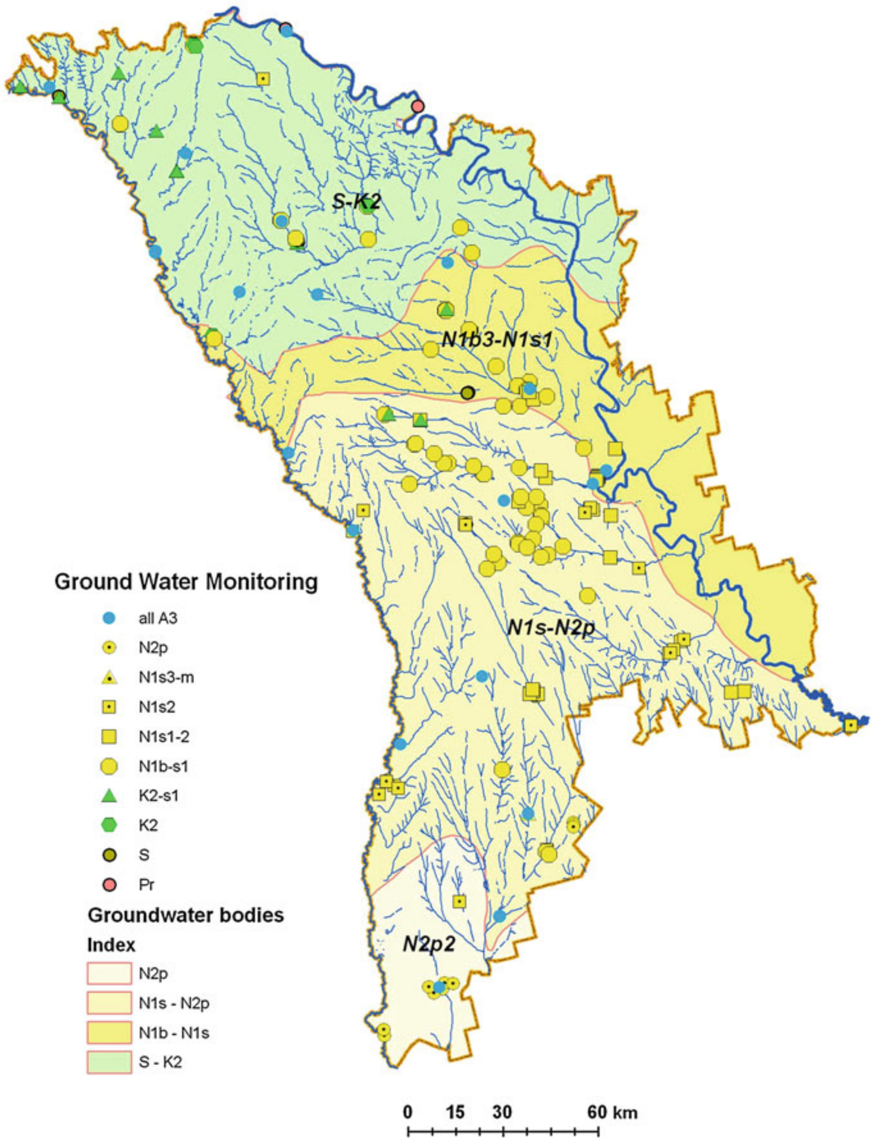

Fig. 1.2 Groundwater monitoring network in Moldova (*Source*: Five-Year Report: Investigation of Groundwater Regime and Balance Elements during 2005–2009, EHgeoM, 2010)

- $N_1t - N_1S_{1\text{-}2}$ Baden-Sarmatian aquifer group
- K Cretaceous karstic limestone
- S_1 Silurian crystalline limestone
- V Vendian crystalline basement rocks.

Some geological formations of the same age may be considered to give rise to different aquifer types in different parts of the country, as a result of lateral changes in lithology which cause the same formation to have different hydrogeological properties in different regions. Groundwater bodies can be identified from one or more of the main stratigraphic units, grouping together geological formations with similar properties and hydraulic parameters and which have both horizontal and vertical hydraulic continuity.

The existing set-up for groundwater resource assessment and monitoring throughout the territory of the Republic of Moldova was established in 1968. This monitoring network is shown in Fig. 1.2. The main aquifers used for water supply are monitored using a network of observation boreholes. The level of water in the boreholes is measured by observers and local residents. The measurements are then sent monthly by post to Chisinau. The correctness of measurements is checked during inspection visits, carried out by the EHgeoM, usually about twice a year.

Unfortunately, in recent years, the number of observation wells appears to have decreased, from 490 boreholes in 1991 to about 170 boreholes in 1997 and 186 in the 2010 report. At the last inventory [12], observations were carried out in 186 observation wells at 33 locations, and the level measurements were made once every 3 days. The instrumentation includes a Roulette WG-LM-30 and 50, level USAC-GL-150 - 200, thermometer TM - 10, and level measuring tools of made in Moldova by the EHgeoM. In the last decade, the frequency of sampling groundwater quality has decreased. Previously, in Soviet times, samples were taken from monitoring boreholes at least once a year, and more frequently in areas with complex hydrogeological conditions. Prior to sampling, water from boreholes was pumped out, following the guidelines established by VSEGINGEO (former Soviet Institute of Hydrogeology and Engineering Geology, Moscow). At present there are no funds for this kind of work.

Two type of groundwater quality analysis are made for there characteristics:

1. Routine sampling of major ions and physical characteristics: sodium, potassium, calcium, magnesium, ammonia, sulphite, sulphate, bicarbonate, chloride, nitrate, fluoride, methane, taste, odor, turbidity, color, dry residue, total hardness, carbonate and non-carbonate alkalinity.
2. Targeted sampling of micro-components when there is known to be a problem: phosphate, manganese, iron, copper, molybdenum, arsenic, lead, selenium, zinc, aluminum and beryllium.

During the last five-year EHgeoM reporting period of 2005–2009, there were 123 chemical analyses of major ions and physical parameters: just over half (i.e. 63) of these samples were collected from operational boreholes, 48 samples from observation boreholes, and 12 samples were collected from dug-wells. On average, this represents a monitoring rate of about 25 samples per year, which is extremely low. For example, in Western Europe, one public water supply source would have at least monthly sampling of raw water, and the sampling frequency would be increased if known pollution problems occurred in the aquifer. The current system in Moldova is therefore grossly inadequate in this respect, and such sampling does not provide effective management.

The analytical laboratory of EHgeoM is not accredited by ISO17025 and quality management of chemical analysis is not corresponds to appropriate normative documents. The obsolete equipment is used for chemical analysis: photocolorimeter MB-2 MB-56 m, Pressure Gauge EV-74 scales, laboratory balance VLA-200, weight F-2 – 210 [12].

The analysis of previous geological and international reports shown a number of water quality problems, they tend to be localized in nature. The main issues involve the following contaminants:

- Fluoride, ammonia, methane, nitrogen [related to oil and natural gas reserves];
- Hardness;
- Iron, Aluminium;
- Sulphates [potassium and sodium];
- Hydrogen sulphide;
- Nitrates [show rising trend at last years];
- Selenium, Strontium.

The electronic archive of groundwater data is compiled by the AGRM in EXEL format, but this work needs a more precise a borehole position. Unfortunately this information also is not exchanged with other stakeholders. EHgeoM produce annual and five-year reports. Apart from the Excel spreadsheet(s), no data are available electronically, and all drawing work is still done manually (no CAD or GIS in the 2010 report).

In addition to groundwater resource assessment, the inventory of boreholes should to be made for the database creation for further GIS modeling, groundwater body delineation and mapping of hydrogeological condition. Due to lack of funds, this work was suspended in 2002 [13]. It was noted in the EHgeoM 5-year report that there has been no progress with this activity [12]. As a result, it is estimated that about 30–40 % of the 7.000 boreholes are not working, and no effort will be made to decommission or backfill such sites. Consequently, such boreholes provide a potential pathway for surface pollutants to contaminate the aquifer.

1.6 Capacity of Analytical Laboratories

The potential of the analytical capacity of State Hydrometeorological Service (SHS) and other stakeholder laboratories (National Centre of Public Health, NCPH) is sufficient for the analysis of most of the physico-chemical parameters included in WFD and Water Law. The number of actually monitored parameters is considerably smaller; due to a combination of factors like lack of reference material and certification standards, specific equipment, and qualified personal.

Moldavian laboratories use a variety of normative documents for analysis of the various parameters, applying rather old standards developed during the Soviet era through recent ISO methods. The analysis' detection limit is not sufficient for some monitoring elements included water regulation documents for the protection of surface and ground waters. The detection limit is determined by a combination of the equipment, method and reagents used for the analysis. For example, the detection limits for aldrin, atrazin, HCH, para-para—DDT by the thin layer chromatography being less sensitive than gas chromatography.

The SHS and NCPH laboratories are accredited to ISO 17025. The lab makes use of Shewhart Control Charts and internal plus external reference material and samples. These laboratories takes part in the QUALCO Danube AQC Scheme, a basin-wide analytical quality control program in which some 35–50 laboratories participate. SHS and NCPH conduct joint sampling exercises with other Moldavian accredited laboratories, Ukraine (laboratories of the State Committee for Water Management in Novodnestrovsk and Odessa) and with Romania. EHgeoM laboratory is not accredited and no has quality management system.

1.7 Conclusions and Recommendation

The appropriate IWRM and IRBM can be realized on the basis of good organized decision making system. The creation of integrated GIS system which will include all information blocks is needed for the water management purposes. The following information should be included: water abstraction and discharge; pollution sources (diffusion and point); water treatment plants; water supply points; surface and groundwater bodies' delineation and characteristics; surface and groundwater monitoring network; water quality and quantity status of water bodies. The monitoring of abstraction and discharge is important for the assessment of water resource availability, management of resources, and collecting fees for water use.

There are a number of software packages which have been developed in developed countries specifically for handling a country's national archive of hydrological and meteorological data. They are all relatively similar, and all fit for purpose, and could easily be implemented in Moldova and linked to the proposed GIS platform. Ground water management is needed the realization of GIS system by the following principal actions:

1. Creation of geological and hydrogeological database as a base for geological GIS and decision making system;
2. Delimitation and characteristic of groundwater bodies for the principal aquifers which should be made in the frame of WFD requirements;
3. Digital mapping of different characteristic of groundwater bodies and aquifers which will include:
    - Distribution of monitoring, observation and production boreholes, and village wells with there characteristic;

- Distribution of the groundwater bodies, hydrogeological regions and principle aquifers, water supply points and other geological and hydrogeological objects;
- Groundwater body classification and quality status.

The groundwater body identification is important in wetland depending ecosystems for the management and the maintaining of the ecological quality of surface waters and terrestrial ecosystems, very often by supporting dry season river flows and wetlands. It is important also for the providing water for agricultural, industrial and domestic use.

The database and GIS systems will need to be used for risk analysis and environmental sustainability assessments later, and the systems will also need to be linked to the other main data-banks, specifically the groundwater licensing system (abstraction and discharge consents). The created hydrogeological GIS key point for whichever system is used is that it should be capable of professional time series hydrological data management using a Relational Database Client–Server platform such as Oracle. It should be capable of operating within the GIS platform and support automatic remote data acquisition from field data loggers, with versatile data import and export tools. The software should be capable of handling meteorological, surface and groundwater components of the hydrological cycle, with a sophisticated graphical data editor and generation of tabular summaries such as yearbook-style reports.

The implementation of GIS system in Moldavian conditions will possible only in the cooperation between all stakeholders with the attraction of the qualified personal from other institutions like universities and Academy of Science. The scientific support of this work is very important because deficiency of qualified specialist is a one of the critical point in this work.

The implementation of modern chemical and physical sensors is a perspective approach for distance monitoring of water quality and quantity. It is important for the obtaining of the digital actual information about the status of surface and ground waters. The scientific support of this activity is needed at all stages from the installation, data transmission, processing and storage in the database.

The analytical capabilities should be improved by the implementation of modern analytical equipment and methods as well as quality management system in all laboratories which participate in monitoring program in Moldova. The participation in the interlaboratory exercises by the international schemes and in local program is an important part of this activity. the organization of local interlaboratory exercises can be executed in scientific laboratories from Academy of Science.

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Chapter 2
Water Structure, Quantum Nature of Hydrogen Bonds and Diffusion of Water Molecules in Chloride Aqueous Solutions

I. I. Geru

Abstract A large variety of water properties is caused by the peculiarities of water clusters and water hydrogen bonds which are quantum mechanical in nature due to a small mass of hydrogen atoms. The concentration dependences of the diffusion coefficient *D* for aqueous solutions were found using the DOSY 2D NMR method. It was shown that with exception of barium chloride solution, which exhibits an anomalous concentration behavior of *D* in the concentration range 0–10 mg/ml, for two other solutions *D* decreases with increasing of the concentration. On basis of the generalized Stokes–Einstein equation the following correlation lengths for water and chloride solutions of the concentration $c = 100$ mg/ml were obtained: $\langle\xi\rangle_{H_2O} = 1.07$ Å, $\langle\xi\rangle_{MgCl_2} = 0.93$ Å, $\langle\xi\rangle_{CaCl_2} = 1.04$ Å and $\langle\xi\rangle_{BaCl_2} = 0.84$ Å. In the model of equivalent clusters of radius *R* the formula for estimation of the averaged time interval τ_0 between decay and creation of the clusters $\tau_0 = \tau_1[(R - \xi_0)/(\langle\xi\rangle - \xi_0) - 1]$ was proposed (τ_1 is the cluster lifetime and ξ_0 is the correlation length of the water without clusters). It was shown that for pure water $\tau_0 \approx 10^{-8} - 10^{-7}$s.

Keywords Water structure · Hydrogen bonds · Water diffusion · DOSY 2D NMR

2.1 Introduction

Water is one of most mysterious substance in a nature with 67 anomalies of physical and chemical properties many of which arise from the nature of hydrogen bonds [1]. It is one of the few known substances whose solid form is less dense

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than the liquid. The behavior of water is due to the properties of hydrogen bond network. There exist intermittent collective molecular motions, influences associated with the rearrangement caused by the hydrogen bonds under strong or extremely week inner or outer interactions.

The hydrogen bond in water is part (about 90 %) electrostatic and part (about 10 %) covalent [2].

Formation of hydrogen bonds between water molecules gives rise to large energetic changes in enthalpy (becoming more negative) and entropy (becoming less positive). This enthalpy-entropy compensation is almost complete with the consequence that very small imposed enthalpic or entropic effects may exert a considerable influence on aqueous systems [1]. It is possible that hydrogen bond between para-H_2O, possessing no ground state spin, are stronger and last longer than hydrogen bonds between ortho-H_2O possessing triplet spin ground state [3].

On very short time scale (less than a picosecond), water is more like a “gel” consisting of a single, huge hydrogen-bonded cluster. On a 10^{-12}–10^{-9} s time scale, rotations and other thermal motions cause individual hydrogen bonds to break and re-form in new configurations. The localized $(H_2O)_n$ clusters may have a fleeting existence, and many theoretical calculations have been made showing that some combinations are more stable than other.

The lower water clusters can enlarge and to form highly symmetric icosahedral water cluster containing 280 water molecules [1]. Water is a network of icosahedral water clusters what can dynamically form continuous networks of open, low-density and condensed structures. The minimum number of possible arrangements of hydrogen bonds in the fully occupied low-density icosahedral network is more than 150-thousand. A fluctuating network of water molecules, with localized and overlapping icosahedral symmetry, was first proposed in 1998 and independently found, by X-ray diffraction, in water nanodrops on 2001 [4].

Water clusters are a considerable interest as models for the study of water structure, and many articles of them are published every year. The principal finding was that 80 % of the water molecules are bound in chain-like fashion to only two other molecules at room temperature, thus supporting the prevailing view of a dynamically-changing, disordered water structure.

The chapter is organized as follows: Sect. 2 provides the water hydrogen-bonds (H-bonds). Water clusters and water H-bonds network are presented in Sects. 3 and 4. Section 5 contains short information about the quantum mechanical properties of hydrogen-bonds network such as zero-point motion, quantum delocalization and quantum tunneling.

2.2 Water Hydrogen Bonds

The water molecule is electrically neutral, but the positive and negative charges are not distributed uniformly. The negative electronic charge is concentrated at the oxygen end of the molecule and to oxygen’s high positive nuclear charge which exerts stronger attractions to the electrons. This charge displacement constitutes an electric dipole. The partially-positive hydrogen atom on the water molecule is electrostatically attracted to the partially-negative oxygen on neighboring molecules.

Each liquid water molecule is involved in about four hydrogen bonds but considerably less than covalent bonds with strength considerably greater than the natural thermal energy. More exactly, the hydrogen bonds between hydrogen and oxygen atoms belonging to different water molecules are 20 times weaker than covalent bounds and 60 times stronger than van der Walls bounds [5].

There is no standard definition for hydrogen bond energy. In liquid water, the energy of attraction between water molecules is optimal about 23.3 kJ mol^{-1} [6] and almost five times the average thermal collision fluctuations at 25 °C. This is energy required for breaking and completely separating the bond, and equals about half of the enthalpy of vaporization (44 kJ mol^{-1} at 25 °C). Just breaking the hydrogen bond in liquid water, leaving the molecules essentially in the same position and still retaining their electrostatic attraction, requires only about 25 % of this energy, recently estimated at 6.3 kJ mol^{-1} [7]. If the excess heat capacity of the liquid over that of steam is assumed attributable to the breaking of the bonds, the attractive energy of the hydrogen bonds is determined to be 9.8 kJ mol^{-1} [8].

This may be considered as an indication of the total extra energy caused by polarization, cooperatively and covalency of the hydrogen bond.

The Gibbs free energy change presents the balance between the increases in bond strength and consequent entropy loss on hydrogen bond formation and may be used to describe the balance between formed and broken hydrogen bonds [9]. Several estimates shown that the Gibbs free energy change needed for the formation of water's hydrogen bonds is about –2 kJ mol^{-1} at 25 °C [10].

The bond lengths and angles will change as consequence of polarization shifts in different hydrogen-bonded environments. The oxygen atoms in water molecule typically passes about 0.7 *e* negative charge and the hydrogen atoms about 0.35 *e* positive charge giving rise to both an important electrostatic bonding but also the favored trans arrangement of the hydrogen atoms. The hydrogen bond strength varies with the hydrogen bond angle (O–H…O). If the hydrogen bond is close to straight, the hydrogen bond strength depends almost linearly on its length with shorter length giving rise to stronger bending. As the hydrogen bond length on water increases with temperature increase but decreases with pressure increase, hydrogen bond strength also depends almost linearly on the temperature and pressure [11].

An important feature of hydrogen bond is that it possesses direction. This direction is that of the shorter O–H covalent bond, the O–H hydrogen atom being donated to the O-atom acceptor on another H_2O molecule. In H-NMR spectroscopy, the chemical shift of the proton involved in the hydrogen bond moves about 0.01 ppm K^{-1} upfield to lower frequency. There is also about 5.5 ppm further upfield to vapor at 100 °C. That is, becomes more shielded with reducing strength of hydrogen bonding [12] as the temperature is raised.

A similar effect can be detected in water's ^{17}O–NMR, moving about 0.05 ppm K^{-1} upfield and 36–38 ppm further upfield to vapor at 100 °C [1].

The spin–lattice relaxation time ($T_1 \sim 3.6$ s, $t = 25$ °C) of the water protons is also function of the hydrogen bonding, being shorter for stronger bonding. However, the effect of solutes shows that the chemical shift and spin–lattice relaxation time are not correlated [13]. The spin–lattice relaxation time has been found to be of three times greater than the spin–spin relaxation time, suggesting the presence of supramolecular structuring in water [14]. These data were confirmed by our measurements of spin–lattice and spin–spin relaxation times for distilled water at 25 °C using the Bruker NMR relaxometer Minispec mq 20: $T_1 = 3.6 \pm 0.2$ s and $T_2 = 1.86 \pm 0.007$ s.

There is substantial cooperative strengthening of the hydrogen bonds in water, which is dependent on long-range interactions [15]. Breaking one bond generally weakens those around whereas making one bond generally strengthens those around. This leads to cluster formation where all water molecules are linked together by three of four strong hydrogen bonds. For the same average bond density, some regions consist mainly of weekly hydrogen-bonded water molecules. This variation is allowed with the water molecules at the same chemical potential as there is compensation between the bond's attractive energy and the energy required for creating the orderliness apparent in cluster formation.

2.3 Clustering of Water Molecules

When the hydrogen bonding is strong, the water network expands to accommodate these directed bonds and where the hydrogen bonding is weak, water molecules collapse into space around their neighbors. Such changes in water's clustering give rise to the so-called anomalies of water. Particularly, this leads to different behaviors of hot water which has weaker hydrogen bonding, and cold (super cooled water), which has stronger hydrogen bonding. It is the clustering of water, due to the directed characteristics of the hydrogen bonding, that is responsible for the very special properties of water that allow it to act in diverse ways under different conditions.

The water molecules form an infinite hydrogen-bonded network with localized and structured clustering. Small clusters of four water molecules may come together to form water bicycle-octamers [1]. The competition between maximizing van der Waals interactions (structure A) and maximizing hydrogen bonding (structure B) is finely balanced, easily shifted with changed physical conditions, solutes and surfaces. The potential energy barrier between these states ensures that water molecules prefer either structure A or B with little time spent on intermediate structure. An individual water molecule may be in state A with respect to some neighbors whilst being in state B with respect to others.

The bicycle-octamers may cluster further, with only themselves, to form highly symmetric 280-molecule icosahedral water clusters that are able to interlink and tessellate throughout space. A mixture of water cyclic pentamers and triciclodecamers can bring about the same resultant clustering [1]. As three of these small clusters are relatively stable, it is likely that their interaction will produce these large icosahedral clusters. Such clusters can dynamically form a continuous network of both open (low density) and condensed structures. The fluctuating self-replicating network of water molecules, with localized and overlapping icosahedral symmetry, was first proposed to exist in liquid water by Martin Chaplin [16].

The liquid water acts in subtly manners as circumstances change depending on variations in physical and molecular environments and occasionally acting as though it were presents more than one liquid phase. Sometimes water acts as a free flowing molecular liquid whilst at other times, in other places or under subtly different conditions, it acts more like a weak gel.

In liquid water, the balance between the directional component of hydrogen bonding and the isotropic van der Waals attractions is finely poised. Increased strength of the hydrogen bond directionality leads to ordered clustering with consequential effects on physical parameters like a glass state, whereas reducing its strength reduces the size of the cluster with the properties of the water when only the van der Waals attraction remain. Quite small percentage changes in the strength of the aqueous hydrogen bond may give rise to large percentage changes in the such physical properties as melting point, boiling point, density and viscosity.

Thus, the water can be presented as an equilibrium mixture of low-density and high-density clusters [17] and examining the consequences of hydrogen bond strength variation on the cluster equilibrium with resultant effects on physical properties. This concept has been shown to explain qualitatively and quantitatively most anomalies of liquid water.

2.4 The Hydrogen-Bonded Network

The anomalous proprieties of the water, most pronounced in the supercooled metastable state [18], can be ascribed to water's unique structure, consisting of a random and fluctuating three-dimensional network of hydrogen bonds [19]. For understanding the water anomalous properties it is necessary to have the novel experimental techniques, detailed theoretical predictions, and computer simulation methods. In particular, the development of pulse neutron sources has allowed the remarkable advance of the deep inelastic neutron scatting (DINS) technique [20–22]. DINS technique is based on measurements at high energy, $\hbar\omega$, and high momentum, $\hbar q$, transfers, thus providing a probe of both the short-time ($t \leq 10^{-15}$ s) dynamics and local ($r \leq 1$ Å) environment of the atoms in materials [20, 21]. The high energy and momentum transfers achieved allows to describe the scattering process within the framework of the impulse approximation [21, 23, 24]. The scattering cross section is the expressed in terms of the single particle momentum distribution, $n(p)$, whose variance is related to the mean kinetic energy

$\langle E_k \rangle$. In the case of water protons the *n(p)* and $\langle E_k \rangle$ provide a richness of information about the potential surface that the proton experiences, including the effects of hydrogen bonding. These possibilities make the DINS technique unique and well established tool to investigate the hydrogen bonding of the water under various conditions [22, 25–29]. In the Ref. [22] the *n(p)* is expressed by explanation [21]

$$n(p) = \frac{e^{-p^2/2\sigma^2}}{(\sqrt{2\pi}\sigma)^3} \sum_n C_n(-1)^n L_n^{1/2}(\frac{p^2}{2\sigma^2}), \tag{2.1}$$

where $L_n^{1/2}$ are generalized Laguerre polynomials. The coefficients C_n and σ can be determined by a least squares fitting procedure. Proton mean kinetic energy $\langle E_k \rangle$, measured in [22] with DINS experiments on water sample under different thermodynamic conditions as a function on temperature, was approximated by dependence $\langle E_k \rangle \sim (\mathrm{T}-\mathrm{T_s})^{\gamma}$, where $\mathrm{T_s} = 228$ K and $\gamma = 2.67$. These data are in good agreement with values found for the description of the divergence of water structural and dynamic properties at $\mathrm{T_s}$ [30].

To highlight the differences between the *n(p)* measured in the supercooled states and those measured in the liquid stable phase [26], the authors of the Ref. [22] have plotted the radial proton momentum distribution, $4\pi p^2 n(p)$, for water under different thermodynamic conditions as a function of p. It has been shown that the stable liquid water (T = 298 K) is characterized by a main narrow peak with maximum at $p = 5.2$ Å^{-1} and by a secondary peak at about $p = 17$ Å^{-1}, in the radial momentum distribution that indicate the quantum delocalization, or coherent interference of the protons over the two sites of a double-well potential [28, 31, 32]. In this case each water proton is shared by covalent bound oxygen and an H-bond one; the proton will be coherent over two separated sites along the H-bond direction. The similarity between the H-bond and the proton mean kinetic energies suggests that each water proton can easily break and reform hydrogen bonds with one of his two first neighboring oxygens. The resulting delocalization of the proton between the oxygen atoms of two neighboring water molecules is consistent with the finding that a proton can become strongly delocalized between two oxygen atoms if the average O–O distance is <2.8 Å, leading to a very broad double-well potential in the energy region, corresponding to the second excited state of the O–H stretch vibration [33].

Recently, Huang et al. [29] used small-angle X-ray scattering (SAXS) over the temperature range 7–77 °C, to show the existence of a shallow minimum in the structure factor, $S(Q)$, at small but finite Q which then rise to the $S(Q = 0)$ value consistent with water's isothermal compressibility at a given temperature [34]. They attribute the minimum in SAXS intensities as being connected with a difference in density between two structural species, which they analyze with a Guinier treatment usually reserved for determining the shape and size of macromolecules in a multicomponent solutions. Furthermore, they shown that a tetrahedral model of water lacks such structural signatures in the same small-Q region, concluding that representation of water as a distorted tetrahedral network is inconsistent with the new SAXS data. Instead, Huang et al. used previously reported X-ray absorption, X-ray Raman and X-ray emission spectroscopy data

[29, 35] which are in themselves controversial [36], to describe the two distinct water structural species as the hypothetical low-density liquid (LDL) and high-density liquid (HDL) that are present in the supercooled region and are observed also at ambient temperatures.

The new SAXS data on ambient liquid water obtained by using the third generation synchrotron source were analyzed in [34]. It was shown that the small-angle region measure standard number density fluctuations consistent with water's isothermal compressibility temperature trends. There is no support or need for heterogeneities in water structure at room temperature to explain the small-angle scattering data, as it is consistent with a unimodal density of the tetrahedral liquid at ambient conditions.

For a homogeneous single component liquid far from any critical region, the small-Q region of the scattering profile of a homogeneous fluid measures the length scale, l_N, over which number fluctuations

$$\lim_{Q->0} S(Q) = \frac{\left\langle (N - \langle N \rangle)^2 \right\rangle}{\langle N \rangle} \tag{2.2}$$

are still observable in Q-space [37]. To determine evidence of enhanced or anomalous density fluctuations, such as that found near a critical point, one can then separate the total intensity or structure factor into normal $S^N(Q)$ and anomalous $S^A(Q)$ components [38]

$$S(Q) = S^N(Q) + S^A(Q). \tag{2.3}$$

The normal component of scattering is either assumed to be Q-independent, i.e., $S^N(Q) = S^N(O)$ over the small-Q region [39, 40], where

$$S^N(O) = k_B T \rho_N \chi_T^N. \tag{2.4}$$

In formula (2.4) k_B is Boltzmann's constant, T is temperature, ρ_N is the molecule number density and χ_T^N is the normal component of the isothermal compressibility.

The anomalous component of scattering allows for the calculation of the correlation length ξ, by fitting it to the following Lorentzian functional form

$$S^A(Q) = \frac{A(T)}{\xi^{-2} + Q^2}, \tag{2.5}$$

where $A(T)$ is the temperature specific constant [38]. For a homogeneous liquid, the correlation length derived from analysis of small-angle scattering data is interpreted to be the size of an observation window in which density fluctuations are still observable in inverse space, but is only valid when $Q \rightarrow 0$ and $S(O) \gg 1$ [34]. It is important to emphasize that far from a critical point, such as that near room temperature, the anomalous component will necessarily be small relative to the normal component.

2.5 Quantum Nature of the Hydrogen Bonds

It is known that hydrogen bonds are complex and because of the small mass of the proton it is often not appropriate to treat the proton in H-bonded system as a classical particle. The small mass of hydrogen atoms means that they are quantum mechanical in nature. Therefore the quantum nature of protons must be taken into account and issues such as zero-point motion, quantum delocalization, and quantum tunneling are relevant [41]. The relevance of quantum nuclear effects to liquid water has been demonstrated. In particular, from the first principle simulations [42, 43] and neutron Compton scattering measurements [44, 45] the impact of quantum nuclear effects on the proton's real space delocalization and water vibrational modes has been established. Upon increasing of H-bonds strength, the proton becomes more delocalized and consequently the OH stretching frequency decreases.

Quantum nuclear effects can also influence the interaction strength and consequently the structure of H-bonded systems [41, 42]. In H-bonded crystals the replacing H with deuterium (D) they causes the change of the O–O distance. The conventional effect yield on elongation of the O–O distance upon replacing H with D, although a negative effect (the shortening of the O–O distance upon replacing H with D) has also been observed [46]. In H-bonded liquids analogous effects take place. In particular, simulations for liquid water shown that the O–O radial distribution function is less sharply peaked when simulations with taking into account the quantum nuclear effects are compared to those with classical nuclei [42] suggesting the decrease in the overall H-bond strength.

Xin-Zheng Li et al. [41] investigated the impact of quantum nuclear effects on a wide range of H-bonded materials. Using state-of-the-art *ab initio* molecular dynamics and *ab initio* path integral molecular dynamics they shown that relatively weak H-bonds, such as those in water, are made weaker if quantum nuclear effects are taken into account. This correlation arises from a simple competition between the anharmonic quantum fluctuations of intramolecular covalent bond stretching (which tends to strengthen H-bonds) and intermolecular H-bond bending (which tends to weaken H-bonds). The influence of quantum nuclear effects was quantified through the radio of the path integral molecular dynamics (PIMD) and molecular dynamics (MD) projections

$$x = (X - H'')^{PIMD} / (X - H'')^{MD}, \tag{2.6}$$

where $(X - H'')$ is the projection of the donor molecule's covalent bond along the intermolecular axis. Since $(X - H'')$ increases upon intramolecular stretching but decreases upon intermolecular bending, it allows the balance between stretching and bending to be evaluated.

The values of x greater than one indicate that quantum nuclear effects lead to more stretching than bending and values less than one indicate than quantum nuclear effects result in more bending than stretching. It was shown that for all systems where H-bond bending dominates ($x < 1$), the heavy-atom distances are longer in PIMD than in MD. In case where, covalent bond stretching is dominant ($x > 1$), the heavy-atom distances are shorter in PIMD than in MD. With the increase of x, quantum fluctuations on the stretching mode become more dominant and quantum nuclear effects turn form weakening the H-bonds to strengthening them. Thus the overall influence of quantum nuclear effects on the H-bonding interaction quantitatively comes down to this interplay between covalent bond stretching and intermolecular bond bending [41].

2.6 Diffusion of Water Molecules in Chloride Aqueous Solutions at Ambient Conditions

Diffusion coefficients are one of the transport parameters which give substantial information about diffusion phenomenon in solutions. These parameters can be obtained using the method of open-ended conductimetric capillary cell [47], the quasi-elastic slow neutron scattering [48] and the direct measurement of diffusion coefficients using NMR field-gradient technique [49].

Below the concentration dependences of the diffusion coefficient D of water molecules in aqueous solutions of manganese, calcium and barium chlorides are presented. The experimental data were obtained on basis of DOSY 2D NMR spectra recorded by means of Bruker NMR spectrometer Avance III 400 MHz. The temperature of solutions in a resonance cavity during measurements of concentration dependences of DOSY 2D NMR spectra was fixed with the precision of ± 0.1 °C. The concentrations of aqueous solutions were changed in the limits 0–100 mg/ml. Thus, at fixed temperature the single perturbation that affect separately self-diffusing water molecules in aqueous solutions is caused by Mg^{2+}, Ca^{2+} or Ba^{2+} cations, because for all three chloride salts the anion Cl^- is the same.

For magnesium chloride the concentration dependence of the diffusion coefficient D in ambient conditions is presented in Fig. 2.1. With increasing of $MgCl_2$ concentration the diffusion coefficient D decreases in a concentration range of 0–100 mg/ml that is in agreement with the standard diffusion theory. Such concentration behavior of the diffusion coefficient is characteristic for liquids in general and therefore the diffusion of water molecules in magnesium chloride aqueous solution can be considered as a normal diffusion.

For calcium chloride aqueous solution the diffusion coefficient D of water molecules also decreases with increasing of the concentration in the same concentration range (Fig. 2.2). However, the concentration dependences for both these aqueous solutions are slightly different (Figs. 2.1, 2 2).

Figure 2.3 exhibits the situation when the diffusion coefficient of water molecules increases with increasing of aqueous solution concentration for a restricted concentration range (0–10 mg/ml) and decreases with increasing of concentration (an anomalous concentration behavior) for the remaining concentration range (10–100 mg/ml). It is the case of barium chloride aqueous solution.

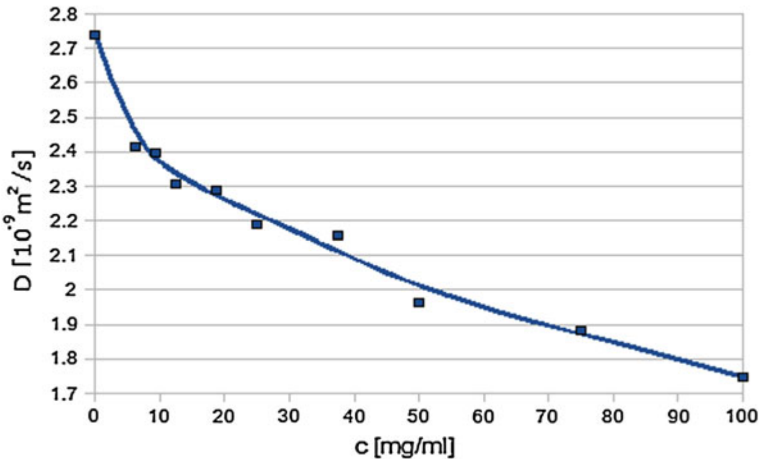

Fig. 2.1 Diffusion coefficient of water molecules versus concentration of magnesium chloride in aqueous solutions at temperature t = 25 °C

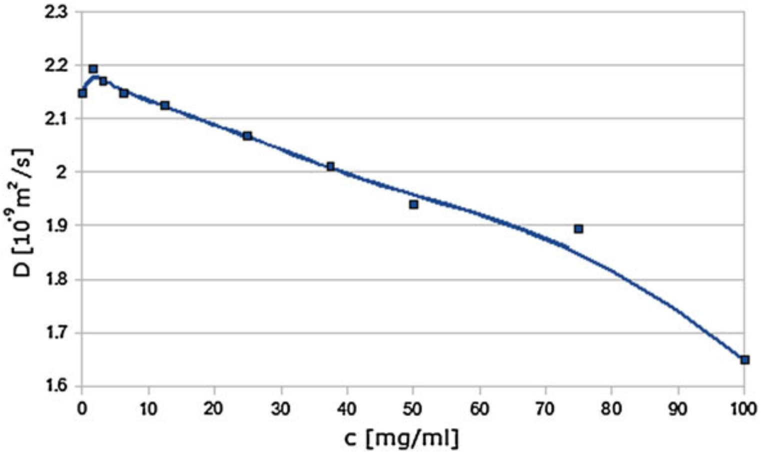

Fig. 2.2 Diffusion coefficient of water molecules versus concentration of calcium chloride in aqueous solutions at temperature t = 25 °C

The diffusion of water molecules into salt solution may be seen as the self-diffusion of water retarded by the presence of the ions in solutions. In the case of the chlorides discussed here the self-diffusion coefficient of water represents a maximum of the diffusion coefficient in the limit of extreme dilution and this tends to zero in the limit of the anhydrous salts.

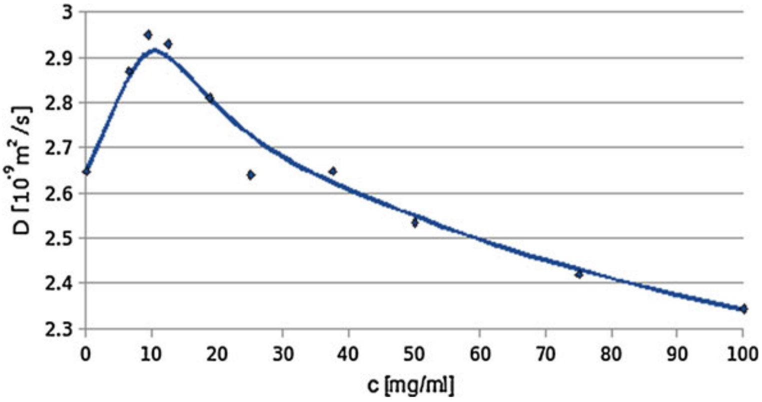

Fig. 2.3 Diffusion coefficient of water molecules versus concentration of barium chloride in aqueous solutions at temperature t = 30 °C

2.7 Discussion

Despite intense experimental and theoretical investigations more than for decades, a complete description of water properties remains elusive.

Each liquid water molecule is involved in a four hydrogen bonds between hydrogen and oxygen molecules belonging to different water molecules. The hydrogen bonds are 20 time weaker than covalent bonds and 60 times stronger than van der Waals bonds. The small mass of hydrogen atoms means that they are quantum mechanical in nature. Therefore issues such as zero-point motion, quantum delocalization and quantum tunneling of protons must be taken into account.

The water molecules form an infinite hydrogen-bonded network with localized and structured clustering. Small clusters may come to form multimolecular clusters including a highly symmetric 280-molecule icosahedral water cluster. These clusters can dynamically form a continuous network of both open (low density) and condensed (high density) structures. Therefore the water can be presented as an equilibrium mixture of low-density and high-density clusters. As consequences of hydrogen strength variation on the cluster equilibrium the resultant effects on physical properties occurs. On the basis of this concept most anomalies of liquid water can be explained qualitatively and quantitatively.

Existence of 67 anomalies of physical and physical–chemical properties of water shows the complexity of the molecular structure of water. Anomalous properties of water can be understood only on the basis of water cluster structure taking into account the quantum nature of hydrogen bonds. The short lifetimes of hydrogen bonds (1–20 ps) causes the short lifetimes of water clusters of various sizes and structures. These clusters decay with the subsequent formation of new clusters of different shapes and structures as a consequence of their short lifetime.

The lifetime of water clusters can be estimated on the basis of the data of 2D IR spectroscopy (a Fourier transfer technique that uses an excitation sequence of femtosecond IR pulses with variable time delay) [50]. However, what is the length of time since the collapse of any one cluster until the formation of another cluster in its place is not currently known.

It is well known that at sufficiently large times the motion if the individual molecules in liquids are well described in terms of ordinary diffusion. Thus, at these times the many-body problem reduces to a one-body stochastical problem in which all many body effects are hidden into a single number, the diffusion coefficient. The question is which time can be considered as sufficiently large to comfortably use the language of diffusion? The diffusion is a proper language for times larger than 2 ps [51].

The diffusion of a Brownian particle in the suspensions at intermediate and high concentration can be understood on basis of the generalized Stokes–Einstein equation [52]

$$D = k_B T / 6\pi\eta\xi,$$

where D is the cooperative diffusion coefficient, η is the suspension dynamic viscosity, $k_B T$ is the thermal energy and ξ is “the correlation length”.

It should be noted that in case of stable particles in the suspension ξ is the radius R of the diffusing particle. If the particles (water clusters) are not stable and the time of measurement is longer than the cluster lifetime (as is in the case of DOSY 2D NMR experiments) the measured correlation length is

$$\langle\xi\rangle = \frac{1}{n}\sum_{i=1}^{n} \xi_i,$$

where n is the total number of short-lived clusters that formed during the registration of the DOSY 2D NMR spectrum.

We should expect that at investigation of water in a liquid state by means of the equipment with the time delay longer than the clusters lifetime they averaged correlation length $\langle\xi\rangle$ should be shorter than the water cluster radius $R\,(\langle\xi\rangle < R)$. The value of $\langle\xi\rangle$ should decrease with increasing of the average time interval τ_o between the collapse of the “old” and the formation of a “new” cluster compared with the average lifetime of the clusters. It can be understood on the basis of a simple model viewing an arbitrary point of the liquid and subnanometric region Ω around it. Let at $t = 0$ (the time moment corresponding to beginning of the registration of the DOSY 2D NMR spectrum) any cluster with the lifetime τ_1 arises in the region Ω. After the time $t = \tau_1$ this cluster decays and during the time τ_o the liquid in the region Ω, that is characterized by the correlation length $\xi_o \ll R$, remains unperturbed. If $\tau_0 \approx \tau_1$ and the processes of creation and decay of the clusters in the region Ω repeated n times each, than we can imagine the existence on a time axis of a finite one-dimensional lattice with the length $t_m = 2n\tau_1$. There are n time intervals during which the clusters exist in the region Ω and the other

n time intervals during which the clusters are not existing in this region. The overage correlation length in this case is $\langle \xi \rangle = (1/2)(R + \xi_0) \approx R/2$.

If during the time t_m only $n_1 \ll n$ clusters arise in the region Ω and, correspondingly, during the time $t_m - n_1\tau_1$ the liquid remain unperturbed in this region with the correlation length $\xi_o \ll R$, then $\langle \xi \rangle = (R - \xi_0)\tau_1/(\tau_0 + \tau_1) + \xi_0$.

Using the data presented on Figs. 2.1, 2.2, 2.3, the generalized Stokes–Einstein equation and taking into account the concentration dependences of the chloride aqueous solutions viscosity [53], we obtain $\langle \xi \rangle_{H_2O} = 1.07$ Å, $\langle \xi \rangle_{MgCl_2} = 0.93$ Å, $\langle \xi \rangle_{CaCl_2} = 1.04$ Å and $\langle \xi \rangle_{BaCl_2} = 0.84$ Å for pure water and chloride solutions at concentration $c = 100$ mg/ml. These data are in the agreement with Ornstein–Zernike correlation lengths that for water at 25 °C are included within the limits 1.2–3.1 Å [34]. Since the diffusion of water molecules into salt solutions may be considered as the self-diffusion of water retarded by the presence of the ions in solutions, we can see that at a given concentration of the most powerful influence on the processes of formation of water clusters have the Ba^{2+} ions.

On the basis of the last formula for $\langle \xi \rangle$, we can estimate the averaged time duration τ_0 between the decay of any cluster and creation in the region Ω of another cluster in the pure water and in aqueous solutions $\tau_o = \tau_1 [(R - \xi_0)/(\langle \xi \rangle - \xi_0) - 1]$. For the parameters of a pure water in the liquid state $\tau_1 = 2.10^{-11}$ s, $R = 3$ nm and $\langle \xi \rangle = 1.07$ Å, taking into account the inequality $\xi_o \ll R$ and supposing that $\langle \xi \rangle - \xi_0 = 10^{-2}\langle \xi \rangle$, we obtain $\tau_o = 5.6 \cdot 10^{-8}$ s, suggesting that τ_o is much longer than the cluster lifetime if $R/(\langle \xi \rangle - \xi_0) \gg 1$. Water proton spin–lattice relaxation time ($T_1 = 3.6 \pm 0.2$ s for distillated water at 25 °C) is a function of hydrogen bonding, being shorter for stronger bonding. It is approximately three times greater that the proton spin–spin relaxation time ($T_2 = 1.86 \pm 0.07$ s), suggesting the presence of supramolecular structuring in water.

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Chapter 3
Electrochemical Solar Cells Based on Pigments

Constantin Turta, Gheorghe Duca, Ion Marin and Dumitru Sirbu

Abstract The intensity of solar radiation at the outer edge of the atmosphere (global illumination on the ground) when the Earth is the average distance from the Sun, is called the solar constant, whose value is 1.37 * 106 ergs/s/cm^2 (1.37 * 103 W/m^2) or about 2 cal/min/cm^2 [1]. As a result the Earth receives a total 1.56 * 1,018 1.2 * 1,017 W or kWh/year. In turn burn energy obtained from 1 kg of hydrogen is 39.4 kWh. So the solar energy which comes to Earth is equivalent to 3.9 * 1,016 kg H_2. During the day-middle solar cell with an efficiency of 10 % produces electrical power 100 W/m^2. Simple calculations show that the annual European solar surface could give 80 kW/m^2. This quantity is equivalent to 2 kg H_2 showing that total energy requirements for world could be met to cover only 0.13 % of Earth's surface with solar panels by 10 % efficiency.

Keywords Solar cells · Photoelectrochemistry · Solar energy · Pigments

The main objective of photoelectrochemistry is to produce hydrogen from water photolysis. Electrochemical reaction of water decomposition requires a potential difference $\Delta V = 1.23$ V which is equivalent to three photovoltaic solar cells.

At the moment there are known eight types of solar cells [2], photovoltaic cells:

(1) silicon cells [(c-Si, monocrystalline, maximum efficiency over 20 %) (mc-Si, polycrystalline, maximum efficiency over 16 %) (a-Si, amorphous thin layer yield 5–7 %)];
(2) Semiconductor-based elements of group III–V [GaAs (GaInP/GaAs, GaAs/Ge, cosmic space, yield 15–30 %)];

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Water Science and Technology Library 69, DOI: 10.1007/978-3-319-02708-1_3,

Table 3.1 Regional variation of the average cost of new generating resources, 2016 [3]

Plant type	Range for total system levelized costs (2009 $/MWh)		
	Minimum	Average	Maximum
Conventional coal	85.5	94.8	110.8
Advanced coal	100.7	109.4	122.1
Advanced coal with CCS	126.3	136.2	154.5
Natural gas-fired			
Conventional combined cycle	60.0	66.1	74.1
Advanced combined cycle	56.9	63.1	70.5
Advanced CC with CCS	80.8	89.3	104.0
Conventional combustion turbine	99.2	124.5	144.2
Advanced combustion turbine	87.1	103.5	118.2
Advanced nuclear	109.7	113.9	121.4
Wind	81.9	97.0	115.0
Wind-offshore	186.7	243.2	349.4
Solar PV	158.7	210.7	323.9
Solar thermal	191.7	311.8	641.6
Geothermal	91.8	101.7	115.7
Biomass	99.5	112.5	133.4
Hydro	58.5	86.4	121.4

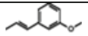
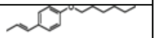
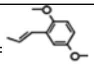
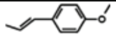
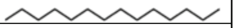
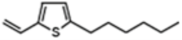
(3) Semiconductor-based elements of group II–VI (CdTe, yield: Lab.—16 %, in practice—10 %);
(4) Cells CIS, CIGS [($CuIn(Se)_2$), ($CuInS_2$), (CuInGa (SeO), maximum yield 42 %];
(5) Solar cells based on organic compounds;
(6) Cells based on pigments (Grätzel' cells);
(7) Cells with semiconductor electrolyte (CuO/NaCl);
(8) Cells based on polymers (in research state).

In Tables 3.1 and 3.2 the prices of one kWh depending on the nature of the source of energy are shown.

Notice that the use of solar energy is currently more expensive than other energy sources.

AM 1.5 size indicates weakening global sunlight at the Earth's surface depending on latitude because browsing a large air masses proportional to the latitude (in this case the 50^{o} latitude is considered). This corresponds to Central European summer conditions—from Northen Italy to central Sweden.

Table 3.2 Absorption coefficients/10^3 M^{-1} cm^{-1}, efficiency and substituents R_i of Dyes [30]

Dye	**Absorption coefficient / $10^3M^{-1}cm^{-1}$**	**Efficiency (%)**	**Radicals**
N3	14.2 (534 nm)(ethanol)	10.0	$R_1=R_2=R_3=R_4=H$
N712	---	8.2	$R_1=R_2=R_3=R_4=TBA$
N719	13.6 (535 nm)	11.2	$R_1=R_2=TBA; R_3=R_4=H$
Z910	16.9 (543 nm) (acetonitrile)	10.2	$R_1=R_2=$ 
K19	18.2 (543nm) (acetonitrile-*t*-butylalchool 1:1)	7.0	$R_1=R_2=$ 
N945	18.9 (550 nm) (acetonitrile-*t*-butylalchool 1:1)	10.8	$R_1=R_2=$ 
K73	18.0 (545 nm)	9.0	$R_1=R_2=$ 
N621	---	9.6	$R_1=R_2=$ 
Z907	11.1 (525 nm)	7.3	$R_1=R_2=$ 
Z955	8.0 (519 nm)	8.0	
HRS-1	18.7 (542 nm) (ethanol)	9.5	$R_1=R_2=$ 
Black dye	(610 nm)	10.8	

3.1 Electrochemical Solar Cells Based on Pigments

This cell type is also known as Grätzel cells. Unlike silicon/semiconductor cells, Grätzel cells' power is obtained by using a light-absorbing pigment on titanium oxide semiconductor [4, 5]. The third component of the cell is the electrolyte [5].

As photoanode other different semiconductors can be used: WO_3, CuI etc. As pigments in principle the rarely metal ruthenium complexes with bipyridyl derivatives as ligands are used, but for demonstration purposes other organic pigments, for instance, chlorophyll or anthocyanins (from berries), which are characterized by a very low lifetime can be used. The operation of this cells type is shown in Fig. 3.1.

At photo-excitation of the pigment molecules absorbed on the surface of n-type/(p-type) semiconductor it is possible to inject electrons (holes) in the conductor (the valence) band forming a cation (anion) [8–12]. This phenomenon is known as sensitization and has been used successfully in the development of photoelectrochemical pigment-sensitizabile cells—Dye-sensitized (DS) photoelectrochemical cells (PECS) [13–15].

Our group is working in synthesis of new complexes as photosensitizers for this type of solar cells.

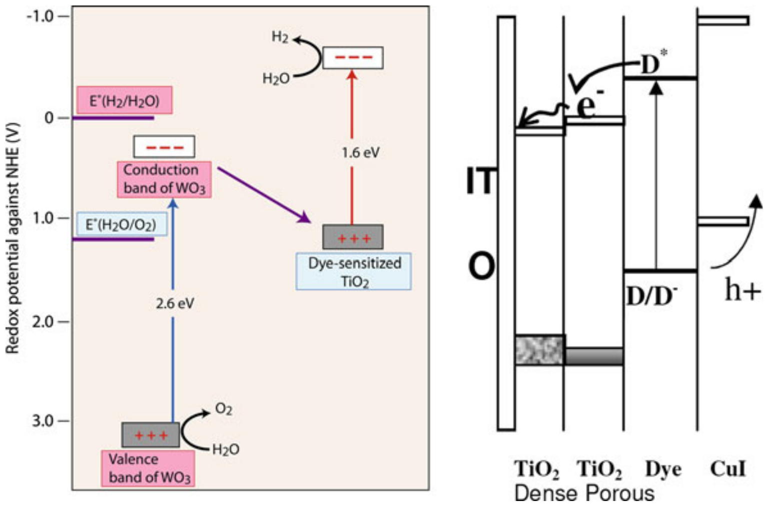


Fig. 3.1 Scheme of photolysis tandem system (*left*) [6] and TiO_2 band positions, the ground and excited states of ruthenium complex with bipyridyl (*right*) [7], illustrating the mechanism of charge separation

3.2 Complexes of Ruthenium with Bipyridine and Terpyridine

3.2.1 Ru(bpy)-Complexes

The achieved progress in optimization of dyes used in dye sensitizer solar cells (DSSC) was performed by systematic variation of ligands, metals and other groups of substituents in the transition metal complexes [16, 17]. This systematic study led to the development of mononuclear dyes [18] and polynuclear [19] based on metals such as Ru^{II} [20, 21], Os^{II} [22], Pt^{II} [23], Re^{I} [24], Cu^{I} [25] the Fe^{II} [26].

For efficient function of DSSC, used dyes must conform to a series of essential requirements of design. They have to form chemical bonds with TiO_2 by a group of “anchor”. This role, as a rule, play groups carboxylic or phosphonic. They provide efficient injection of electrons in the conduction band of TiO_2 and prevent its gradual shift in the electrolyte. To achieve the charge injection on TiO_2 energy level, Lowest Unoccupied Molecular Orbital (LUMO) of the dye should be greater than the energy of the conduction band of TiO_2, and for regeneration of oxidized dye his energy levels Highest Occupied Molecular Orbital (HOMO) must be lower than the redox energy level.

Another requirement to dye is intense absorption of solar radiation in the visible spectrum or close to IR region, preferably covering a wide range of wavelengths. It is necessary for electron transfer from the dye on TiO_2 conduction band to be faster compared with the time of the dye excited state deactivation.

Family complexes $\{[(4,4'\text{-COOH})_2\text{-bipy}]_2\text{RuX}_2\}$ (bipy = 2,2′-bipyridyl, X = Cl, Br, I, CN, SCN) works well [27] but the most efficient DSSCs demonstrated to date by the Grätzel group are: the N719 (Fig. 3.2), N3 and 'black' dyes (Fig. 3.3).

Today N_3 dye is still widely employed as a reference, the reported efficiency of 10 % could only be slightly improved since then. DSSCs sensitized with terpyridil-Ru^{II} complex so-called "black dye", have a higher short circuit current. The conversion efficiency of 10.4 % (1 cm^2) and 11.1 % (0.26 cm^2), are the

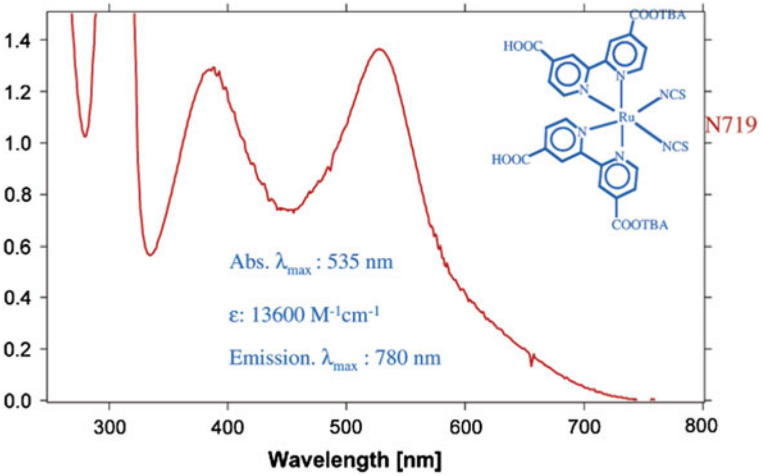


Fig. 3.2 Absorption spectrum of N719 in ethanol. [28]

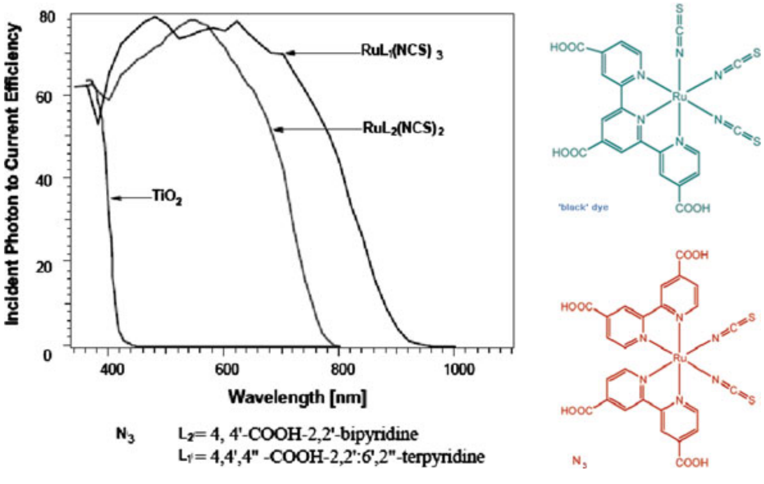
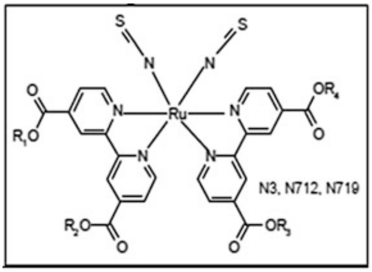
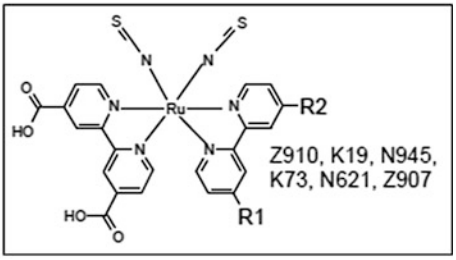


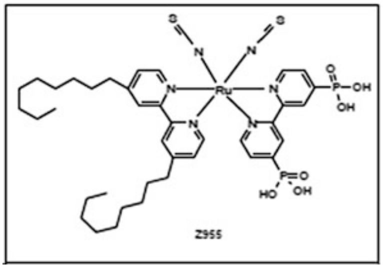
Fig. 3.3 Absorption spectrum of N3 and black dye [29]

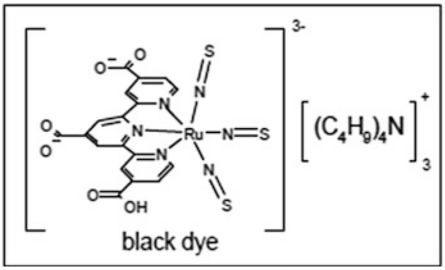
highest certified efficiencies so far. However, the stability of the dye has not been proven yet.

Some of good results are achieved with styryl-ligands attached to the bipyridil ring and presented in Table 3.2. The performance of these novel sensitizers on thick electrodes and with volatile electrolytes is about the same as for the N3-reference (e.g. Z910 10.2 % and N945 10.8 %), but applied on thin electrodes and with non-volatile electrolytes, the conversion efficiency is significantly higher. At the same time a remarkable stability at 80 °C in darkness and at 60 °C under AM1.5 is observed. The excited state of these dyes is between −0.71 and −0.79 V versus NHE, which is sufficiently more negative than the conduction band of TiO_2 (ca. −0.1 V vs. NHE) to ensure complete charge injection [30].









The most remarkably feature about the Ru-dyes is their extraordinary stability when being adsorbed on the TiO_2-surface. For example, the widely employed complex N3 sustains only 200 excitation cycles in solution, but between 10^7–10^8 cycles on a metal oxide surface. The difference between the dye in solution and on the TiO_2-surface is an ester bond in the periphery of the molecule. Obviously the electronic state of the Ru-complex is significantly altered by the adsorption. The dye is probably not simply attached by physic sorption or chemisorption, but creates a charge transfer complex (CTC) with Ti^{3+}-surface states, which are partly present in the semiconductor or are created upon charge injection. The CTC might induce a π-backbonding, which allows the local export of entropy and thus stabilizes the Ru-complex.

3.2.2 Ru(tpy)-Complexes

Sauvage, Balzani and their groups discussed a great number of terpyridine (tpy) derivatives which had been used for preparing of Ru(II) complexes [31]. As can see from Table 3.3, ligand substituents cause considerable variations in the absorption and electrochemical properties. It is clear that phenyl substituents in the 4, 4′, and 4″ positions increase the molar absorption coefficient, as expected on simple theoretical grounds [32]. The substituent effect on the energy of the absorption and emission bands results from a combined perturbation of the LUMO (ligand π^*) and HOMO (metal t_{2g}, in octahedral symmetry) orbitals. The effect on the luminescence quantum yield and lifetime is likely related to the above-mentioned perturbations as well as to the substituent effect on the ligand field strength. In general, (i) both the electron-withdrawing and donating substituents stabilize the Metal Ligand Charge Transfer (MLCT) excited state, with a consequent red shift on the absorption and emission maxima, and (ii) the electron-withdrawing substituents increase the excited state lifetime and the luminescence intensity at room temperature [31].

The $Ru(tpy)_2^{2+}$ complexes are electrochemically active. They exhibit a reversible $Ru^{II,III}$ oxidation process and a variable number of reversible or quasi-reversible reductive ligand-centered processes. Some of the electrochemical data are presented in Table 3.3. The excited state of all these dyes are more negative than −0.9 V versus NHE, that satisfies condition of complete charge injection in the conduction band of TiO_2.

Table 3.3 Photoelectrochemistry characteristics of Ruthenium complexes [31]

Number	Dye	Absorption		Electrochemistry $E_{1/2}$, V	
		λ(nm)	ε (10^3* M^{-1} cm^{-1})		
1.	$Ru(tpy)_2^{2+}$	476	17.7	+1.30	−1.24
2.	$Ru(Cl\text{-}tpy)_2^{2+}$	480	16.0	+1.0	−1.53
3.	$Ru(Me_2N\text{-}tpy)_2^{2+}$	490	15.4	+0.42	−1.90
4.	$Ru(HO\text{-}tpy)_2^{2+}$	485	12.7	+0.73	−1.81
5.	$Ru(EtO\text{-}tpy)_2^{2+}$	485	17.5	+0.74	−1.76
6.	$Ru(ph\text{-}tpy)_2^{2+}$	488	30.0	+0.90	−1.66
7.	$Ru(Cl\text{-}phtpy)_2^{2+}$	490	24.6		
8.	$Ru(HO\text{-}phtpy)_2^{2+}$	496	26.1		
9.	$Ru(MeO\text{-}phtpy)_2^{2+}$	495	24.4		
10.	$Ru(tphtpy)_2^{2+}$	501	38.4	+1.22	−1.19
11.	$Ru(4,4'\text{-}dptpy)_2^{2+}$	495	28.3		
12.	$Ru(6,6''\text{-}dptpy)_2^{2+}$	477	6.85		
13.	$Ru(ttpy)_2^{2+}$	490	28.0	+1.25	−1.24
14.	$Ru(tppz)_2^{2+}$	478		+1.51	−0.88
15.	$Ru(tpy)(tppz)_2^{2+}$	470	20.1	+1.50	−0.95
16.	$Ru(ttpy)(phbp)^{+}$	523	9.96	+0.54	
17.	$Ru(ttpy)(dpb)^{+}$	550	8.25	+0.49	−1.61

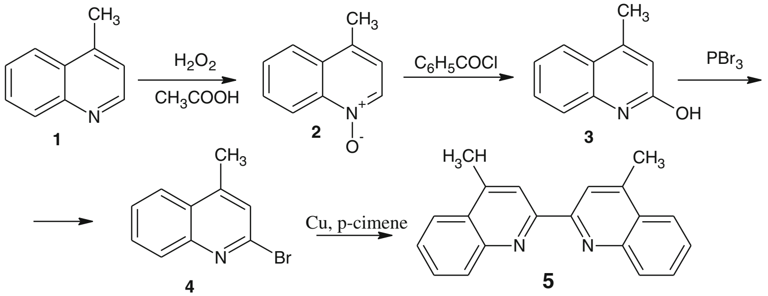
3.3 Synthesis and Characterization of Ligands Based on Bipyridine and Terpyridine (Our Investigations)

3.3.1 Synthesis of 2,2′-Bilepidine Ligand

According to literature, diquinolin complexes have a very high interest to study it in photovoltaic applications [18]. In literature, several methods are noted for the synthesis of 2,2-bipyridinic compounds as ligands, One type of methods was interaction of quinolin with metals in inert gas atmosphere where are obtaining partial hydrogenated isomers of 2,2′-diquinolins, which are oxidized in nitrobenzene and are obtaining diquinolins mix, components of that is depending of metal nature.

In the first method 4-methyl-quinolin was boiled for 8 h with aluminium powder in inert gas atmosphere, activated with $HgCl_2$ [33]. After separation was obtained 8 different isomers in small amounts, that provoke decreasing of yield of target compound 2,2′-dilepidine (7 %).

Other method of synthesis of ligand could be chosen in a longer pathway. Proceeding of 4-methylquinolin (1) was synthesized 2-bromo-4-methyl-quinolinei (4) according to Scheme 1. The synthesis of N-oxylepidine (2) was performed according to the method used by Midjoian [34] with a yield of 55 %. In order to activate the C-2 position of lepidine compound (2) was isomerized and obtained 2-oxilepidine (3), again according to the Midjoian method [35]. The next step of substitution was made according to the Kaslow and Marsh method [36], finally was obtained was 2-brom-lepidine (4) with a yield of 70 %.

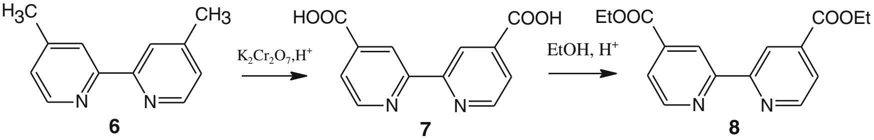


The final step of obtaining 2,2′-bilepidine represents coupling reaction of 2-brom-lepidine with a low active metal, such as Cu. According to the literature that method was also applied to obtain 2,2-bipyridin having a 52–54 % yield [37], but after experience 2,2′-bilepidin was obtained with a yield of 12 % and excessive consumption of the intermediate reactive which motivates to process the proposed methodology in future.

Based on IR and H′-NMR spectra, the presence of compounds (1–4) was demonstrated by the appearance and disappearance of characteristic bands. Compound (2) was demonstrated by the appearance of the absorption band of the oximes group ν (NO) 1,146 cm^{-1}, a methyl group 1,395 cm^{-1}, and aromatic groups of quinolin are in 1,300–1,510 cm^{-1} region. In spectrum of compound (3) disappears absorption band of oximes group and appear –OH group band at 3,190–3,929 cm^{-1} region. Group –OH from position 2 in lepidine also has been demonstrated by H^1-NMR spectroscopy, where the –OH group proton peak observed at 11.28 ppm. Compound (4) was also demonstrated by the disappearance of the absorption band of –OH group and the appearance of *ν* (C–Br) bond at 500–600 cm^{-1}, the aromatic methyl group of lepidine was observed in 1,395 cm^{-1} and quinolin rings at 1,300–1,510 cm^{-1} region. Final compound (5) was demonstrated from H^1-RMN spectrum with appearance of singlet of two protons from C3 position, at 7.8 ppm region.

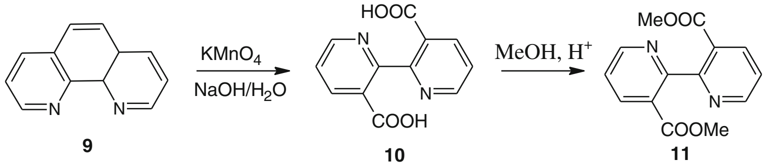
3.3.2 Synthesis of the Ligand 4,4′-Dicarboetoxi-2,2′-Dipyridyl

The aim of this synthesis is the further use of this dye, named N3, as etalon for sensiblisation of titanium oxide (IV) semiconductors. As the starting compound was used 4,4′-dimethyl-2,2′-dipyridyl (6). It was oxidized with potassium dichromate in acid medium according to described method [38]. The reaction was carried out quantitatively (yield 95 %). The obtained 2,2′-dipiridil-4, 4′-dicarboxylic acid (7) was further esterificated in acid solution of ethanol according to described method [39].



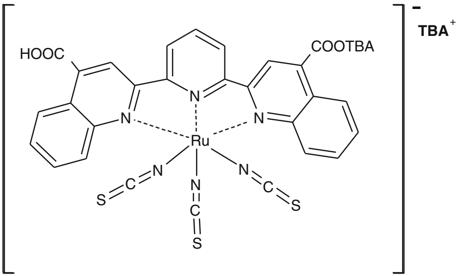
3.3.3 Synthesis of the Ligand 3,3′-Dicarbometoxi-2,2′-Bipyridyl

The bibliographic study [18] showed that is necessary to study new metalorganic chromophore efficient for photovoltaic applications. In order to obtain more accessible ligands was initiated synthesis of compounds 2,2′-dipyridyl-3,3′-disubstituted. The synthesis of acid diethyl ester, 3,3′-dicarbometoxy-2, 2′-dipiridil (11) from the 1,10-phenanthroline (9) was done according to the next scheme.



The synthesis of 2,2′-bipyridyl-3,3′-dicarboxylic acid (binicotinic acid) by the oxidation of 1,10-phenanthroline with alkaline permanganate was first described by Smith and Inglett [40]. The preparation of binicotinic acid by this method has subsequently been reported by several workers [41] with yields varying from 50–85 %. We used here the same simplified preparation of binicotinic acid in good yield (65–80 %) with the elimination of the tedious work-up procedure [42]. The esterification method of nicotinic acid was made in methanol and sulphuric acid solution, refluxed, neutralized, separated and dried in vacuum with approximately 50 % yield like in Dholakia procedure [43].

3.3.4 Synthesis of the Ligand 2,6-bis(4-Carboxyquinolin-2-yl)Pyridine



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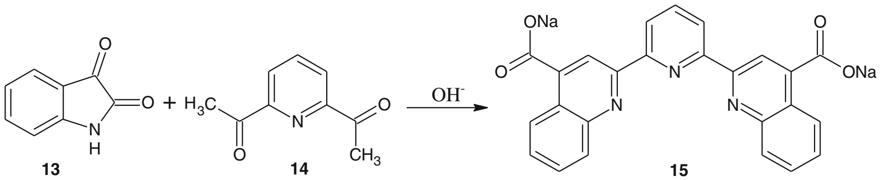
Onozawa-Komatsuzaki report the synthesis and photochemical properties of a new ruthenium complex (12) with a 2,6-bis(4-carboxyquinolin-2- yl)pyridine. This ligand has an extended aromatic structure owing to the existence of two quinoline rings linked with the pyridine ring; therefore, the delocalization and electronegativity of this ligand were expected to lower the energy of the π^*-level and extend the absorption envelope of 12 well into the IR region [44]. This complex exhibited better light-harvesting properties and higher absorbance than those observed for black dye in the near-IR region. DSCs sensitized with 1 showed 35 % Incident-Photon-to-electron Conversion Efficiencies (IPCE) at 900 nm; this is the highest IPCE value reported for ruthenium–polypyridyl complexes in the near-IR region. This demonstrated light-harvesting efficiency makes 12 an attractive candidate as a high-performance sensitizer under near-IR irradiation.

Compound (15) was prepared through a Pfitzinger reaction of isatin (13) and 2,6-diacetylpyridine (14). Simply stirring the reactants in the presence of sodium hydroxide results in the formation of sodium salt (15). As is the case with carboxylate derivatives of related heterocycles, purification of (15) can be troublesome due to its insolubility in all acids, but soluble in bases [45].

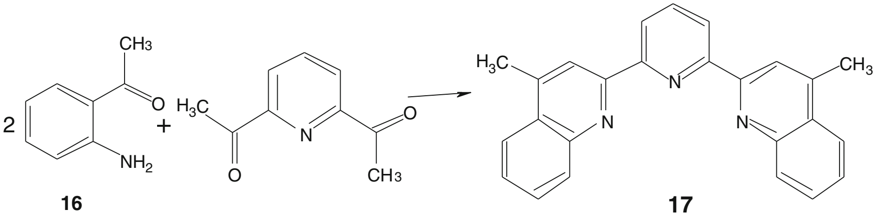


13 **14** **15**

C^{13}-NMR was more useful, than proton NMR in the characterization of (15). While the proton NMR contained only aromatic protons the signals were extremely broad and detailed structural information was lacking.

3.3.5 Synthesis of the Ligand 2,6-Bis(4-Methylqinolin-2- il)Pyridine

The Friedlander condensation is an extremely useful and versatile method for the direct construction of a quinolin ring [46]. The condensation of an aromatic o-aminoaldehyde with an enolizable ketone proceeds directly with the loss of two molecules of water. By varying the nature of the aromatic ring, a variety of annulated qunolines can be prepared. Guiding by this method, at the interaction of o-aminoacetophenone (17) with 2,6-diacetilpyridine was obtained 2,6-bis(4-methylqinolin-2-il)pyridine.



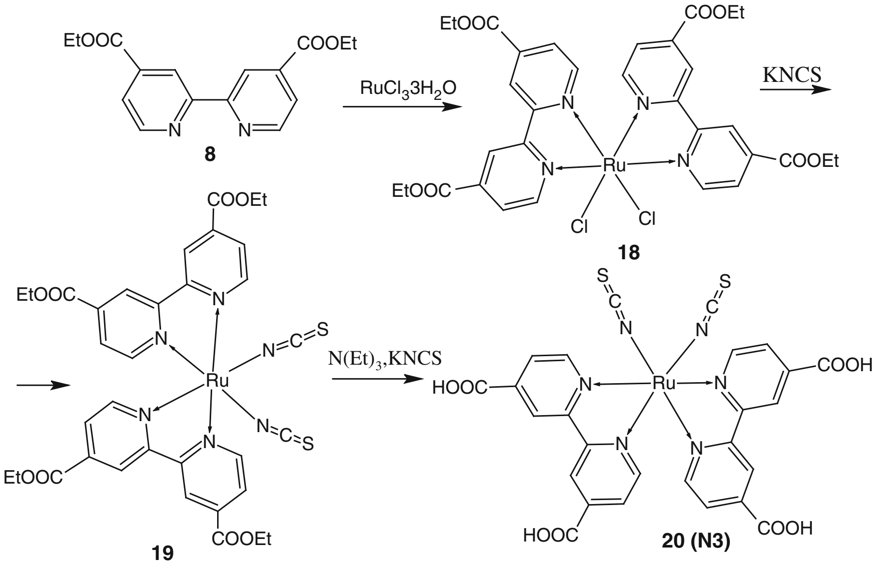
16 **17**

Its structure was demonstrated by IR, C^{13}-NMR, H^1-NMR, COSY-45 but to say that was formed quinolin ring in 2-C position of pyridine was easily by H^1-NMR, where was observed a singlet at 8.60 ppm of 2 protons in C^3 position of quinolin rings.

3.4 Complexation of Obtained Ligands

3.4.1 Synthesis of the Etalon-Dye N3

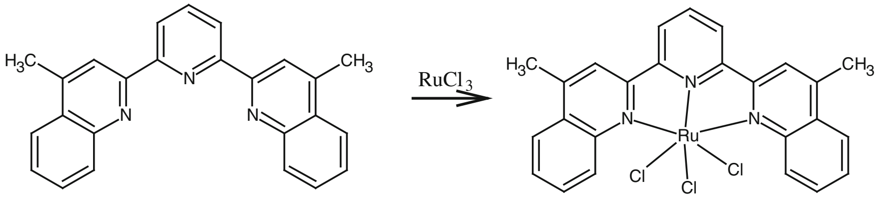
The next scheme shows the stages developed by Grätzel group of researchers [47] for the synthesis of this complex N3. Substances interim and final products were characterized by spectroscopy (^{13}C, ^1H) NMR. This compound is very good known in literature and was discussed before.



3.4.2 Complexation of 3,3′-Dicarbometoxi-2,2′-Bipyridyl

After literature investigation [43, 47] was concluded that complexation methods of 4,4′-disubstituted-2,2′-bipyridyn ligands with Ru^{III} can be applied for complexation of 3,3′-disubstituted-2,2′-bipyridyn ligands. The last step was made in the same procedure described higher (p. 3.4.1).

3.4.3 Complexation of the Ligand 2,6-Bis(4-Methylqinolin-2- il)Pyridine



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Ligand 2,6-bis(4-methylqinolin-2-il)pyridine was complexed with Ru(III) and was observed that it has peak in visible region of spectrum at 530 nm, which can be used in photocatalytical water splitting processes (Fig. 3.4).

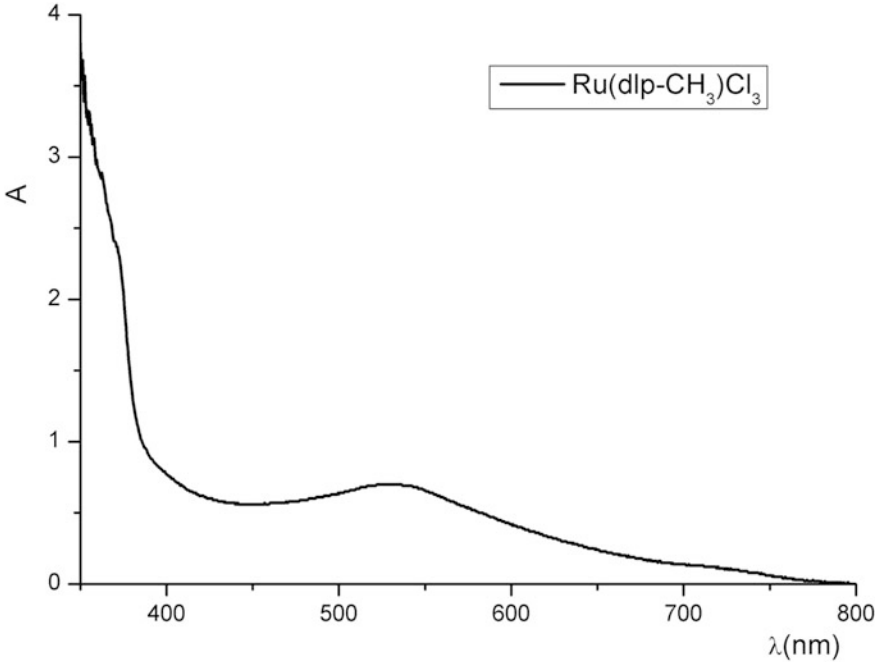
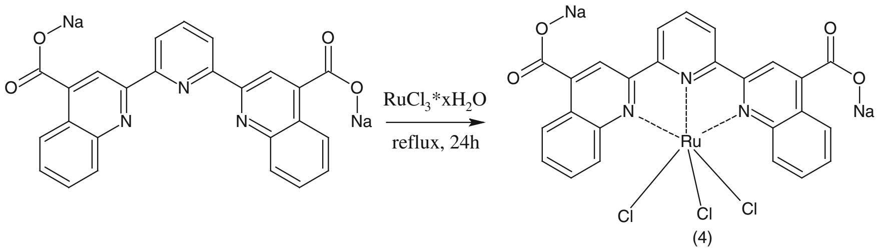


Fig. 3.4 Absorption spectrum of Ru(dqp-CH$_3$)Cl$_3$ complex (22)

3.4.4 Synthesis of the Complex Disodiu-2,6-Bis(4-Carboxilat-Quinolin)Pyridinat of Ruthenium (III)



(4)

After refluxation of ligand 2,6-bis(4-carboxyquinolin-2-yl)pyridine (15) with ruthenium cloride it is obtained complex disodiu-2,6-bis(4-carboxilat-quinolin)piridin rutenat (III) (Ru(dqp)COONa) (23). From UV-Vis spectrum it is observed an large absorbtion peak (690 nm) in UV and visible region (Fig. 3.5).

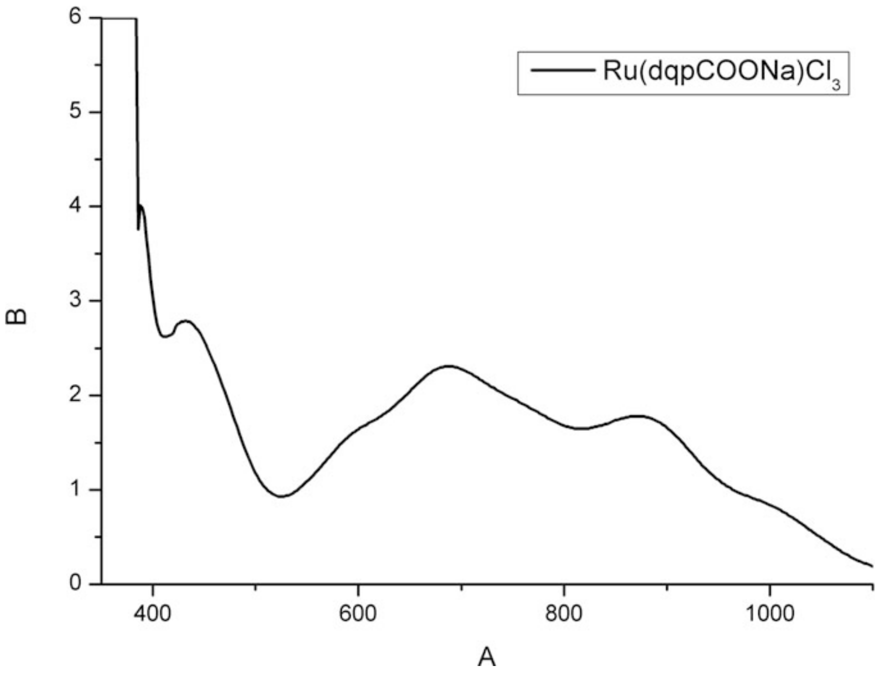


Fig. 3.5 Absorbtion spectrum of Ru(dqp-COONa)Cl_3 complex

3.5 Metalo-Phorphirins Complexes

The use of porphyrins as light harvesters in various solar cells is quite reasonable because of an intense absorption in the Q band at low energy as well as in the Soret band at higher energy. On the other hand, numerous attempts to use porphyrins in conversion of solar energy into chemical or electrical energy represent an attempt to mimic the photosynthetic systems found in plants and some bacteria. Chlorophylls (Chls)—the extremely important molecules in natural photosynthesis which absorb light and transfer that light energy by resonance energy transfer in the Photosystems I and II, are compounds based on the modified chlorine macrocycle (dihydroporphyrin) (Fig. 3.6).

In 1993 it was firstly described [48] Chl-*a*/TiO_2 couple in a DSSC. Using chlorophyll *a* and compounds obtained by its chemical modification (pheophorbide *a*, Mg-chlorin e_6, H_2-chlorin e_6, Cu-chlorin e_6 and Cu-2-α-Oxymesoisochlorin e_4) IPCE of up to 70 % were obtained. Maximum overall energy conversion efficiency of 2.6 % (under simulated sunlight illumination) was obtained for chlorophyll *a*.

Using a derivative of chlorophyll *a* (Fig. 3.7) another group [49] has obtained an improved overall energy conversion efficiency of 3.1 %. By adding carotenoids as a conjugated spacer they achieved optimization of the overall energy conversion efficiency up to 4.2 % [50].

Fig. 3.6 Structure of chlorophyll a [48]

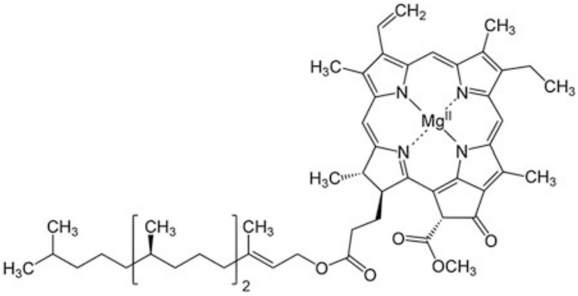
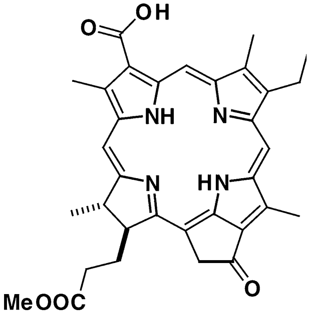


Fig. 3.7 Methyl 3-carboxy-3-devinyl pyropheophorbide a [49]



The influence of carotenoid moiety was investigated by the same group [51]. The authors concluded that introduction of carotenoid moiety to the pheophorbide molecule may result in an electron transfer and singlet-energy transfer from the carotenoid to the chlorin moiety and suppression of the singlet–triplet annihilation reaction. As a result the performance of the cell was enhanced from 1.4 to 1.8 %.

The maximum overall energy conversion efficiency (η) was further improved to 6.5 % by extension of π-conjugation length along the Q_y axis (Fig. 3.8) [52]. This improvement can be explained by two factors: (1) concentration of the electron density in the Q_y direction on the LUMO + 2 for electron injection and (2) better Q_y absorption together with a smaller E_{ox} value for light-harvesting.

Using the knowledge accumulated during the last years a series of new chlorin based compounds was obtained (Fig. 3.9) [53].

The overall energy conversion efficiencies for all DSSCs sensitized with chlorin based dyes exceed 6 % and reach 8 % for dodecyl trans-3^2-carboxypyropheophorbide *a* (**3**, Fig. 3.9).This is the highest η value among chlorophyll and porphyrin sensitizers published to date.

Another approach to the cyclic tetrapyrrole molecules for DSSCs sensitizing is the obtaining of synthetic porphyrins. The porphyrin sensitizer with the highest overall energy conversion efficiency ($\eta = 3.0$ %) until 2004 was tetra(4-carboxyphenyl)porphyrin (Fig. 3.10) [54]. The relatively low η value of the sensitizer was explained by the highly symmetrical structure and aggregation of porphyrin molecules.

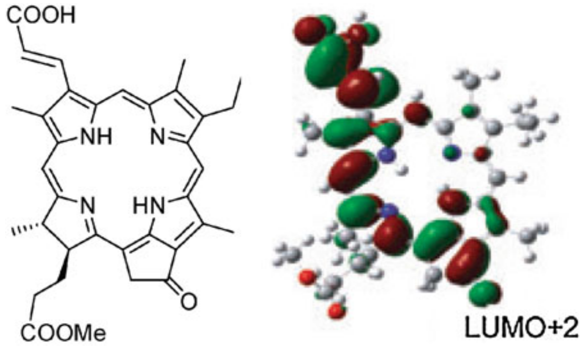


Fig. 3.8 Methyl trans-32-carboxypyropheophorbide a and its LUMO + 2 molecular orbital [52]

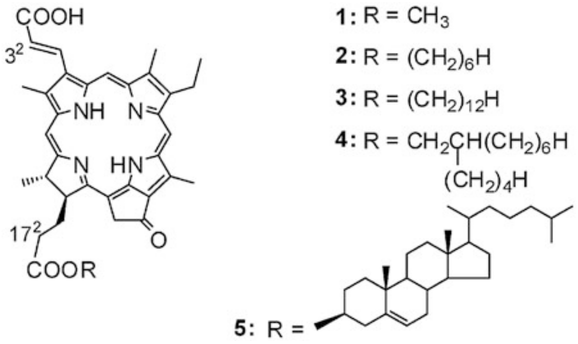


Fig. 3.9 Chemical structures of chlorin based sensitizers [53]

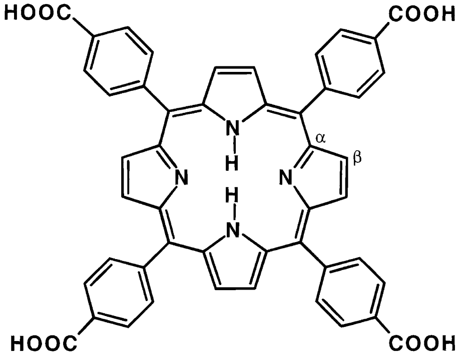


Fig. 3.10 Structure of tetra(4-carboxyphenyl)porphyrin [54]

By unsymmetrical π-elongation of the porphyrin and connection of the linker moiety to the β-position of the porphyrin the Japanese researchers [55] designed a naphthyl-fused zinc porphyrin with a conversion efficiency of 4.1 % (50 % higher comparatively to the unfused porphyrin reference).

In a more recent paper researchers from Taiwan synthesized a *meso*-substituted porphyrin sensitizer with Donor-π-Acceptor configuration (Fig. 3.11) [56].

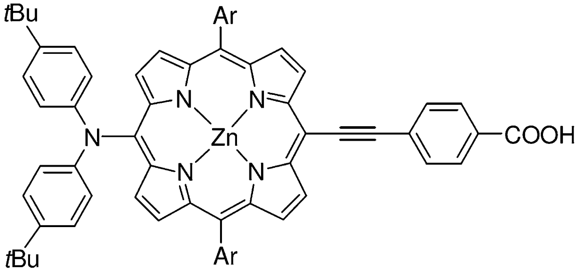


Fig. 3.11 Zinc(II) 5,15-Bis(3,5-di-tert-butylphenyl)-10-(bis(4-tert-butylphenyl)amino)-20-(4-carboxylphenylethynyl)porphyrin [56]

This molecule shows very high η value of up to 6.0 % under standard global AM 1.5 solar conditions, which is similar to *cis*-Ru(dcbpy)$_2$(NCS)$_2$ dye (**N3**) under the same experimental conditions. It clearly shows that porphyrins can compete with traditional Ru-polypyridil dyes.

Many groups have studied the influence of donor and acceptor moieties on the photosensing properties of sensitizing dyes. Hiroshi Imahori, Shunichi Fukuzumi and co-workers have obtained molecular photovoltaic devices with the porphyrins and fullerenes as the main building blocks [57]. Fullerenes is an electron acceptor with small reorganization energies during the electron-transfer reduction. The porphyrin-fullerene dyads with sulfur-containing group were adsorbed on the gold surface. As a result the charge separated state is formed (Fig. 3.12) and the photocurrent is generated.

The photocurrent intensity in Au/2/MV^{2+}/Pt device was enhanced fivefold compared to that in the porphyrin device without C_{60}. This clearly shows that introduction of donor group in the photosensitizer may be useful for optimization of photosynthetic systems mimicking nature. These dyads were extended to ferrocene (Fc)-porphyrin (P)-fullerene (C_{60}) triads (Fig. 3.12).

The introduction of ferrocene group leads to Fc$^+$-P-C_{60}—charge-separated state as a result of photoinduced electron transfer (Fig. 3.13). The internal quantum yields of the photocurrent generation for these systems are one of the highest for the donor–acceptor linked molecules at monolayer-modified metal electrodes and in artificial membranes.

The same group has developed photosynthetic system based on boron-dipyrrin (bodipy) and Fc-porphyrin-C_{60} triad (Fig. 3.14) [58]. The boron dipyrrin thiol was chosen as a light-harvesting molecule (λ_{max} 500 nm, $\varepsilon \sim 10^5$ M^{-1} cm^{-1}) which enhance the absorption of light in green and blue region. The mixed dyes were tuned so that bodipy emission ($\sim$510 nm) overlaps with the absorption of the porphyrin Q bands (500–700 nm) and an efficient singlet–singlet energy transfer from bodipy moiety to the porphyrin moiety leads to efficient photocurrent generation. But, in these systems the porphyrin exited state is strongly quenched by the gold surface. That is why gold surface was replaced by indium tin oxide (ITO) and as a result the electron injection from P* to fullerene was achieved, without quenching by the ITO surface. The internal quantum yields obtained by Hiroshi Imahori and Shunichi Fukuzumi group reach 50 %, however the power-conversion

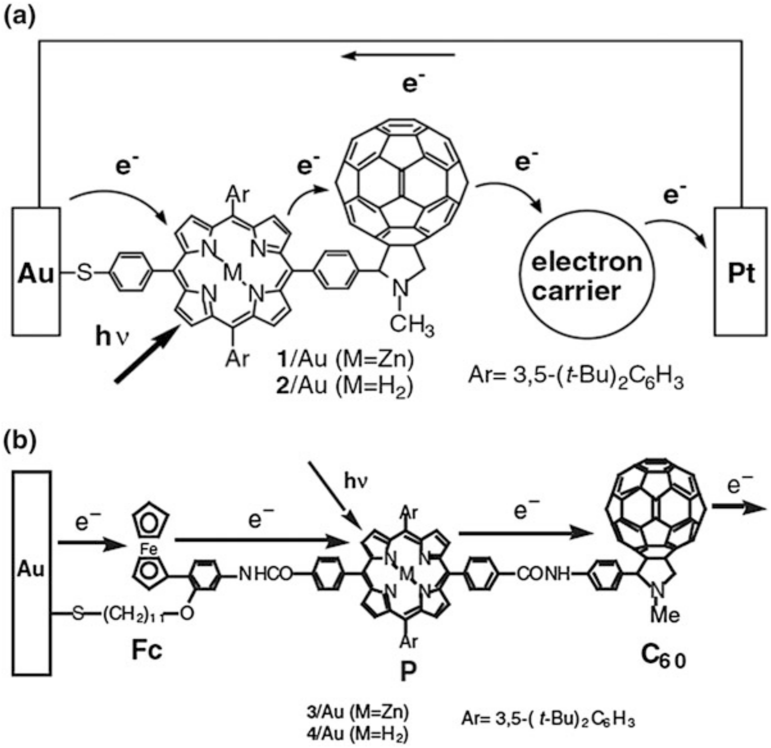


Fig. 3.12 **a** Photoinduced electron transfer at gold electrodes modified with self-assembled monolayers of porphyrin-C60 dyads [57] **b** Photoinduced electron transfer at gold electrodes modified with self-assembled monolayers of Fc-porphyrin-C60 [57]

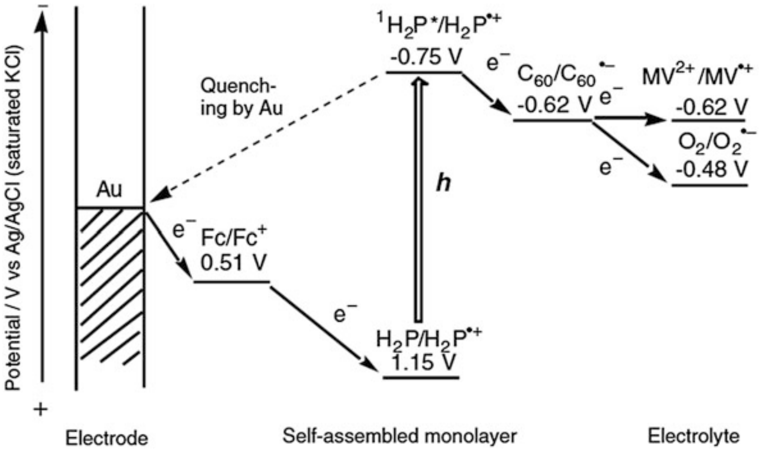


Fig. 3.13 Photoinduced electron transfer at gold electrodes modified with self-assembled monolayers of Fc-porphyrin-C60 alkanethiols [57]

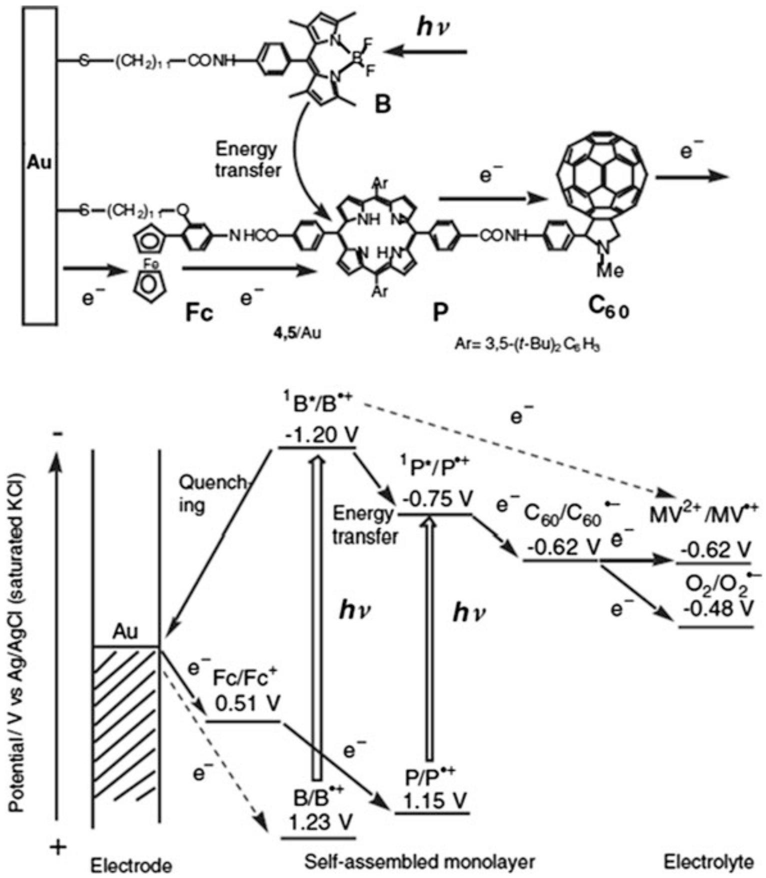


Fig. 3.14 Photoinduced energy transfer and at gold electrodes modified with mixed self-assembled monolayers of ferrocene-porphyrin-C60 alkanethiol and boron dipyrrin thiol [58]

efficiency of these systems (~1 %) is still lower than that of typical inorganic solar cells.

Another approach for design of synthetic porphyrin based dyes is introduction of anchoring, π-extending moieties at the β-positions. The Officer and coworkers have designed a series of β-susbstituted porphyrins for sensitization of TiO_2 surfaces [59]. The Cu porphyrins and those with phosphonic acid as anchoring group showed low η values, but the Zn porphyrins with β-susbstituted ethenylbenzoic acid as anchoring moiety (Fig. 3.15) give high overall energy conversion efficiency of up to 4.8 %. It is to be emphasized that the introduction of *m*-methyl substituents on the *meso*-phenyl groups give rise with 16 % of η value (4.11 → 4.8 %), probably by preventing π–π stacking between porphyrin molecules.

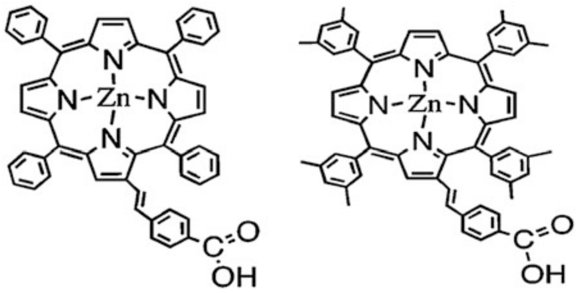


Fig. 3.15 Zn porphyrins with *β*-susbstituted ethenylbenzoic acid as anchoring moiety [59]

In the [60] is described synthesis of a series of porphyrins *β*-substituted with carboxylate anchoring groups (Fig. 3.16) for sensitization of nanocrystalline TiO_2 films.

The Incident Photon to electron Conversion Efficiencies (IPCE) of the obtained porphyrins reach 85 % (Fig. 3.17). Among the reported porphyrins, the porphyrin **1** shows the best conversion efficiency of 5.2 % under standard AM 1.5 sunlight. By analyzing obtained results can be revealed the influence of the anchoring group on the photovoltaic properties of the photosensitizer.

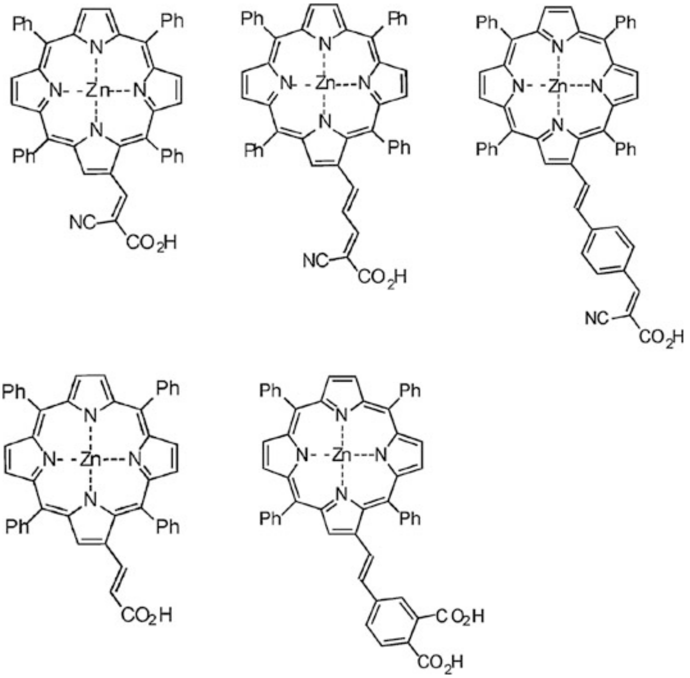


Fig. 3.16 *β*-Modified porphyrins 1–5 [60]

Fig. 3.17 Photoaction spectra of porphyrins 1–5 [60]

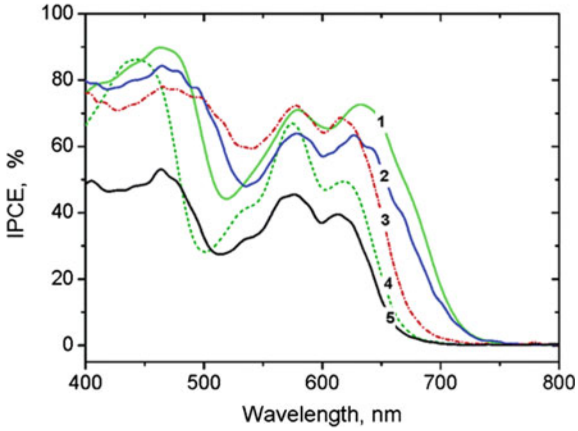
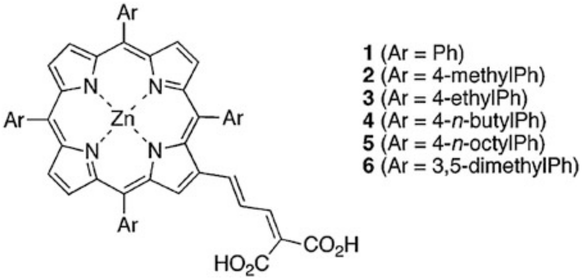


Fig. 3.18 *β*-Modified porphyrins 1–6 [61]



In the following work [61] the same group has changed the aryl substituent in *meso*-position of porphyrins (Fig. 3.18) to determine its influence on the IPCE of the dyes.

The porphyrin **2** of this set shows high IPCE values (Fig. 3.19) and the overall conversion efficiency of 7.1 % (3.6 % for solid state cell) under standard global AM 1.5 solar conditions, which is the best η value among the present and reported synthetic porphyrin sensitizers for DSSCs. However, all of the dyes **1–6** exhibit efficiencies ≥ 5 %. It is indicating that the nature of the substituents of the aryl group is not a major factor in determining photosensing properties of dyes.

Conclusion: Porphyrins of different metals with substituents in meso and beta-pyrrole positions are the perspective dyes for DSSC devices.

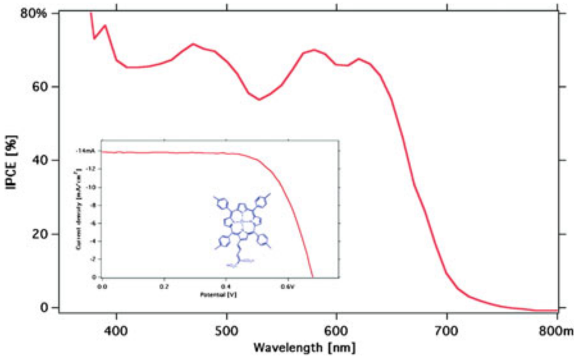


Fig. 3.19 Photoaction spectrum of porphyrin 2 [61]

3.6 Synthesis and Characterization of Tetra (Ferrocene) Porphyrins (Our Investigations)

Pd and Cu tetra(ferrocenyl) porphyrins were obtained in our laboratory (Fig. 3.20). Their UV–Vis spectra (Fig. 3.21) show very high absorption in the entire visible region of light. A new band ($\lambda_{max} = 475$, 480 and 486 nm for free-metal, Pd (II) and Cu (II) tetra(ferrocenyl) porphyrins, respectively) appeared in comparison with tetra(phenyl) porphyrins.

As a result these porphyrins show high harvesting properties for 300–700 nm spectrum of light.

The Cyclic voltammetry (CV) spectra (Fig. 3.22) of the synthesized porphyrins show reversible processes in the potential window −2 to +1 V in THF and DMF vs Ag/AgCl.

Two reversible peaks in the negative (reductive) potential region were attributed to the one electron reductions of the porphyrin ring. The quasireversible peak in the positive (oxidative) potential region was attributed to the oxidation of the four ferrocenyl moieties. The reduction of the obtained ferricinium moieties shows a wave with a very large area which was attributed to the desorption processes of the positively charged species deposited on the electrode surface.

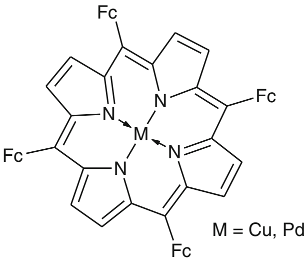


Fig. 3.20 Tetra(ferrocenyl)-porphyrine of Cu and Pd

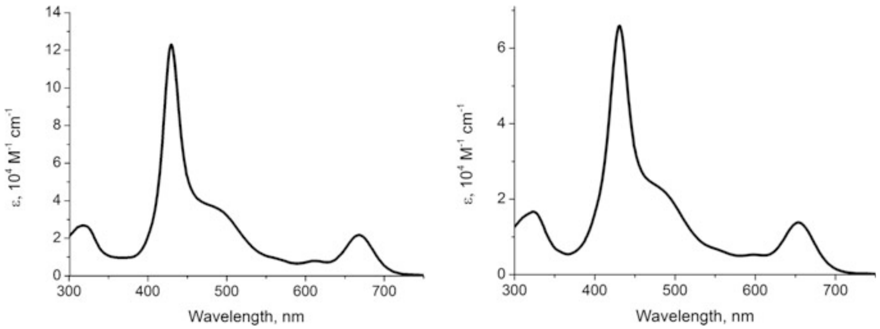


Fig. 3.21 The UV–Vis spectra of tetra (ferrocenyl)-porphyrine of Cu (*left*) and Pd (*right*) in THF

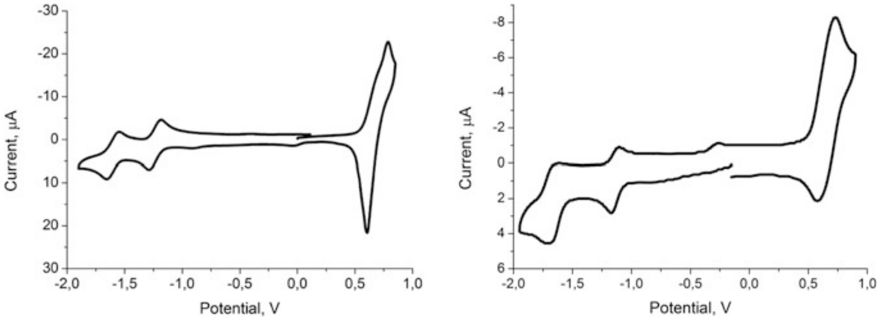


Fig. 3.22 CV spectra of Cu tetra (ferrocenyl) porphyrin in THF and Pd tetra (ferrocenyl) porphyrin in DMF (0.2 M TBATFB) at a glassy carbon working electrode. Scan rate = 100 mV s^{-1}

The obtained results indicate that meso-ferrocenyl porphyrins have potential to be used as molecular sensitizers for harvesting the sunlight.

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Chapter 4
The Opportunity of Recognition of the Right to Water as a Fundamental Human Right

Ion Guceac and Igor Serotila

Abstract Although the issues relating to human rights and liberties are one of the oldest, they remain one of the most researched themes in the contemporary period, the research being conducted by diverse scientists and scholars, especially by those pertaining to jurisprudence. The increased attention human rights are granted is due to the fact that these rights are established in numerous and various sources of law, which often are stated in an evasive language to the reader. We can conclude that one of the main priorities of the scholars of legal sciences is to interpret and make known to each individual the correct meaning of these rights.

Keywords Human rights · Constitutionalism · Water rights · Right to water

The conceptualization of fundamental rights resides in the fact that these rights are subjective, representing a faculty of a person to do or not to do something, privilege bestowed on to him by law, pursuant to this the holder of the right can carry out a certain conduit, can claim protection of his right against third parties in order to capitalize a legitimate interest. An important particularity of fundamental rights is that these rights are established in the supreme law of a state, as is a constitution, evidence that states the essential character of these rights and their abundant protection.

Although contemporary international law as well as national law is gifted with a large variety of human rights, doctrine and jurisprudence is signaling a reanimation process for human rights. An eloquent example of the evolution of the legal institution of human rights is the establishment of the right to water as a new fundamental right, an indispensable component of life and human dignity.

Nevertheless, in order to ensure the complete and effective achievement of the human right to water and to establish clear and compulsory obligations to

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governments to satisfy minimal quantities of water, this right has to be acknowledged explicitly and clearly defined. International normative regulations in the matter of water resources have found their purpose in the declaration of the right to water as a fundamental right. The solemnity was instrumented by the United Nations Organization by means of Resolution A/RES/64/292 on the human right to water and sanitation [1].

Simultaneously, it is necessary to nominate regulation that oriented the legal evolution of the human right to water as is the Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy, which substantiate water as a heritage which requires protection and needs to be treated as such and not as a commercial asset. The aforementioned directive fortifies the normative content assembled by the General Commentary nr.15 of the Covenant on economic, social and cultural rights established by the UN Committee on economic, social and cultural rights. The general commentary tends to clarify the content of the rights incorporated into the Covenant, of potential breaches of those rights as well as obligations of signatory states.

The fundamental right to water is an integral part of international law. The supremacy of international law to that of the national is uncontestable; this reality is proven by the provisions of article 8 of the Constitution of the Republic of Moldova which establishes the state obligation to respect the UN Charter and signed treaties, to establish relations with other states conducting by unanimously accepted principles and norms of international law [2]. Therewith, as there are no international authorities who have the responsibility to ensure the proper application of rights relating to water resources, states, individually have to ensure the respect of such rights [3]. In our point of view a mean to incorporate the right to water in a national legal order is to root it by constitutional means. It is known that one of the concerns of national constitutionalism is the legal institution of human rights. In the national constitutional system, this institution has been established in a modern conception far later than the constitutional practices of other states. This circumstance does not serve as a detriment to the state of the Republic of Moldova; on the contrary the constituent legislator of 1994 has included in the Constitution the whole spectrum of human rights and liberties which by that time were proclaimed by international documents, referential to this domain. Moreover, according to article 4 of the Constitution, provisions on human rights and liberties will be interpreted in accordance with the Universal Declaration of Human Rights of 1948; with covenants and other treaties of with the republic is part of. If a certain discrepancy between covenants, treaties of which Moldova is part of and regard fundamental human rights and national law arise, international sources will have priority [4].

Viewing the right to water by contemporary constitutional means, it is relevant to observe the fact that the effectiveness of its application is conditioned by the efforts of both the international community and national legislature. In recent cases, direct applicable law, which ensures the implementation of any international treaty, is the national law. In this jurisdiction, the legislative process as well as the law hierarchy is established by constitutional arrangements. Traditionally, national law of a state may include normative provisions regarding the legal regime of water (as an example: pollution control or licensing activity). These provisions, excluding the formal legal framework, contain regulation on water rights [3].

It is natural that Moldova has viable legislation on water. Such legislation is: the Water Code [5], Law on the protection of water in zones, strips, rivers and water basins [6], Law on hydrometeorological activity [7] and Law on drinking water [8]. One of the most important legislative instruments on the matter of water was established by the ratification of the Protocol on water and health of the 1992 Convention on the protection and use of Transboundary Watercourses and International Lakes, signed on the 10th of March 2000 [9]. Currently the legal framework on water is composed of 24 documents, 14 of which were adopted in the past decade. It is with regret that we conclude that water legislation of Moldova is limited as opposed to the EU legal framework which consists of 682 documents [10].

The high disparity can be considered a hindrance in the fulfillment of the assumed commitment of Moldova to the European Union and specifically the achievement of compatibility of national legislation with the European one, by means of harmonization.

Moreover, it is important to mention that the scientific community strives to enrich and improve national legislation in matters regarding sustainable development, water resource management and access to safe drinking water, implementation of modern wastewater treatment, discharge and reutilization technologies and irrigation as well. An example of such actions is the State Program "Research and Management of Water Quality". Under the state program, actions were undertaken to create a legal framework for the proper management, protection and use of water in Moldova, based upon evaluation, planning and participative decision making process. Other goals of the program is to establish the right to use water and to promote investments in water infrastructure; establish mechanisms of protection of water quality, prevention of water degradation, protection and restoration of water resources, convergence with international measures of water management; establishment of a legal framework for the bilateral and multilateral cooperation on matters related to water resources.

One of the essential features of constitutionalism in Moldova is the promotion of the concept of rule of law (article 1 of the Constitution). This concept implies the supremacy of law and enforcement of certain rigors in regulation of social relations. The constitution becomes the primary source of law in the national law system, thus most important values and attributes are regulated by this source. It is to note that one of the primary functions of the Constitution of the Republic of Moldova is to enshrine rights, liberties and fundamental duties of the citizens, directing relations between them, between citizens and public authorities. Therewith, the legal framework subordinate to the Constitution is created in respect of the basic law and is uniform. Considering this, the legal framework becomes the extension of the constitutional provisions. The relevance of the aforementioned is based on the fundamental principle of lawmaking and general mandatory conditions pertaining to a legal act, which establish that a legal act has to conform to the provisions of international treaties of which Moldova is part of, unanimously acknowledged principles and norms of international law. The legal document must conform to **constitutional provisions** and be in accordance with existing legal documents, with the codification and unification systems. The protection of **rights, liberties, legitimate interest of citizens,** equality and social equity, compatibility with EU legislation is a compulsory condition of any legal document [11]. From these provisions we can foresee the Europe-oriented direction of Moldova, the tendency to enshrine European values in the national legal framework.

In order to constitutionalize this right water it is necessary to create a conceptual rationale of this right. Thus, appealing to the General Commentary Nr.15 of the UN Committee on economic, social and cultural rights, articles 11 and 12, we subtract fundamental provisions on the right to water [12].

The primary element of the right to water is the correlation between access to water and sufficient quantity necessary for life, human dignity and health. This characteristic cannot be interpreted in a restrictive manner, due to the simple reference to volumetric quantities and applied technology. Water should be treated, primarily, as a social and cultural asset and not as economic one. The realization of rights relating to water should be sustainable, ensuring future generation use.

As aforementioned, the Protocol on water and health of the Convention on the protection and use Transboundary Watercourses and International Lakes, signed by Moldova in 2000 is extremely important [9].

We should recognize the effort of Moldova to fulfill the assumed commitments in order to improve water quality. Starting from august 2009, by means of the Implementation Facility Mechanism of the Protocol on water and health, created near the Mixt Secretariat of the Protocol WHO/EEC UN, Moldova is the beneficiary of financial and methodological support for the drafting, in accordance to article 6 and 7 of the Protocol, of target indicators and of implementation plans of the Protocol in Moldova. Currently, with support from the Government of Switzerland through the Swiss Agency for Development and International Cooperation and some international experts, national target indicators are being drafted for the implementation of the Protocol. After the drafting process is finished, these indices will be publicly discussed with all actors, including civil society. After their enactment, these indices will be achieved gradually, in concordance with national deadlines. Concurrent, in order to coordinate this activity a Coordination Group has been established, comprised of interested parties, approved by a joint ordinance of the ministers of health and environment [13].

Analyzing the national legal framework, the efficiency of water policy implementation and the research in these matters, it is necessary to realize that in lack of a constitutional provision on the right to water the development and sustainable management of natural resources as well as ensuring all citizens unconditional access to these resources is practically beyond reach, if we establish that water is indispensable to any form of life.

Arguments that support the aforementioned are related to various aspects, one of which is **poor water quality**. The necessity to strengthen the legal framework around the right to water in Moldova is conditioned by water quality. The quality aspect of water is vaguely regulated in national law, the accent being set on dominantly on commercial water use. Therewith, it is relevant to point out that the population of Moldova is supplied with drinking water mainly from local sources (wells, springs etc.). According to recent research, water quality from these sources year to year is degrading is maintaining at an under par level, manifesting a threat to population health. One study of the matter has shown that 58.9 % of all local sources of water indicate a high chemical value of nitrates [14].

From a regional, socio-economic point of view these indices vary in the spectrum of significantly high contamination, from a 51.6 % contamination in Chisinau to a 80.3 % contamination in Gagauzia.

As a result of monitoring of these indices, in recent years, a constant high pollution level is revealed in local water sources and those measures directed to pollution reduction and water quality improvement do not prove to be efficient.

Chemical pollution of water in local sources is dominant in the northern and central region.

According to results obtained in this study, it was established that the population exposed to the influence of pollutant factors from water is around 1.9 million people. The share of people using non-complying water sources is 72.7 % in the central and northern region, including Chisinau with 3.6 %.

One of the reasons behind water quality degradation as well as ineffectiveness of the measures undertaken is that the national legal framework does not establish clear responsibilities to authorities to ensure qualitative and quantitative access to water. Concurrently, it is relevant to strengthen user responsibility, to those groups of users who utilize water in commercial activities. These responsibilities need to be crystallized according to the unanimously acknowledged principle of international law – **the polluter pays**.

Our tentative to constitutionalize the right to water is empowered by the experience of other states in dealing with such issues. An example of an attempt to constitutionalize the right to water can be found in Belgium. Being a federal state, Belgium is divided into three parts: Flamandia, Wallonia and Brussels region. In all those regions, strong legislation on water is enforced and in order to achieve the Millennium Development Goals (MDG), on issues relating to poverty, public health, reduce mortality among women and children it is attempted to constitutionalize the fundamental right to water. This right, in a Belgian envisage, is an instrument to achieve proposed targets. In 2005, federal government has adopted a resolution stating that access to drinking water is a fundamental right of a person, which should be included in the constitution [15]. Some relevant rationale must be mentioned:

1. Water is indispensible for life and in small quantities it can affect the level of development of a state, thus access to water is a stringent problem for underdeveloped states.

2. Privatization of water objects will not produce positive effects and a strong possibility of tax increases is persistent. High taxes impose a threat on water accessibility and quality.

The text of the resolution also enables a primary role for international institutions, such as European Parliament, which has stated in favor of non-privatization of water objects. The resolution addresses water issues and proposes constitutional amendment by adding the right to water as a fundamental human right.

Concurrently, the importance of identification and respect for state guarantees and responsibility in achieving this right is also found in this resolution. Currently, according to MDG, Belgium is showing perfect indices on share of population using improved water sources and share of population using improved sanitation services [16].

In an ample view, the human right to water exists without any legal validation, in case we admit that water is vital for life and is the sole basis for the existence of human rights is the existence of human beings.

An eloquent example of combating water scarcity is the Constitution of South Africa. This document was enacted in 1996. Among essential elements, the constitution ensures the right to life and dignity, the right to a healthy environment and the right to water [17]. The South African constitutional framework has enabled government by means of the Department of Water Affairs and Forestry to draft and enact a series of normative documents and policies which strengthen constitutional order, a relevant example is the National Water Act, enacted on 20th of August 1998 [18]. A concurrent analysis of constitutional provisions and the aforementioned document can open up the view on the South-African legal framework which has necessary instruments to guarantee access to safe drinking water, to be responsible for the protection of this right as well as to initiate consistent reforms in order to implement a sustainable water policy in the benefit of society.

All provisions of aforementioned laws are directed towards improving water quality. It is remarkable that by a joint effort of government and society to strengthen national legal framework has brought impressive results. According to MDG, share of population with access to improved water sources has risen from 83 % in 1990 to 91 % in 2011. Regarding sanitation, share of population which uses improved sanitation services has risen as well from 69 % in 1990 to 77 % in 2011 [16].

The experience of the African states, considering geographical positioning, is tied to water issues and progress has been encountered not only in South-Africa. Ethiopia, in its constitution, enacted in 1995, establishes in Chap. 10 the title of principles and objective of national policies and consequently article 90 relating to social objectives mentions the following: policies, in the limit of natural resources, will be oriented towards ensuring all Ethiopians with access to education and public health, **safe drinking water**, shelter, food and social security [19]. After the constitutional referendum in Kenya on the 4th of August 2010 by a sweeping majority of 67 % has voted upon the enactment of a new constitution. This event is relevant due to the fact that among all essential provisions the new Kenyan constitution establishes the right to water as a fundamental human right, incorporated into the category of social rights, guaranteed by state [20]. Thus, the constitutional guarantee of the right to water strengthens national legal framework and enables the possibility to prioritize water issues, which according to MDG are poor. Share of population to safe drinking water is 59 % [16].

We consider the experience of the African state meaningful and viable due to the fact that these states are always faced with water scarcity issues; this experience is beneficial both to the international community and Moldova. International efforts to improve water quality and combat water related issue are measured by the MDG, which at section 7, Ensuring environmental sustainability sets out target goals to cut by half by 2015 the share of population without access to safe drinking water and sanitation. Concurrently it is worthwhile to point out that the constitutional substantiation of the right to water in those states opened to such opportunity can facilitate these processes as well establish definite responsibilities to state authorities towards the people, the holder of sovereignty.

The impact of national water law on international law can be deduced by consulting national constitutional constructions as well as ratification instruments for the treaties the state is open to. One of the most viable instruments available is the Protocol on water and health of the Convention on the protection and use Transboundary Watercourses and International Lakes. In the absence of sources that will develop the fundamental right to water we con not converge to a state of involution of sustainable water management as well as partially guarantee access to drinking water, on the contrary it is necessary in all cases to develop national law on water both doctrine and practice.

Constitutional experience of states is an important component in the formation of international practices. Guarantee and protection of a fundamental right by means of the constitution represent an advantage towards the fulfillment of crucial objective such as establishing the rule of law or European integration.

The realization of the right to water cannot be perceived separately from the constitutional protection of life, physical and mental integrity, a sufficient reason for the extent of the development of the right to water as means of protection of a person's life and health. The connection between human and water is incontestable and is due to the connection of humans to the natural environment, their habitat. In a wider perspective, the right to water concerns man and natural elements which surround him to an extent that both form an inseparable whole. Concurrently, the right to water should be perceived as a qualitative right. Accesses to water resources enable the balanced development of the person.

The guarantee of the right to life, the right to physical and mental integrity can be affected or threatened or even become inoperative in situations such as pollution or accidents with devastating effects to water. As an example to this we can reference to events occurred in Hancesti, where devastating floods ravaged the region. Likewise, we can mention the drinking water issue in Mingir, where after the construction of an aqueduct, the quality of water has degraded to an extent that it became undrinkable.

The category of arbitrary ways to end life should include all actions and activities which as a consequence lead to environmental degradation, especially water. The responsibility to protect is persistent to all natural persons as well as to the state [21]. This responsibility is directed toward the respect of the right to life of another by interdiction of certain activities that may lead to environmental degradation, underlining the importance of water.

From our point of view the opportunity to constitutionalize the right to water would guarantee the respect of this right by means of other subordinate normative document. The constitutional existence of the right to water and its guarantee can have the most beneficial effects: strengthening of public responsibility to protect water resources, ensuring an efficient protection of subjective rights related to water, establishment of a solid legal framework for the sanctioning of infringements brought upon water resources.

Without a constitutional rationale upon this right, actions taken by authorities and society in order to solve key water issues are irrelevant.

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Chapter 5
Hygienic Evaluation of Water Quality and Health State of Children

Grigore Friptuleac and Vladimir Bernic

Abstract A lot of attention is given to the issue of supply of population and especially to children with drinking water as in national programmes as well as globally. In Moldova, risk of diseases is conditioned by nonconformed water quality which is at high levels; this has great impact especially to children, which are very sensitive to the action of environmental factors. The present work tries to elucidate health issues of children in relation with drinking water quality. Measures of diseases prevention are proposed which are conditioned by water quality, developed based of scientific researchers; these measures will be applied in the future by specialists of the Centre of Public Health of Moldova, primary health care units and local authorities.

Keywords Diseases · Hygienic indicators · Water quality · Drinking water

One of the priority issues for children's health is drinking water, especially in rural areas [1, 4]. Usually, rural areas of Moldova are supplied with water from underground sources, the quality of which in most cases do not meet hygienic standards [5, 6]. Consumption of water with excessive content of some chemical compounds or microbiologically polluted conditions risks to human health [2]. Considering immature adaptation mechanisms and the anatomical and physiological age of the growing organism we can consider children as the most vulnerable stratum of the population affected by the action of environmental factors, especially noncompliant water [4].

Water quality does not remain constant over time and can therefore vary due to many factors, either man-made (anthropogenic factors) or natural origin. A

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peculiarity of changes in water quality over time allows us to predict and monitor its impact on the health of the population [4, 6].

Setting priorities and methods for environmental factors impact mitigation, including water quality on health of the population is and continues to be one of most pressing issues of society. The most effective way to maintain satisfactory health is risk prevention at early stage, in childhood [3, 4].

The present work focuses on sources of water supply in rural areas, territorially distributed in different areas of Moldova (South Zone—Cahul; Centre Zone—Chisinau, North Zone—Briceni), children (1–17 years) in select locations, statistical data on child morbidity, seasonal weather patterns and water quality.

Investigative methods used pertain to hygiene, epidemiology, sanitary chemistry, mathematics. Morbidity was studied in aspect of morbidity after addressing complex clinical examination; drinking water quality was examined in a sanitary chemical laboratory. Accumulated data was processed using statistical methods.

Drinking water in Moldova is acute issues since water sources are territorially unevenly distributed and its quality in very frequent cases did not meet sanitary regulations.

Surveyed children use drinking water from both deep layers (artesian wells) as well as from groundwater (wells). Artesian wells are dominant in the south and groundwater wells in the north. Water from wells is characterized by high mineralization conditioned by sulfates, hydrocarbonates, and chlorides. Higher concentrations of these indices are typical for the south and north of the country.

According to statistical reports of the State Supervision Service for Public Health, the country maintained a high level of noncompliance of water quality sources and distribution systems. The share of noncompliant samples of groundwater of centralized sources in 2010 was 67.8 % compared with 58.3 % in 2008, water samples from wells noncompliant to sanitary-chemical parameters amounted to 84.2 and noncompliant microbiological parameters 41.2%.

Water from wells frequently contains an increased amounts of nitrates (75 % samples), sulfates (65.0–100.0 %) dry residue (65.0–87.0 %), boron (6 %) and fluorides (7 %).

In terms of organic pollution of water is found the most significant concentrations of nitrogen, showing excessive values across the country. Higher average values were recorded in south and north of the country, trends accounting for 173.95 and 111.15 mg/dm^3 respectively. The average concentration of nitrates in the central zone is lower representing 95.7 mg/dm^3, however beyond permissible limits, more than 1.8–2 times.

A particularity to note is the seasonal variation in water quality. Thus, organic water pollution indices are unfavorable during the warm season (summer–autumn).

Inadequate share of microbiological parameters in water samples is less in the winter, trends account from 6.3 to 12.5 %. The largest share of noncompliance was recorded in spring, representing 47.2–63.6 %, remaining at this level, with small deviations, in summer and fall.

In order to highlight peculiarities of health, possibly influenced by the chemical content and bacteriological pollution of water used for drinking purposes, one of the first steps is to analyze general and specific morbidity of children in 2003–2009 dynamics.

The evolution of general morbidity of children in Moldova shows a significant increase in both incidence and prevalence. In 2003, general morbidity of children was 5393.5 cases per 10,000 children, prevalence—7238.4 ‰, increasing significantly in 2009, 8085.3 cases or 6350.9 ‰ per 10,000 children.

Evaluation of average structure of child morbidity in the country by incidence and prevalence of nosologic groups that directly or indirectly may influence water quality have shown increased values in infectious and parasitic diseases (corresponding to 683.9 and 700.2 cases per 10,000 children). Incidence and prevalence of digestive diseases (i.e. 243.1 and 534.5 cases per 10,000 children) come second to the abovementioned. Here it is necessary to mention the chronic predominant character of most digestive diseases.

An important part of the structure of general morbidity are diseases of blood and hematopoietic organs, which are on average 223.1 and 424.9 ‰ and of the genitourinary system (105.3 and 271.1 ‰ accordingly).

There were some territorial dependent particularities of general and specific morbidity in key areas of the country: Southern, Central and North Zone.

Average morbidity of children by main nosologic groups indicate increased values in the south, compared to central and northern regions by infectious and parasitic diseases, diseases of the skin and subcutaneous tissue. In the central zone digestive, genitourinary system diseases and nervous and circulatory system diseases prevail. In northern region, respiratory, blood, osteoarticular and endocrine diseases are prevalent as well as diseases relating to nutrition.

A growing dynamic characteristic for all locations are the digestive and blood system diseases.

An important scientific value is submitted by the connection between sanitary-chemical indices of drinking water and morbidity indices.

This section has found that overall morbidity has a strong direct link with water alkalinity ($r = 0.84$) and fluoride concentration ($r = 0.75$), a direct link with average and low water content of sulphates, magnesium, nitrate and total hardness (respectively $r = 0.62$, $r = 0.57$, $r = 0.38$ and $r = 0.26$). Calcium salts in water content is in an average inverse correlation with overall morbidity.

Diseases of the circulatory system directly correlate with carbohydrate concentration in water ($r = 0.84$), and the concentration of sulfates, fluorides, magnesium, nitrates and total hardness manifest direct average dependencies (i.e. $r = 0.63$, $r = 0, 59$, $r = 0.49$, $r = 0.35$ and $r = 0.30$). With calcium salts, cardiovascular diseases manifest a low inverse relation $r = -0.26$.

The same regularity is characteristic for osteoarticular system diseases with a significantly higher correlation index for nitrates and total hardness (respectively $r = 0.58$ and $r = 0.51$).

In order to develop strategies and prioritization of disease prevention dependent on environmental factors was attempted using modern methodology to estimate the relative risk of illness. Research conducted in this specific context revealed important features. Level of hydric relationship between exposition risk factors and threat of disease expressed by relative risk allowed us to arrange classes of diseases in the following sequence: firstly, circulatory system diseases (RR = 3.6), followed by diseases of the osteoarticular system (RR = 2.24), congenital malformations (RR = 2.1) and digestive diseases (RR = 2.03).

Based on the results of state of children health it is recommended to implement a comprehensive preventive measures directed toward improving water supply of locations, mainly primarily pre-school and pre-university educational institutions. To this end activities will be carried out of several services representatives responsible for this section: State Supervision Service for Public Health, Primary Health Care Services (PHCS) central government and local representatives of ministries and departments, local community, NGOs, educational institutions, health workers (doctors, nurses etc.) family members.

Centre for Public Health (CPH) specialists are performing health monitoring in regard to drinking water, centralized and decentralized supply systems and institutions. The activity involves monitoring, analysis, interpretation and dissemination of data on health of pupils, in particular diseases conditioned by water, drinking water, in regard to which priorities are and risks identified as well as measures for public health improvement are developed and implemented.

These activities will include hygienic measures for more favorable conditions for child water supply.

CPH specialists must organize continual intersectoral collaboration between partners including family physicians, municipalities, authoties entitled with supplying communities and child care institutions with water. There is a need for health education means by familiarizing people with the negative effects caused by improper water use and ways to improve its quality.

Main activities carried out by monitoring experts of CPH are:

- Monitoring child health indicators (morbidity, physical development, disability);
- Monitoring health of water resources, centralized and decentralized water supply;
- Study and description of drinking water useage to scoolchildren;
- Highlighting hydration risk factors for children health;
- Development of prophylactic measures and familiarization of pupils, teachers with risk factors;
- Development of a set of recommendations for medical activities for school and family doctors regarding safe drinking water.

Primary health care service activities are carried out at health centres, where special attention is paid to reflect the premorbid state, early diagnosis and treatment of WRI, and noncontagious infectious diseases, both acute and chronic, including medical monitoring of children with chronic diseases. The medical staff is required to regularly visit families and children with chronic diseases conditioned by water.

Simultaneously, family doctors work with CPH physicians in monitoring health status in relation to the environment; develop specific recommendations for improving water supply, hygienic conditions of preschool and university institutions, as well as the community in general.

Representatives of the primary health care system will focus on the following activities:

- Demonstration and assessment of hydric risk factors in the community;
- Intersectoral activities between families and CPH experts aimed at exchanging information on the subject of water related illnesses (WRI) and water quality, joint development of preventive measures;
- Conducting surveys on WRI of children;
- Conducting surveys on WRI of adults;
- Confirm the diagnosis of WRI;
- Request a consultation expert (depending on the diagnosis) for the ambulatory or stationary patient;
- Perform activities of health promotion and health education.

Central and local government is responsible for creating harmonized legislative basis with European standards concerning construction, arrangement and operation of water resources and water supply installations, water quality monitoring, initiate and support national development programs systems water supply and sanitation communities to combat WRI and health promotion. Financial planning is important to ensure material population, health and social conditions that would enable to achieve the necessary preventive measures. It is also important to ensure training and recycling of medical, pedagogical staff in combating WRI.

Main activities of local government are:

- Strengthening intersectoral collaboration between partners in the issue of health promotion and disease prevention, including WRI;
- Initiating programs to develop local water supply systems and sanitation;
- Providing preschool and pre-university institutions, communities with sufficient water quantities, permanent monitoring of this action;
- Each local administrative unit will develop a policy on the prevention of WRI;
- Coordinating the activities of individuals and businesses in implementing measures to ensure public health;
- Ensuring safe conditions and services for health protection of water sources, water quality consumed by children and adults.

Management of educational institutions shall be responsible for compliance with water quality standards, sanitary regulations on aqueducts, safe drinking water, small water systems and sanitation, housing the equipment necessary for ensuring water supply, drinking water quality, taking all preventive measures of WRI prevention, enactment of decisions made by State Supervision Service for Public Health (SSSPH).

Main activities of teachers in schools are:

- Knowledge of WRI symptoms, isolation of WRI children, parental and medical notification;
- Compliance with drinking and antiepidemic regime for the protection of child health during lessons and breaks;
- Organization of a systematic cleaning of the study room, ventilation of premises during each break;
- Thematic seminars with representatives of CPH for pupils and parents.

The medical staff of educational institutions (doctors, nurses) is responsible for compliance with sanitary regulations on drinking water and is compelled to take all preventive measures for hydric dependent diseases. Main activities of the medical staff are:

- Organizing regular medical exams and placement of sick children;
- Isolation of sick, first aid and notification of doctors or entitled authorities;
- Highlighting actual frequency of illness, take preventive measures, collaborate with parents;
- Raising awareness of teachers and parents about pupils health (pupils manifesting diarrhea, abdominal pain, fever, vomiting etc.).
- Cooperation with entitled health authorities and CPH experts;
- Health promotion and health education of students.

An important role in preventing WRI at children lies with parents, which must comply with sanitary regulations for drinking purpose in consultation with hygienists, in order to ensure necessary housing facilities with water supply.

Drinking water quality, in Moldova, in most cases does not comply with hygienic standards, in respect to sanitary-chemical indices (concentration of nitrates, sulphates, hydrogen carbonates, chlorides) as well as microbiological indices. Estimated noncompliant indices relate directly to a number of diseases that occur mainly at children due to morpho-functional peculiarities of age and immature adaptation mechanisms. Mitigation of disease risk due to noncompliant water quality requires the participation of all stakeholders, promotion and respect for preventive measures.

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Part II
Surface Water

Chapter 6
Chemical Composition of Right Bank Tributaries of Nistru River and Their General Impact

V. Gladchi, N. Goreaceva, Gh. Duca, E. Bunduchi, R. Borodaev, O. Şurîghina and A. Lis

Abstract The work represents the preliminary results of the study on the chemical composition and general impact of the right bank tributaries of Nistru river. The results describe the impact of the tributaries on the formation of the chemical composition of Nistru as well self-purification capacity of its waters. It was shown that Raut, Ichel, Bic and Botna rivers have a different anthropogenic impact on the main artery of the country, Nistru.

Keywords Dniester · Tributaries · Chemical composition · Water quality

For our country the study of the formation of the chemical composition of the Nistru river waters and their chemical self-purification capacity becomes a current issue, which is motivated by the fact that Nistru is the main source of surface water, which provides urban and rural as well as agriculture and industry.

Currently, the chemical composition and hydrological regime of Nistru waters suffer undesirable changes caused by human impact, especially in Ukraine. Many hydraulic structures changing of the riverbed have negative consequences for the natural processes of formation of hydrological, thermal and chemical regime of the Lower and Medium Nistru. These effects are studied by many scholars from Moldova [1–3]. Transdniestrian Moldovan territory waters penetrate with a disrupted thermal regime and dissolved oxygen; they are polluted with poorly degradable organic substances, various forms of biogenic elements and heavy metals [4–7].

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Among risk factors that amend the chemical composition and water self-purification capacity of Nistru in Moldova an important role is attributed to the tributaries, which are formed in the region. Increased risk, in this respect, is attributed to the most important right tributaries of Nistru—Raut, Ichel, Bic and Botna. The total area of these tributaries is 63.44 % of the accumulation basin of Nistru in the country, including 40 % which is the storage basin of Raut, 4.24 %—Ichel, 11.2 %—Bic and 8 %—Botna. Alongside these rivers live about 1.5 million people working at various industrial and agricultural enterprises. These rivers are collecting sewage and poorly treated or untreated wastewater, water runoff, etc. The high level of pollution of these rivers is confirmed by multiannual research [8–11]. Based on the aforementioned, the need for research on chemical composition of waters of these tributaries and smaller rivers impact on Nistru river becomes clear.

As object of research the tributaries of the right bank of Nistru were selected—Raut, Ichel, Bic and Botna, at their rivermouths of flow into Nistru as well as Nistru itself, mainly the sector near the town Dubasari—Chitcani, upstream and downstream of the rivermouths of the small river.

The river Raut flows into Nistru at the 342 km of its source near the village Ustia and the town Dubasari. The river length is 286 km; surface water accumulation basin is 7760 km^2, average slope—0.59 ‰. Raut basin contains several streams with a length between 40–95 km, the main ones being at Copaceanca (50 km), Cubolta (92 km), Cainari (95 km), Ciulucul Mic (61 km) and Cula (65 km). Raut tributaries contribute to the increase of mineralization and total hardness of its waters; waters from this river are attributed to the hydrogencarbonate or sulphates class, magnesium or sodium group and are advancelly polluted by biogenic substances and of organic nature [11, 12]. In addition, at 212 km from the spring, malice sewage accumulates from Balti city.

The river Ichel flows into the Nistru a mile below the village Cosernita, Criuleni region, at 322 km from the rivermouth. The tributary has a length of 101 km; accumulation basin area is 814 km^2, average slope—2.21 ‰. In the capture point of Goieni village, river waters are attributed to hydrogencarbonate class, magnesium group with increased mineralization (900–1100 mg/dm^3) and total excess hardness (8.6–10.5 mmol/dm^3) [11, 12].

The river Bic flows into Nistru downstream of Gura Bicului village. The river length is 155 km; basin accumulation area is 2150 km^2, average slope—1.13 ‰. Hydrological and hydrochemical regime of the the river is heavily disrupted as a result of flow regulation after the Ghidighici dam and river discharge into the poorly treated or untreated sewage from the city from Causeni, Straseni and Chisinau cities. The anthropogenic impact on river waters is manifested in the increase of sulfate ions and alkaline metal ions. Chisinau wastewater volume exceeds 3–4 times the natural flow of Bic, which in consequence leads to the reduction of total hardness and mineralization of water content backgrounded by the increase of chloride ions downstream of the cities wastewater treatment plant [11, 12].

The river Botna length is 152 km; basin accumulation area is 1540 km^2, average slope—1.15 ‰. Flow and chemical composition determined by natural factors is practically disturbed by complete river course regulation. On the river three dams were built in a cascade, each with its own reservoir, situated near Ulmu, Costesti and Rezenti villages. 1 km from the mouth into Nistru riverbed, Botna is blocked by a dam with gates, which currently do not function and has a small water drainage capacity into Nistru. Nevertheless, in high water periods of Nistru, waters enter the riverbed of Botna and outreach the aforementioned dam. The content of the main ions in the river is rising from the spring to the rivermouth, simultaneously the content of sulfate and magnesium ions as well as alkaline metal ions increases [11, 12].

The studies of the chemical composition of the waters in Raut, Ichel, Bic and Botna have included the determination of water flow and analysis of samples of water from the rivermouths into Nistru. For the assessment of the influence of the rivers on Nistru, water samples have been collected from the tributary rivermouths, upstream and downstream. Samples have been gathered in the same conditions.

In order to study the impact of the water flow of the tributaries of the right bank of Nistru on the quality of water of Nistru itself, the following methodologies were used:

- Seasonal study of the chemical composition of water from each tributary in the capture point, situated near the outpouring mouth (at a distance of 200–300 m up to outpouring into Nistru) and Nistru waters capture points located upstream and downstream to the mouth of outpouring at a 500 m distance of;
- Simultaneously, samples measurements were made related to the mouth bed morphology and water flow speed;
- Tributaries flow was calculated in the time of sampling for analysis;
- Tributaries and Nistru water analysis was performed by the following parameters: temperature, pH, Eh, rH values, content of hydrogen peroxide, OH radical content, dissolved oxygen, soluble forms of nitrogen, CBO_5, CCO. The principal feature of the project is the quantitative determination of redox status, concentration of OH free radicals and other parameters that characterize the redox state of formation of waters that are subject to anthropogenic influence;
- Calculation of chemicals in river discharges from each tributary;—Establish dependencies between water flow and chemical composition of water tributaries capture points at the confluence with the river;
- Screening Nistru water quality in Dubasari up to Chitcani;
- Analysis of data, temporal and spatial variability characteristic, statistical processing, clearing dependencies correlation coefficients calculation for irrigation.

While performing hydrochemical analysis traditional methods were used, analytical methods specifically (HACH, USA), atomic absorption spectroscopy for the determination of heavy metals, methods for determining the buffering capacity of water, kinetic methods of analysis [13–17].

6.1 Chemical Composition and Water Self-Purification Processes in Raut, Ichel, Bic and Botna

Main ions content. The right-bank tributaries waters at rivermouths can be characterized as having increased mineralization and advanced total hardness. Average values of main ions content varied insignificantly from 892 up to 1,039 mg/dm^3. Main ions content variations over the years were insignificant for all rivers except Botna, whose waters have considerable fluctuations in mineralization (Table 6.1). Raut and Ichel waters are characterized by the corresponding hydrochemical index of C_{II}^{Mg} and C_{III}^{Mg}. In Bic waters among anions, hydrogen ions are most dominant and Na^++K,$^+$, Ca^{2+}, Mg^{2+} cations were present in similar amounts [18]. Botna waters are classified as hydrogencarbonate and chloride class, type III magnesium group.

For Raut, Ichel and Botna a well-defined linear dependence of hydrogen ions and the total content of main ions was identified. These tributaries have shown a clear trend of increasing concentration of ions of Cl^-, SO_4^{2-}, alkaline metal ions (Na^++K^+) while dealing with increased mineralization. Bic waters have shown no correlation to the aforementioned.

Total average water hardness for Raut, Ichel and Botna constituted 11.0–11.9 mmol/dm^3 and Bic—8.3 mmol/dm^3. Hardness values for the three tributaries are mainly conditioned by the presence of magnesium salts; also Bic's intake of calcium and magnesium salts in total hardness was approximately equal.

Water mineralization dynamics of Raut, Ichel and Bic during the timeframe was similar and deviate insignificantly from average annual values (Fig. 6.1). Botna waters summary content of main ions varied in a wider range.

In Botna waters a drop in mineralization and total hardness values was recorded, in cases of Nistru high waters and their penetration into the rivermouth.

For Raut waters a good correlation between mineralization and water flow was found (Fig. 6.2), for Ichel and Botna this dependence has a low degree of correlation.

Buffering capacity. Research related to acid–base balance of waters and their buffering capacity (after Van-Slaic) have shown the danger of acidification. For all investigated rivers is characteristic relationship stability Alk > Acid, buffering capacity indicator has exceeded the alkalinity. However, water samples of Bic have revealed a high content of carbon dioxide, indicating intensive pollution with organic substances during high speed their oxidation processes. CO_2 content at its mouth in river varies between 4.9 and 32.6 mg/dm^3, averaging 12.13 mg/dm^3. In river waters pH was always lower than other tributaries of Nistru (Table 6.2).

Oxygen regime. Oxygen content in water tributaries studied and the degree of saturation of water with oxygen (GS) during the investigation underwent essential changes. The most favorable situation was recorded at the mouth of Raut, where the degree of saturation of water with oxygen remained favorable, except from July 5, 2010, when this parameter has lowered to 61.7 %. In rivermouths of Botna and Ichel oxygen regime was unstable, ranging from oxygen-deficient situations

Table 6.1 Main ions content (Σi) and total hardness ($D_{tot.}$) of right bank tributaries of Nistru in 2009–2010 (the numerator—average values, the denominator—the limits of variation)

Tributary	$D_{tot.}, \frac{\text{mmol}}{\text{dm}^3}$	Ions, mg/dm^3						Σi, mg/dm^3
		Ca^{2+}	Mg^{2+}	Na^{+}+K^{+}	HCO_3^-	SO_4^{2-}	Cl^-	
Raut	$\frac{10.9 \pm 0.4}{8.1 - 12}$	$\frac{67.8 \pm 4.2}{52 - 90}$	$\frac{91.5 \pm 4.1}{60.8 - 102}$	$\frac{76.9 \pm 5.4}{55 - 96}$	$\frac{486 \pm 15.9}{403 - 546}$	$\frac{171 \pm 4.6}{149 - 187}$	$\frac{88.6 \pm 4.6}{63.8 - 106}$	$\frac{982 \pm 25.9}{849 - 1082}$
Ichel	$\frac{11.6 \pm 0.6}{8 - 13.5}$	$\frac{78 \pm 4.8}{58 - 100}$	$\frac{92.7 \pm 6.5}{49.9 - 116}$	$\frac{33.9 \pm 8.4}{10.8 - 75}$	$\frac{446 \pm 19.8}{342 - 531}$	$\frac{161 \pm 9.8}{86 - 182}$	$\frac{80.4 \pm 3.4}{64 - 92.6}$	$\frac{892 \pm 36}{650 - 994}$
Bic	$\frac{8.3 \pm 0.61}{6.8 - 10.5}$	$\frac{87 \pm 4.16}{76 - 102}$	$\frac{48.3 \pm 5.4}{31 - 65.7}$	$\frac{118 \pm 11.9}{69.8 - 147}$	$\frac{426 \pm 9.6}{387 - 451}$	$\frac{147 \pm 10.8}{120 - 180}$	$\frac{107 \pm 4.23}{95.7 - 124}$	$\frac{933.7 \pm 16}{868.8 - 989}$
Botna	$\frac{11.9 \pm 1.8}{3.7 - 17.9}$	$\frac{74.6 \pm 9.5}{42 - 122}$	$\frac{100 \pm 17.9}{15.8 - 158}$	$\frac{101 \pm 26.2}{17.5 - 238}$	$\frac{368 \pm 4.1}{150 - 519}$	$\frac{144 \pm 17}{57.6 - 189}$	$\frac{251 \pm 48.4}{42.5 - 489}$	$\frac{1039 \pm 132}{356.7 - 1470}$

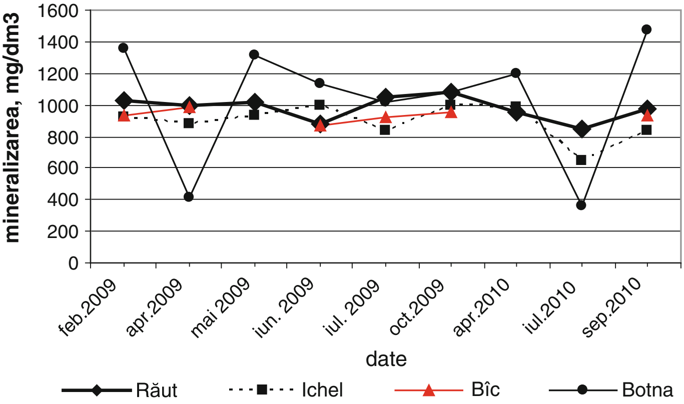

Fig. 6.1 Dynamics of main ions content in tributaries water during 2009–2010

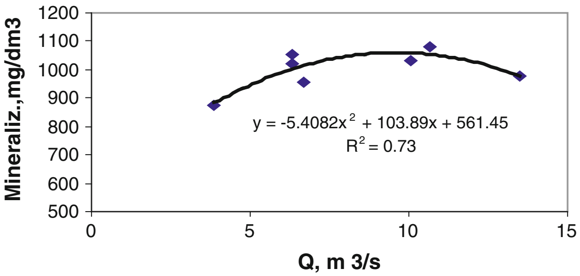

Fig. 6.2 Correlation between mineralization and water flow values for Raut

(GS 45.4–69.6 %) to supersaturation (GS 128–168 %). At the mouth of the Bic oxygen regime was negative throughout the monitoring period; the degree of saturation in 2009 did not exceed more than 69 % and in 2010 vary from 0.0 to 5.7 % range.

Organic and biogenic matter. The studied river waters flowing into the river sections are considerably polluted with organic and biogenic substances. Average values of organic matter (SO), which were determined using indicator CCO_{Cr}, is 24.2 mg_O/dm^3 in Raut, 29.0 mg_O/dm^3 in Botna, 43.5 and 40.2 mg_O/dm^3 in Ichel and Bic respectively. Maximum values were recorded in Ichel waters—126.0 mg_O/dm^3.

CCO_{Mn} and CCO_{Cr} relationship between parameters shows that tributaries waters contain 18–24 % of humic substances. For all tributaries are characteristic increased values of the parameter CBO_5, which characterize biodegradable organic substances [19]. The highest values of the parameter in 2009–2010 were recorded in Bic waters, where CBO_5 values ranged from 5.0 to 34.0 mg_{O_2}/dm^3 (Table 6.3). On average, in Bic waters the share of fresh organic substance formed in all organic matter is 41 %. In Ichel waters this ratio is lower—18 % and in Raut and Botna biochemically degradable organic matter content are respectively 25 and 28 % (Table 6.3).

Table 6.2 Acid-base balance parameters and buffering capacity (β) of water ($\frac{media}{\text{min.} - \text{max.}}$)

Location	pH	HCO_3^- mmol-equiv/l	Acid	Alkaline	β	pK	K* 10^7	CO_2 mg/l
Raut	$\frac{8.42}{8.2-8.9}$	$\frac{8.33}{6.9-10.0}$	$\frac{0.21}{0.0-0.94}$	$\frac{8.33}{6.9-10.0}$	$\frac{0.44}{0.3-0.86}$	$\frac{6.88}{6.4-7.6}$	$\frac{1.54}{0.03-3.6}$	$\frac{3.48}{1.3-6.4}$
Ichel	$\frac{8.25}{7.8-8.4}$	$\frac{7.52}{5.2-9.1}$	$\frac{0.23}{0.0-0.33}$	$\frac{7.52}{5.2-9.1}$	$\frac{0.51}{0.33-0.8}$	$\frac{6.76}{6.5-7.2}$	$\frac{1.92}{0.6-3.4}$	$\frac{5.12}{1.7-9.9}$
Bic	$\frac{7.83}{7.3-8.1}$	$\frac{7.18}{6.4-8.3}$	$\frac{0.61}{0.3-1.14}$	$\frac{7.18}{6.4-8.3}$	$\frac{0.91}{0.6-1.31}$	$\frac{6.56}{6-6.8}$	$\frac{3.24}{1.8-9.1}$	$\frac{12.13}{4.9-32.6}$
Botna	$\frac{8.44}{8.0-8.8}$	$\frac{6.15}{2.4-8.5}$	$\frac{0.16}{0.0-0.62}$	$\frac{6.15}{2.4-8.5}$	$\frac{0.36}{0.2-0.48}$	$\frac{7.18}{6.6-7.8}$	$\frac{0.83}{0.17-2.4}$	$\frac{2.18}{0.6-4.2}$

Table 6.3 Content of organic and biogenic substances in tributary waters of Nistru ($\frac{\textit{valorile medii}}{\text{min.– max.}}$)

River	CCO_{Cr} mg_O/dm^3	CCO_{Mn} mg_O/dm^3	CBO_5, mg_{O_2}/dm^3	$\frac{CBO_5}{CCO_{Cr}}$	$N–NH_4^-$ mg/dm^3	$N–NO_2^-$	$N–NO_3^-$	PO_4^{3-}
Raut	$\frac{24.2 \pm 5.87}{8.0 - 45.0}$	$\frac{5.05 \pm 0.66}{2.6 - 7.55}$	$\frac{4.4 \pm 0.59}{2.0 - 7.0}$	$\frac{0.25 \pm 0.1}{0.07 - 0.75}$	$\frac{0.54 \pm 0.24}{0.01 - 1.91}$	$\frac{0.042 \pm 0.02}{0.003 - 0.150}$	$\frac{2.72 \pm 0.73}{0.50 - 7.02}$	$\frac{2.64 \pm 1.33}{0.43 - 11.4}$
Ichel	$\frac{43.5 \pm 17.8}{6.0 - 126.0}$	$\frac{7.9 \pm 1.7}{3.8 - 16.5}$	$\frac{7.75 \pm 1.41}{4.0 - 17.0}$	$\frac{0.18 \pm 0.04}{0.05 - 0.38}$	$\frac{0.91 \pm 0.38}{0.03 - 3.75}$	$\frac{0.082 \pm 0.03}{0.033 - 0.26}$	$\frac{2.88 \pm 0.71}{0.10 - 7.74}$	$\frac{2.39 \pm 1.03}{0.08 - 7.51}$
Bic	$\frac{40.2 \pm 7.9}{14.0 - 56.0}$	$\frac{8.4 \pm 1.15}{6.0 - 12.3}$	$\frac{16.0 \pm 4.9}{5.0 - 34.0}$	$\frac{0.41 \pm 0.15}{0.10 - 0.97}$	$\frac{12.54 \pm 3.29}{2.55 - 18.2}$	$\frac{0.064 \pm 0.040}{0.004 - 0.200}$	$\frac{2.26 \pm 1.10}{0.10 - 6.50}$	$\frac{9.15 \pm 2.12}{1.13 - 11.8}$
Botna	$\frac{29 \pm 12.9}{4.0 - 45.0}$	$\frac{7.02 \pm 0.84}{2.56 - 13.1}$	$\frac{7.1 \pm 1.39}{3.0 - 18.0}$	$\frac{0.28 \pm 0.06}{0.13 - 0.48}$	$\frac{0.26 \pm 0.09}{0.0 - 0.74}$	$\frac{0.071 \pm 0.0.03}{0.0 - 0.170}$	$\frac{2.29 \pm 0.81}{0.10 - 8.82}$	$\frac{2.12 \pm 1.3}{0.0 - 11.67}$

Analysis results for Raut waters measurements revealed strong correlation between CCO_{Cr} and CCO_{Mn} parameters and a lower correlation between CCO_{Cr} and water flow parameters in the sampling section (Fig. 6.3).

Ichel waters correlation were found between parameters CCO_{Mn} and CCO_{Cr} and water flow (Fig. 6.4).

Permanent biogenic elements were present in all tributary waters. In very rare cases Botna lacked ammonia and nitrite ions. The most advanced level of ammonia nitrogen pollution of water was added to rivermouths of the Ichel and Bic, with corresponding average values 0.91 MGN–NH_4^+ /dm^3 and 12.54 MGN–NH_4^+ /dm^3. Minimum content of the forms of nitrogen in waters beyond 1.6 times Bic allowable concentration limit and maximum values exceeded 11.6 times CLA.

Nistru tributary waters contain large amounts of phosphates. The average value of this parameter was 2.12 mg/dm^3 in Botna, Ichel—2.39 mg/dm^3, Raut—2.64 mg/dm^3, Bic—9.15 mg/dm^3. Ichel waters and Raut highlighted a strong correlation between the content PO_4^{3-} ions and water flow (Q).

In the case of Ichel the appropriate relationship is: $PO_4^{3-}, \mathrm{mg}/\mathrm{dm}^3 = 12.25 \cdot Q - 1.159;\ r = 0.81$.

For Raut : $PO_4^{3-},\ \mathrm{mg}/\mathrm{dm}^3 = 0.383 \cdot Q + 2.628;\ r = 0.64$.

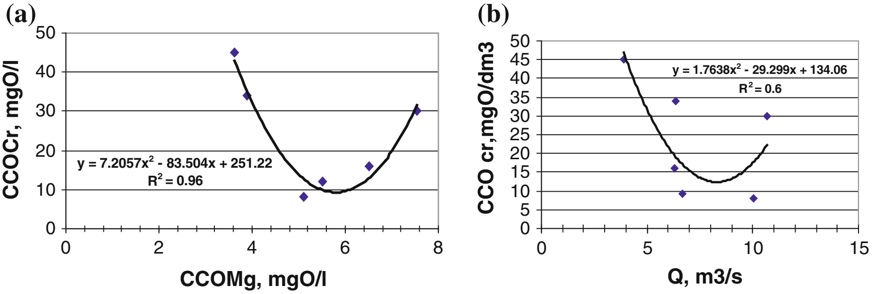

Fig. 6.3 Correlation between water quality parameters of Raut: **a** CCOCr şi CCOMn; **b** CCOCr şi debit (Q)

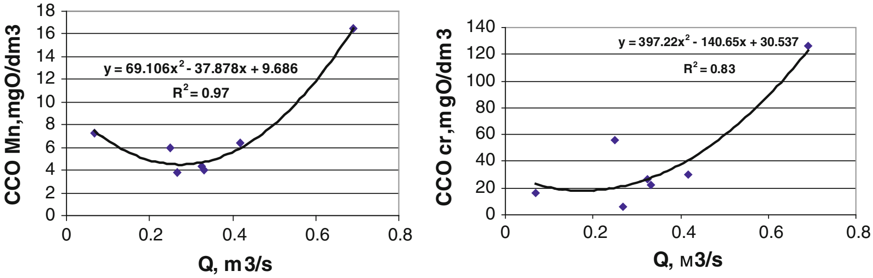

Fig. 6.4 Correlation between CCO_{Mn}, CCO_{Cr} parameters and water flow of Ichel

Metals The trend of total content of various forms of copper and iron in tributary waters content was decreasing from northeast to southwest. Ichel and Raut waters the total content of copper and iron is higher in comparison with Bic and Botna waters. Average total copper content in waters was 11.2 $\mu g/dm^3$ Raut, and r Ichel—11.55 $\mu g/dm^3$. For iron in these rivers average values were respectively 313.7 and 282.3 $\mu g/dm^3$ (Fig. 6.5).

Copper was present in water in form of suspensions and colloidal–soluble form, their weight is about the same. Iron predominant form of suspensions register (from 96.6 to 98.86 %) (Table 6.4).

Kinetic parameters. By investigating kinetic parameters, tributary waters can be characterized as aquatic objects unfavorable environmental situation, i.e. the biological value of livable water for hydrobionts was reduced (Table 6.5).

Redox water state of Raut, Ichel and Bic was more often reducing; water samples were missing to detect hydrogen peroxide and reducing substances with properties (DH_2). The mean values indicate that the highest content of peroxidase substrates has been documented in waters Ichel (1.53 µg/l), followed by those of Bic (1.30 µg/l), in Botna waters the amount was lower (0.64 µg/l) and the lowest amount was determined in Raut waters (0.11 µg/l). It is worth mentioning that during monitoring, Botna waters, on September 27, 2010, superoxide was certified status, which indicate the presence of the tributary waters of appreciable quantities of semi-finished products and technological cycles, i.e. anthropogenic impact on aggressive enough. Setting both oxidative status, as well as reduction one, shows the significant depreciation of the ecological status of an aquatic ecosystem.

$\Sigma k_i \cdot [S_i]$ (5.01 s^{-1}) parameter analysis, which characterizes the effective constant interaction with OH radicals reducing substances of nature shows that the radical self-purification process had a low share in the overall process of self-purification of water Raut. Average values of inhibition capacity of their water-Ichel (4.38 s^{-1}) and Botna (4.22 s^{-1}) show that in the monitored period content of substances that disrupt radical chain process of self-purification in the waters of both rivers was about the same. Although the concentration of these substances in waters Bic r was lower, however their amount was sufficient to reduce speed to radical self-purification process (3.38 s^{-1}).

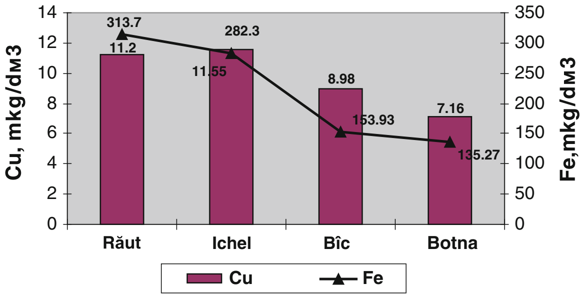

Fig. 6.5 The average content of copper and iron in Nistru tributary waters in 2009–2010

Table 6.4 The average content of different forms of copper and iron in Nistru tributary waters in 2009–2010, $(\frac{medie}{\text{min.–max.}})$

River	Cupru				Fier			
	FS[a]		FCS[b]		FS[a]		FCS[b]	
	μg/dm^3	%	μg/dm^3	%	μg/dm^3	%	μg/dm^3	%
Raut	$\frac{6.2}{1.5 - 12.75}$	$\frac{50.4}{27.3 - 76.1}$	$\frac{5.0}{2.0 - 8.0}$	$\frac{49.6}{23.9 - 80}$	$\frac{310.5}{183 - 482}$	$\frac{98.86}{98.4 - 99.6}$	$\frac{3.2}{2.0 - 4.0}$	$\frac{1.14}{0.41 - 1.61}$
Ichel	$\frac{7.15}{1.25 - 14.2}$	$\frac{53.6}{20 - 78.1}$	$\frac{4.4}{3.0 - 6.0}$	$\frac{46.4}{21.9 - 80}$	$\frac{279.7}{109.5 - 469}$	$\frac{98.76}{97.3 - 99.6}$	$\frac{2.6}{2.0 - 3.0}$	$\frac{1.24}{0.42 - 0.67}$
Bic	$\frac{4.23}{1.25 - 6.5}$	$\frac{44.22}{23.8 - 61.9}$	$\frac{4.75}{4.0 - 6.0}$	$\frac{52.78}{38.1 - 76.2}$	$\frac{150.18}{55.5 - 167.5}$	$\frac{96.65}{94.6 - 98.9}$	$\frac{3.75}{3.0 - 6.0}$	$\frac{3.35}{1.09 - 5.42}$
Botna	$\frac{3.56}{1.48 - 6.75}$	$\frac{46}{22.8 - 77.1}$	$\frac{3.6}{2.0 - 5.0}$	$\frac{54}{22.9 - 77.1}$	$\frac{131.9}{76.2 - 208.7}$	$\frac{96.6}{93.1 - 98.1}$	$\frac{4.00}{2.0 - 6.6}$	$\frac{3.37}{1.88 - 6.88}$

[a] Suspension form (FS)

[b] Soluble-colloidal form (FCS)

Table 6.5 Average kinetic parameters of the Nistru tributary waters in 2009–2010, ($\frac{medie}{\text{min.–max.}}$)

River	$[H_2O_2]$, μg/dm^3	$[DH_2]$, μg/dm^3	$OH_{h\nu} \cdot 10^{14}$, mol/dm^3	$OH_{bio} \cdot 10^{17}$, mol/dm^3	$\Sigma k_i \cdot [S_i] \cdot 10^{-5}$, s^{-1}
Răut	0.0 0.0 – 0.0	0.11 0.0 – 0.39	1.94 0.1 – 3.8	14.98 1.1 – 110.0	5.01 2.96 – 8.97
Ichel	0.0 0.0 – 0.0	1.53 0.0 – 2.42	2.15 0.31 – 8.8	4.54 1.2 – 13.8	4.38 3.4 – 6.82
Bîc	0.0 0.0 – 0.0	1.30 0.82 – 1.90	1.4 0.0 – 3.2	6.26 2.04 – 19.0	3.38 1.9 – 4.9
Botna	1.06 0.0 – 8.5	0.64 0.0 – 2.4	1.96 0.0 – 5.1	7.94 2.4 – 23.0	4.22 1.6 – 9.2

It should be noted that for all monitored rivers was found tend to dominate the redox agents, formed as a result of photochemical reactions in comparison with their training towards biotic ($OH_\lambda > OH_{bio}$). This shows that the waters redox conditions were not optimal for intensive development of microorganisms that eliminates outdoors products of vital activity with strong reducing properties and toxicity.

Right tributary influence on the chemical composition of the Nistru River. The results obtained indicate about the negative influence of tributary waters on chemistry and chemical self-purification capacity of water fl. Nistru. The most obvious negative impact showed Raut and Bic waters. In Nistru waters downstream of rivermouths of these tributaries are detected increased contents ions as it determines mineralization of waters (Mg^{2+}, $Na^+ + K^+$, SO_4^{2-}, Cl^-) and the values of total hardness of waters, on average by 41 % for Raut and 26 % for r Bic (Fig. 6.6).

Raut and Bic waters contribute to increasing pollution of Nistru with phosphates, nitrogen compounds, biodegradable organic substances (after parameter CBO_5). Downstream of the mouth of Raut, Ichel and Botna waters, Nistru dichromatic oxidisability is increased the (Figs. 6.7, 6.8).

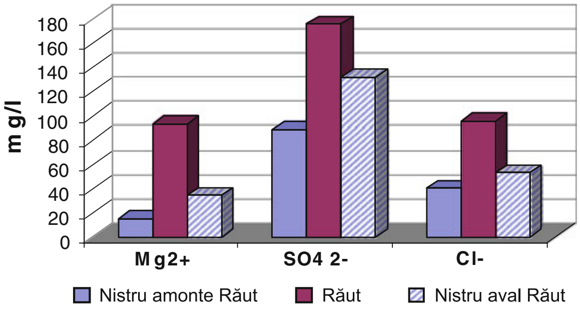

Fig. 6.6 Influence of Raut waters on main ions content in Nistru

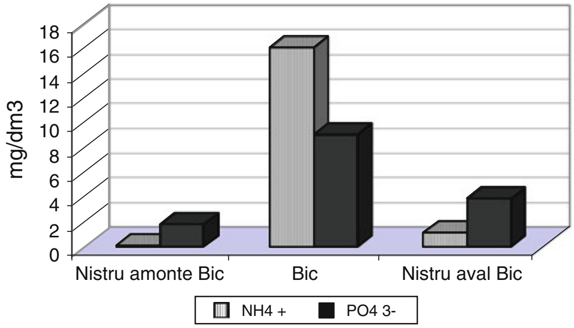

Fig. 6.7 Bic influence on the content of biogenic substances in Nistru waters

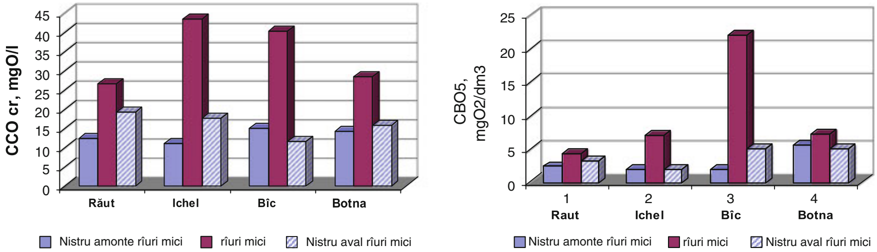

Fig. 6.8 Tributaries impact on the content of organic substances in Nistru waters

Essential influence on the chemical composition of small rivers Nistru water is demonstrated diurnal flows of chemical substances entering the waters Raut (Table 6.6).

Polluted waters from tributaries entering in Nistru helps to reduce the intensity of self-purification processes of river water chemical dominance peroxidase reductant type, the reduction of the OH radicals and increased inhibition of waters to conduct active processes involving these particles.

Thus, research conducted in 2009–2010 showed that Nistru tributaries may be considered risk factors for river and research in this area should continue to consider all factors that will contribute to improving the situation.

Table 6.6 Average values of diurnal flow of substances entering Nistru waters from Raut during the years 2009–2010, in t/day

Year	Q, m^3/s	Σi	SO_4^{2-}	Cl^-	C_{org}	$N–NO_3^-$	$N–NH_4^+$	PO_4^{3-}
2009	8.41	752.4	129.1	69.59	8.66	1.65	0.464	1.065
2010	10.14	848.6	144.8	68.3	5.88	1.44	0.76	4.56

6.2 Conclusions

1. Nistru tributaries data on water chemical composition have been obtained (Raut Ichel, Bic, Botna) in sections of the river pouring over the years, and the chemical composition of Nistru downstream and upstream of the estuary mouth of the tributaries and the contribution in the formation of the chemical composition of tributaries river waters.
2. The data obtained show a considerable influence on the content Raut main ions in waters Nistru. Raut shedding downstream of Nistru shows increased content of mineral salts in waters by 41 %.
3. Raut and Bic rivers contribute essentially to the change of the chemical composition of Nistru River:
   - Increase in total mineralization and hardness of Nistru waters downstream of the tributaries is observed;
   - In summer Bic and Raut waters do not meet standards prescribed by regulation on hygiene protection of water bodies against pollution (Chisinau 1997);
   - Advanced Pollution of Bic with biogenic substances (N–NH_3, N–NO_2^- and PO_4^{3-}) contribute essentially to the aquatic biocenosis disturbance, decreased dissolved oxygen content and chemical disruption of self-purification processes of Bic and Nistru water;
   - During the summer-autumn coloring register Bic in brown waters and the presence of strong smell of water.
4. Ichel and Botna rivers influence on Nistru water quality is insignificant:
   - Ichel has a dispensable flow rate that does not cause significant changes in the chemical composition of Nistru;
   - Botna is heavily regulated and tributary the mouth of in Nistru a dam is built which basically stops the penetration of Botna waters into the river;
   - Both rivers are characterized by advanced mineralization and increased content of various forms of biogenic elements, which suggests a degree of anthropogenic pollution pronounced.
5. Nistru tributaries waters are polluted with mineral compounds of biogenic elements—ammonium, nitrite, nitrate, phosphate ions. Maximum concentrations were found at the mouth of the Bic. It was established a trend of increasing concentrations of various forms of biogenic elements in Bic downstream waters of shedding into Nistru.
6. Researched tributaries have an important influence on Nistru waters according to CBO_5 and CCO_{Cr} parameters.
7. It was estimated redox state Nistru tributaries and intensity of chemical self-purification processes tributaries at the confluence with the Nistru waters. By kinetic redox state indicator (H_2O_2/DH_2), river waters were characterized by unstable redox state (Raut) or reducing (Ichel, Bic and Botna). Tributaries waters were almost always attested reducing substances with peroxidase type

that were oxidized by H_2O_2 and thus favored the establishment of quasi-reductive status of these waters. RH_2 redox potential values and shows that the state's waters and those Transnistrian region of Raut, Ichel, Botna was oxidant, and those from the mouth of Bic-reducing. Tributaries waters of Nistru contained high amounts of substances peroxidase, which led to the establishment unstable redox status of these waters.

8. Average oxidation of OH radicals is effective under transdniestrian waters, but is slow. Dynamics of kinetic indicators show that tributaries water purification capacity is lower than the river water.

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Chapter 7
Hydrobiocenosis State of the Prut River in the Sculeni–Giurgulesti Sector

Elena Zubcov, Laurentia Ungureanu, Ion Toderas, Lucia Biletchi and Nina Bagrin

Abstract Prut is the second largest river in Moldova. It takes its beginning from the South-East side of Goverla peak, 15 km South-Southwest of Vorokhta village in the woody Carpathian mountain massif Cernogora. The total length of the river is 967 km, in Moldova's borders—695 km, the catchment area is 27,540 km^2; Prut waters pours in the Danube at 164 km from its mouth, being thus the last left large tributary of one of the largest rivers of Europe (Fig. 7.1). Prut River has a rate of water flow of about 2.9 km^3 determined by its character of river feeding and its hydrological regime. Prut mountain region has a V-shaped valley with a width of 3 km and from Lipcani city down the river—in the form of a trapezoid, with width from 3.7 to 12 km in the delta. The bed of the river forms a large number of meanders—the sinuosity coefficient is 1.7–2.2.

Keywords Prut · Danube · Water quality · Sculeni-Giurgiulesti

7.1 Materials and Methods of Research

Water samples and biological samples were collected seasonally, in spring, summer and autumn, from key biotopes of Prut River (Braniste, Sculeni, Leuseni, Cahul-Cislita) in 2009–2011 in the frames of the research projects of the Laboratory of Hydrobiology and Ecotoxicology of the Institute of Zoology of the Academy of Sciences of Moldova (ASM). The investigations were focused on the assessment of diversity, quantitative structure, production peculiarities of bacterio-, phyto-, zooplankton, and zoobenthos, destruction of organic substances, determination of trophic status and water quality of the Prut River.

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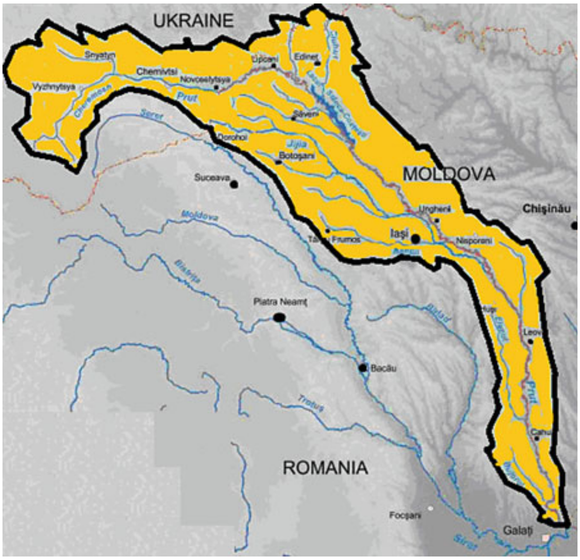
Fig. 7.1 Map of Prut River basin



The dynamics of dissolved oxygen, main ions (hydrocarbon, sulphates, chlorides, calcium, magnesium, sodium, potassium ions), nutrients (nitrogen and phosphorus compounds) was investigated, values of permanganate and dichromate oxidability were determined, as well as content of microelements. The results obtained were compared with the materials from previous years.

The field samples collection and their chemical analysis were performed according to the established methods in hydrochemistry and hydrobiology [1, 49]. Dissolved oxygen was determined by iodometric method [49], the samples were fixed directly in the field; this method is adapted to ISO 5667-6:2005 [10] and ISO 5667-2009 [11, 14].

The contents in suspensions was determined by the gravimetric method (weight loss after drying at 80 °C and after calcination) with water filtration through the filters with the known mass.

The contents in hydrocarbonate ($HCO3^{-}$) and carbonate ($CO3^{2-}$) ions or alkalinity was determined by classical titration method, which corresponds to ISO 9963-1:1994 [21] and 9963-2:1994 [22]. The chlorides were studied by silvermetric titration in accordance with ISO 9297:1989 [20]. Sulphate ion concentration (SO_4^{2-}) was determined by gravimetric method using barium chloride according to ISO 9280:1990 [19]. The determination of total contents in calcium and magnesium, or hardness, as well as calcium ions, was carried out by complexometric EDTA-titrimetric method (ISO 6059:1989 [13] and 6058:1984 [12]). The contents in magnesium ions (Mg^{2+}) was determined as the difference between the hardness values and contents in calcium ions. Sodium and potassium ions were studied by the standard method [49], some samples—by atomic absorption method—ISO 9964-2:1993 [23, 24].

The nutrients (N–NH_4^+, N–NO_2^-, N–$NO_3^{-)}$ were studied by using the spectrometric methods, which complies to ISO 7150-1:1984 [16], ISO 6777:1984, ISO 7890-3:2006 [17]. Mineral nitrogen (Nmin) was calculated as the sum of ammonia nitrogen, nitrate and nitrite nitrogen. Total nitrogen (Ntot) was determined by Kjeldal method using the selenium indicator, thus corresponding to ISO 5663:1984. The difference between total and mineral nitrogen corresponds to organic nitrogen. Total phosphorus (Ptot) and mineral phosphorus (Pmin) were determined by the ammonium molybdate spectrometric method, which corresponds to ISO 6878:2004 [15]. The difference between total and mineral phosphorus accounts organic phosphorus (Porg).

The total amount of organic matter and correlation of stable organic matter and unstable forms was assessed by determining permanganate and dichromate oxidability—ISO 8467-2009 [18].

The studies on bacterioplankton consisted of determining the total density of bacterioplankton (N_{tot}), saprophytic bacteria (N_{sapr}), some groups of bacteria involved in nitrogen, phosphorus, and carbon cycles, and also of phenolitic and petroleum degrading bacteria.

The samples were collected in sterile vessels with a volume of 0.5 l in the surface layer of water (up to 0.5 m). Immediately after collection, in order to determine the total density of bacterioplankton, samples were filtered through membrane filters (Synpor), pore size 0.26 μm.

The bacterial biomass production (P) and bacterial destruction of organic matter (R) were determined in glass bottles with a volume of 125 ml, filled with natural water, which was primary filtered of phyto- and zooplankton through membrane filters (Synpor), pore size 2.5 μm. The vessels were exhibited in the water body for 12–24 h, depending on the water temperature. It is important to note that the intensity of microbial destruction (R) was determined by Vinberg method and more specifically, by Winkler oxygen modification, which consists in the iodometric measurement of dissolved oxygen concentration.

In order to determine saprophyte bacterioplankton, seedings on nutrient media (fish peptonic agar) were performed and density of some eco-physiological groups of bacteria was determined by using the selective liquid and solid nutrient media [1]. In particular, the Fyodorov's medium (with various carbon sources- mannitol, glucose) was applied for determining of aerobic nitrogen fixing bacteria, mineral medium № 70- for ammonifying bacteria, Van-Itersen medium- for denitrifying bacteria and medium consisting of starch and ammonia—for amylolytic bacteria (The unified methods of the study quality water [58].

The collection and processing of phytoplankton samples was performed according to the unified methods [1]. The algae species identification was performed using microscopes ("Jenaval" and Lomo "Mikmed 2") and widely used identifications guides.

The phytoplankton density was estimated by counting cells of algae on Goreaev counting camera (0.9 cm^3). A cell was considered as unit of counting and assessing of phytoplankton density, the results being expressed in thousand cells/l or mln cells/l. During the microscopic analysis of samples, necessary parameters for assessing algal cell volume and individual mass were measured. In each analyzed sample the algae species were determined and all their cells were counted at least in three counting chambers. The phytoplankton density was calculated for each investigated sample. The phytoplankton density was calculated using the formula:

$$N = nv_1/v_2w$$

where:

N—number of cells in 1 cm^3 of water,
n—number of cells in a chamber with a volume of approximately 1 mm^3,
v_1—concentrate sample volume,
v_2—chamber volume,
w—initial sample volume.

The phytoplankton biomass was calculated by summation of populations. biomass. With this purpose, the average mass of algae cells that form the given sample populations was initially estimated. The algae body was likened to figures or combinations of geometric figures. The algae volumes were calculated according to the formulas known in geometry, based on the linear dimensions of specific algal cells. The relative density of freshwater algae is considered equal to 1.0–1.05 [1]. The calculated volume of each cell was multiplied to the cells number and biomass value resulted, expressed in mg/l or g/m^3 with accuracy of 0.01. The biomass was calculated for each species and then summed to obtain the total biomass of phytoplankton in the given sample.

The phytoplankton primary production and destruction of the organic matter was estimated by the method of exposed vessel in oxygen modification [1]. The integral phytoplankton production (ΣA) under 1 square meter of aquatic area was calculated according to the obtained experimental values, taking in account the transparency and, respectively, the euphotic layer depth [34, 48] and integral destruction (ΣR)—by multiplying the mean R value by the water body depth.

With the scope to estimate the trophicity dynamics of Prut River, the seasonal and multiannual values of phytoplankton biomass and primary production were used [45].

For estimation of pollution and water quality accordingly with hydrobiological indices, the methods based on systems of indicator organisms were used [43]; The unified methods of the study quality water [8, 32, 33, 58]. Based on the list of indicators, the Rotschein saprobic index was calculated by using the Zelinka–Marvan saprobic valence method, calculated by formula, which was modified by Toderash [59].

$$S_R = \sum_{i=1}^{i=n} N_iG_iS_i / \sum_{i=1}^{i=n} N_iG_i$$

where:

N_i—density,
G_i—weight indicator,
S_i—saprobic valence.

The saprobic index was calculated with the accuracy of 0.01. For the xenosaprobic zone it ranges between 0 to 0.50, oligosaprobic zone—0.51–1.50, β-mesosaprobic zone—1.51–2.50, α-mesosaprobic zone—2.51–3.50, polysaprobic zone—3.51–4.00 [44].

Zooplankton samples were harvested according to the unified methods ([1], Handbook on Methods…, [2]). The filtering of 100 l of water was performed by using Apstein zooplankton net, with sieve no. 68. The samples were fixed with 4 % formalin solution. The organisms were counted in Bogorov camera, density (N) was reported in thousands of individuals to 1 m^3. The species' biomass (B, mg/m^3) was calculated by multiplying the density of species by mass of one individual of given species (mg/m^3) [5, 57]. The taxonomic diversity was identified using the identification guides [26, 29, 61, 62, 64, 67].

The saprobic index was calculated by Pantle and Buck method as modified by Sladeček [32, 33, 46, 50, 51]. Based on the list of indicators [50, 51], the saprobiologic characteristic of studied water bodies was given. Estimation of water quality in the studied ecosystem was performed according to unified methods for classifying natural water quality [44].

The collection, processing and determination of benthic invertebrate samples was performed according to the methods generally accepted in hydrobiology [1, 25, 29, 63, 65–67]. Benthic invertebrates were sampled in the shallower bank zone of Lower Prut with depths up to 1.2 m, using the Petersen grab (area of capture—250 cm^2 or 1/40 m^2) and dredge (area of capture—8 m^2). For qualitative samples a hand—net for different substrates was used, including macrophytes. For the preservation of the samples 4 % formaldehyde was used. The sorting of the samples and identification of the organisms was performed using MБC-9 binocular and microscope *Jenaval*. The biomass of benthic organisms was determined via their weighting on electronic balance *TYPE ABS 80-4 Kern* (with 0.0001 g sensitivity), being previously dried up on a filter paper till the disappearance of wet spots. The density and biomass of the organisms was calculated into ind./m^2 and g/m^2, respectively.

In order to assess the water quality, a range of indexes were used: Oligochaetes Index [9], TBI—Trent Biotic Index [72], EBI—Extended Biotic Index ([73], BMWP—The Biological Monitoring Working Party [4], Saprobic Index of Pantle and Buck [46] in modifications made by Zelinka and Marvan [74]. Also, the software (www.fliessgewaesserbewertung.de) was applied.

For the mathematical calculation of saprobic index was applied formulae:

$$\text{Saprobic index S} = \sum_{i=1}^{n} (s_i \cdot a_i \cdot g_i) / \sum_{i=1}^{n} (a_i \cdot g_i)$$

where:

i = number of the taxon;
s_i = saprobic value of the ith taxon;
a_i = relative abundance value of the ith taxon;
g_i = indicative weight of the ith taxon;
n = number of taxa.

Mathematical and statistical analysis methods using Biostat applications, Statistics 7 for Windows, Excel-7, Asterisk/Perlodes were used to establish the veracity of the hydrobiological data.

7.2 Results and Discussion

The chemical composition and quality of Prut River water was determined, considering the natural and anthropogenic factors. The natural factors include the structure and composition of rocks, soils, relief of hydrographic basin, hydrobionts community structure and abundance, which until now were poorly investigated. Obviously, a huge influence had the drought in 2007, hot temperatures and floods in 2008 and 2010. The major anthropogenic factors are water and waste discharge in hydrographic basin of Prut River, construction and operation of Giurgiulesti terminal.

The studies performed have shown that in 2009 and 2011 the dissolved oxygen contents was relatively satisfactory for the development of hydrobionts, being on the Braniste-Giurgiulesti sector within 8.1 and 11.8 mg/l, or 90–118 % of

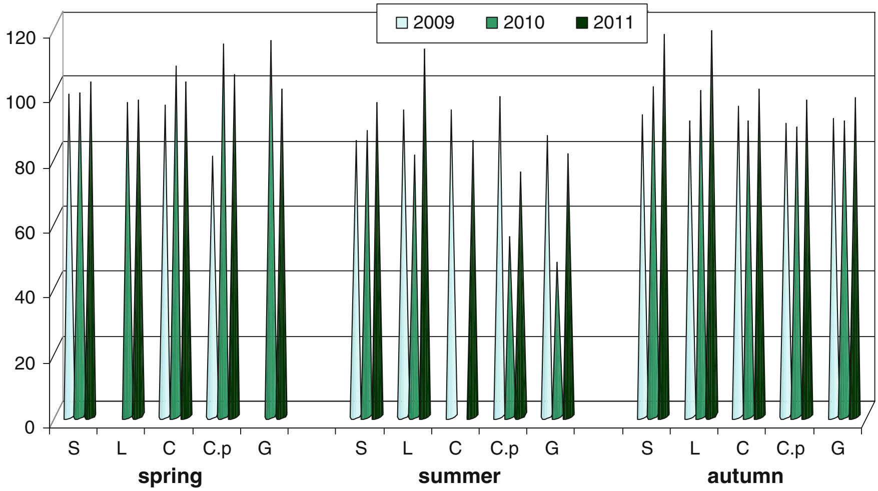


Fig. 7.2 The dynamics of dissolved oxygen in % of saturation in Prut waters (*B* Braniste, *S* Sculeni, *L* Leuseni, *C* Cahul, *Cp* Cislita-Prut, *G* Giurgiulesti), 2009–2011

saturation (Fig. 7.2), the highest values were recorded in spring and autumn, and the lowest—in the summer. During the 2010 summer floods the dissolved oxygen content decreased to 56 % of saturation, despite of a water's high speed and high level, but after floods it went down to 46–48 % of saturation, reaching in the Lower Prut the value of 3.9 mg/l and being unsatisfactory for several species of hydrobionts, including fish. Namely in those periods a lots perished hydrobionts were observed on the river banks.

The suspension contents in the river waters is an important indicator of erosion processes intensity in the catchment area, as well as of waste and wastewater pollution. During the research period the obvious influence of the right tributary—Jijia—was observed: downstream its confluence with Prut River: the suspension contents was 10 times increased (Fig. 7.3).

While in most cases the concentrations of mineral suspensions in Prut waters were much higher than those of organic ones, in the summer of 2010 (after the flood) an opposite situation was observed—the contents in organic suspensions was higher than that of mineral suspensions. This phenomenon, together with the increasing concentration of organic matter in general has reduced the dissolved oxygen contents up to the critical values for Prut flora and fauna (less than 4 mg/l) and only in autumn of the same year the situation has returned to multiannual, with the prevalence of mineral suspensions. The autumn of 2011 was dry, the water level in the river was quite low and yjr suspension contents did not exceed 20 mg/l, which is not characteristic for the Lower Prut.

The increase in the suspension contents in Prut waters negatively influences the production and destruction of organic matter and planktonic organisms [75, 76, 78].

Mineralization, as well as the main ions contents, is a conservative indice and depends mostly on the natural factors. It is known that water mineralization decreases during the floods and increases during the low flows. Despite the fact that during the flood an enormous amount of different waste penetrated into the river bed, the mineralization of Prut water was the lowest, especially during the flood period (Fig. 7.4); the highest value of mineralization was recorded in 2011 in Cahul-Giurgiulesti sector, and thus the classical trend of mineralization growth along the river was preserved.

It is worth to mention the obvious increase in the contents of sulfate (145 mg/l), magnesium (30.4 mg/l) and sodium (68.5 mg/l) ions in the autumn of 2009, which, along with the hydrogen carbonates, determined a quite high level of mineralization for this season—up to 750 mg/l. In 2010 the highest mineralization values were recorded in autumn (640 mg l) and in 2011 (775 mg/l)—in spring.

The ratio between the equivalent values of anions of hydrogen carbonates, sulfates, chlorides and calcium, magnesium, sodium and potassium cations forms the ground for several classifications of surface waters [42].

In the autumn of 2009 in the Cahul-Giurgiulesti sector the contribution of sulfates, sodium and potassium ions in the mineralization of Lower Prut water increased and, opposite, the contribution of hydrogen carbonates and calcium ions significantly decreased; this phenomenon served as evidence of metamorphosis of water chemical composition, linked with river pollution. As result, Prut River

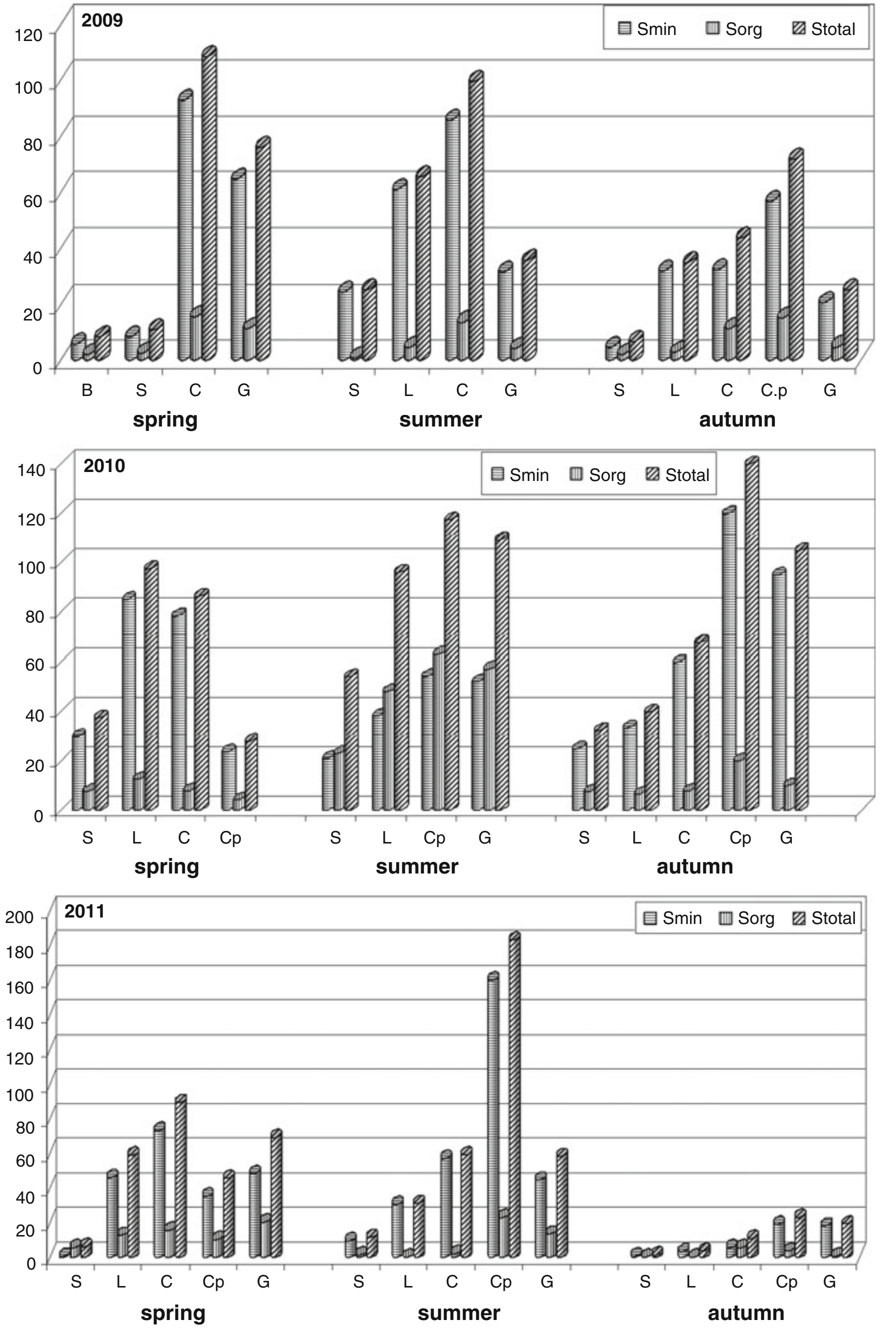


Fig. 7.3 The dynamics of mineral (Smin), organic (sorghum) and total (Stot) suspensions in Prut River (*B* Braniste, *S* Sculeni, *L* Leuseni, *C* Cahul, *Cp* Cislita-Prut, *G* Giurgiulesti), 2009–2011, mg/l

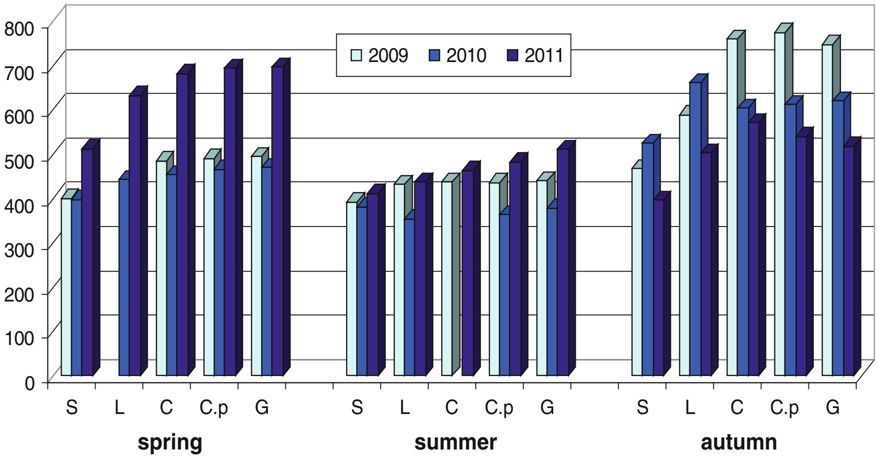


Fig. 7.4 The dynamics of mineralization in Prut river waters (*B* Braniste, *S* Sculeni, *L* Leuseni, *C* Cahul, *Cp* Cislita-Prut, *G* Giurgiulesti), 2009–2011, mg/l

waters, which in most cases refer to the hydrogen carbonate class, calcium group, type II, according to Alekin classification [42], passed in hydrogen carbonate class (almost hydrogen carbonate-sulfate), sodium group, type II, which is not characteristic for Prut River (Figs. 7.5, 7.6).

Thus, the anthropogenic influence on the ecological state of Prut River was obvious enough; perhaps, at that time, there was a source of very high pollution of Prut River with salty wastewater or other waste, which caused an increase in sulfate anions and sodium and potassium cations contents (Figs. 7.5, 7.6).

The contents in nutrients is one of the most important indicators of water quality, which determines both the development of several aquatic organisms, as well as trophicity level, intensity of production-destruction processes of aquatic ecosystems. The concentrations of mineral nitrogen compounds (ammonium ions, nitrites, nitrates) depend on a range of factors, but during the given research period the content of these compounds was much lower than in previous years (Table 7.1). Low levels of ammonium nitrogen and nitrite nitrogen were recorded in the summer of 2009 and 2010 and autumn of 2011, and the highest—in the autumn of 2009, 2010 and the summer of 2011. Nitrate nitrogen concentration was higher in spring and lower in summer (Table 7.1).

Nitrate nitrogen forms, in most cases, more than 90 % of the mineral forms of nitrogen, and only because of the increased concentration of ammonium nitrogen during the floods of 2010 and in the following period, the share of nitrate nitrogen dropped at 50–75 %, and in the summer of 2011—up to 72–70 %.

The ratio between mineral and organic nitrogen is an integrated index that reflects not only nitrogen flow processes, but also the intensity of purification processes, secondary pollution and trophicity level of aquatic ecosystems. It is known that in autumn share of organic nitrogen increases, a phenomenon caused

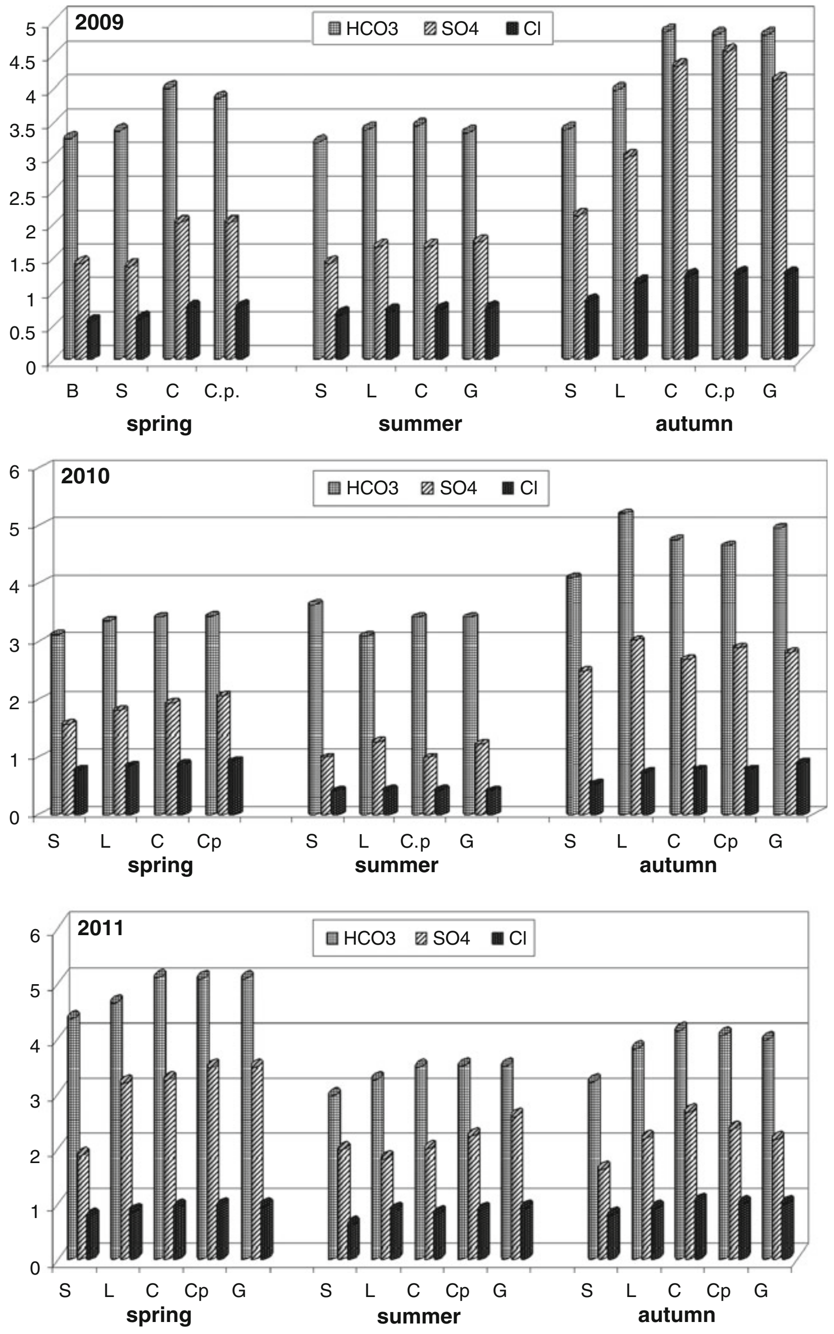


Fig. 7.5 The dynamics of hydrogen carbonate, sulfate and chloride ions in Prut (*B* Braniste, *S* Sculeni, *L* Leuseni, *C* Cahul, *Cp* Cislita-Prut, *G* Giurgiulesti), 2009–2011, mg-ecv/l

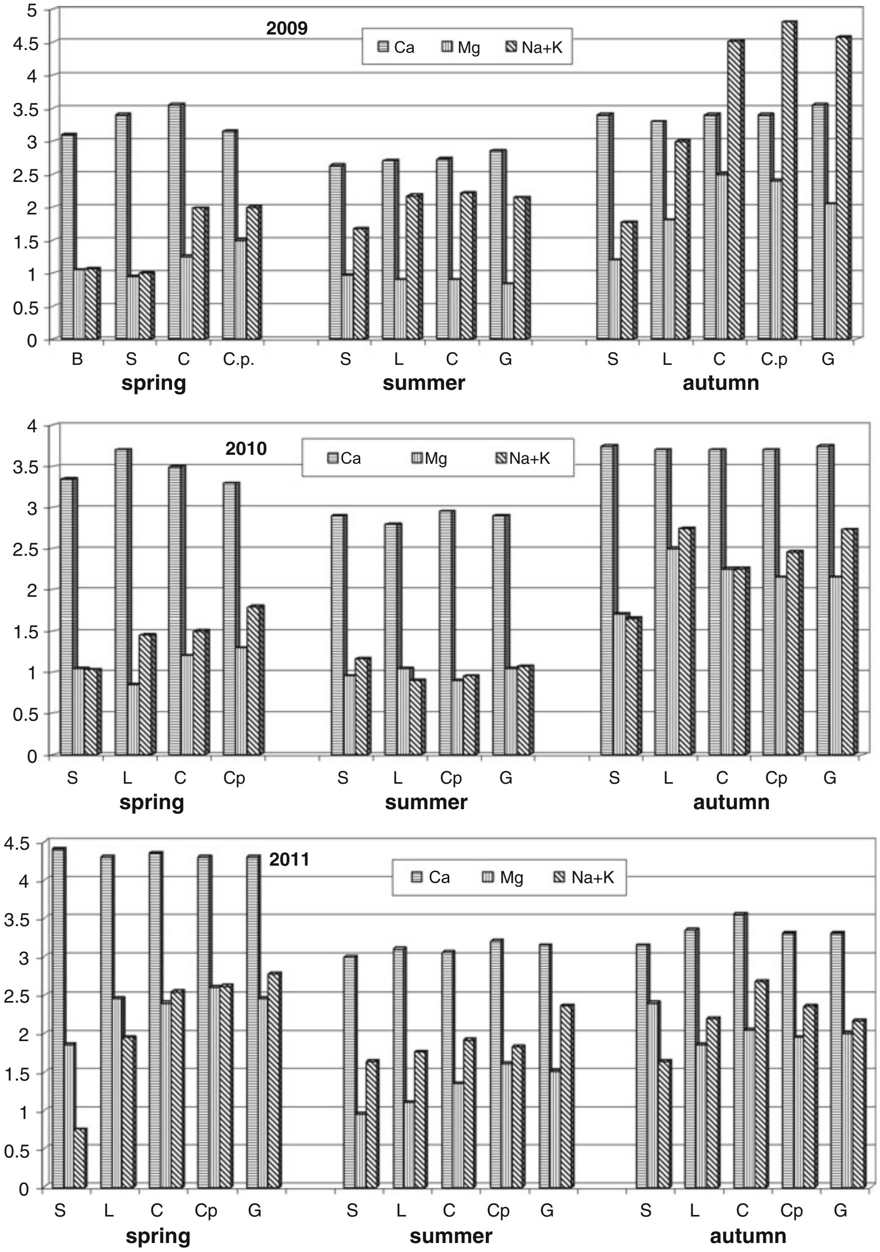


Fig. 7.6 The dynamics of calcium, magnesium, sodium and potassium ions in Prut (*B* Braniste, *S* Sculeni, *L* Leuseni, *C* Cahul, *Cp* Cislita-Prut, *G* Giurgiulesti), 2009–2011, mg-ecv/l

Table 7.1 Dynamics of mineral nitrogen concentration: ammonium (N–NH_4), nitrite (N–NO_2) and nitrate nitrogen (N–NO_3) in Prut waters, mg/l

	Year	Season	Sculeni	Leuseni	Cahul	Cislita Prut	Giurgiulesti
N–NH_4^+	2009	Spring	0.070		0.002	0.020	0.002
		Summer	0.002	0.002	0.002		0.002
		Autumn	0.110	0.002	0.002	0.010	0.070
	2010	Spring	0.10	0.170	0.210	0.100	
		Summer	0.020	0.080		0.060	0.180
		Autumn	0.010	0.170	0.210	0.200	0.230
	2011	Spring	0.040	0.002	0.002	0.002	0.110
		Summer	0.127	0.131	0.135	0.198	0.124
		Autumn	0.002	0.070	0.050	0.060	0.110
N–NO_2^-	2009	Spring	0.011		0.02	0.024	0.022
		Summer	0.005	0.006	0.003		0.013
		Autumn	0.004	0.037	0.021	0.014	0.013
	2010	Spring	0.011	0.026	0.018	0.020	
		Summer	0.008	0.004		0.009	0.011
		Autumn	0.085	0.255	0.230	0.215	0.15
	2011	Spring	0.014	0.018	0.009	0.012	0.014
		Summer	0.019	0.021	0.025	0.031	0.029
		Autumn	0.005	0.009	0.002	0.009	0.002
N–NO_3^-	2009	Spring	1.080		1.250	0.94	0.91
		Summer	0.810	1.020	0.960		0.92
		Autumn	0.680	0.980	1.280	1.090	1.110
	2010	Spring	1.310	1.430	1.480	1.180	
		Summer	0.690	0.590		0.150	0.180
		Autumn	0.820	1.130	1.090	0.980	0.980
	2011	Spring	1.630	1.960	1.630	1.530	1.580
		Summer	0.547	0.628	0.553	0.537	0.558
		Autumn	0.390	1.080	1.160	0.740	1.210

by the decomposition of many aquatic organisms. During the floods in the summer of 2010 the increase of share of organic nitrogen in Prut River was caused by leakage of pollutants from its hydrographic basin (Fig. 7.7). In spring of 2011 downstream of Cahul it was registered an obvious pollution with organic substances and the trend remained the same in summer-autumn, but at a lower level (Fig. 7.7).

Currently, phosphorus concentrations are much lower than in 80–90th years of past century, but the ratio of mineral phosphorus and organic phosphorus is reversed. Organic phosphorus content in 2009–2011 exceeded the mineral one by ten times (Fig. 7.8). For unpolluted rivers from research area the ratio of mineral and organic forms of nutrients is opposite.

It is evident the pollution along the Prut River with easily degradable organic substances, which were assessed according to the values of permanganate oxidability, as well as poorly degradable, which were determined on the base of values

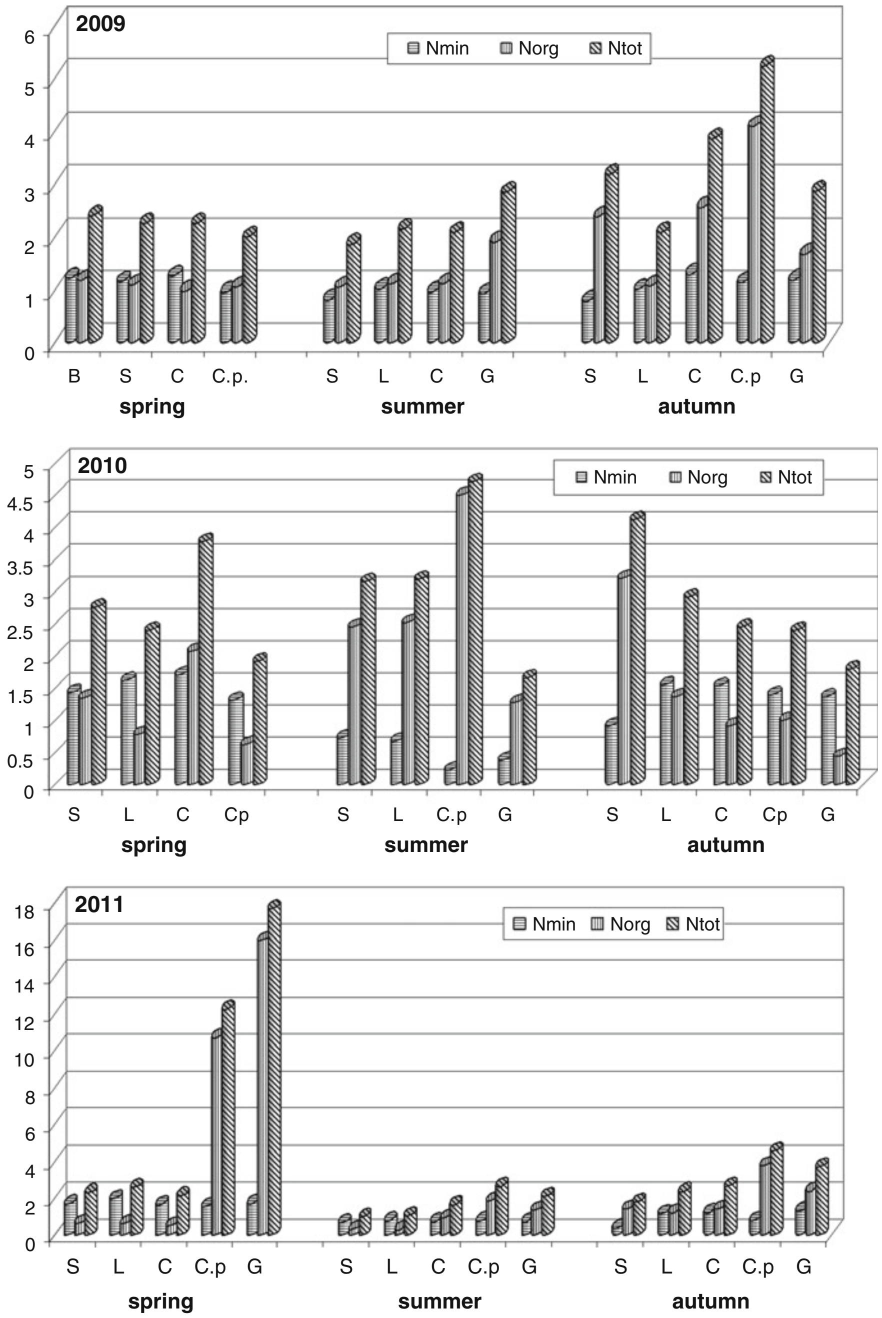


Fig. 7.7 Dynamics of mineral (Nmin), organic (Norg) and total (Ntot) nitrogen in Prut (*B* Braniste, *S* Sculeni, *L* Leuseni, *C* Cahul, *Cp* Cislita-Prut, *G* Giurgiulesti), 2009–2011, mg/l

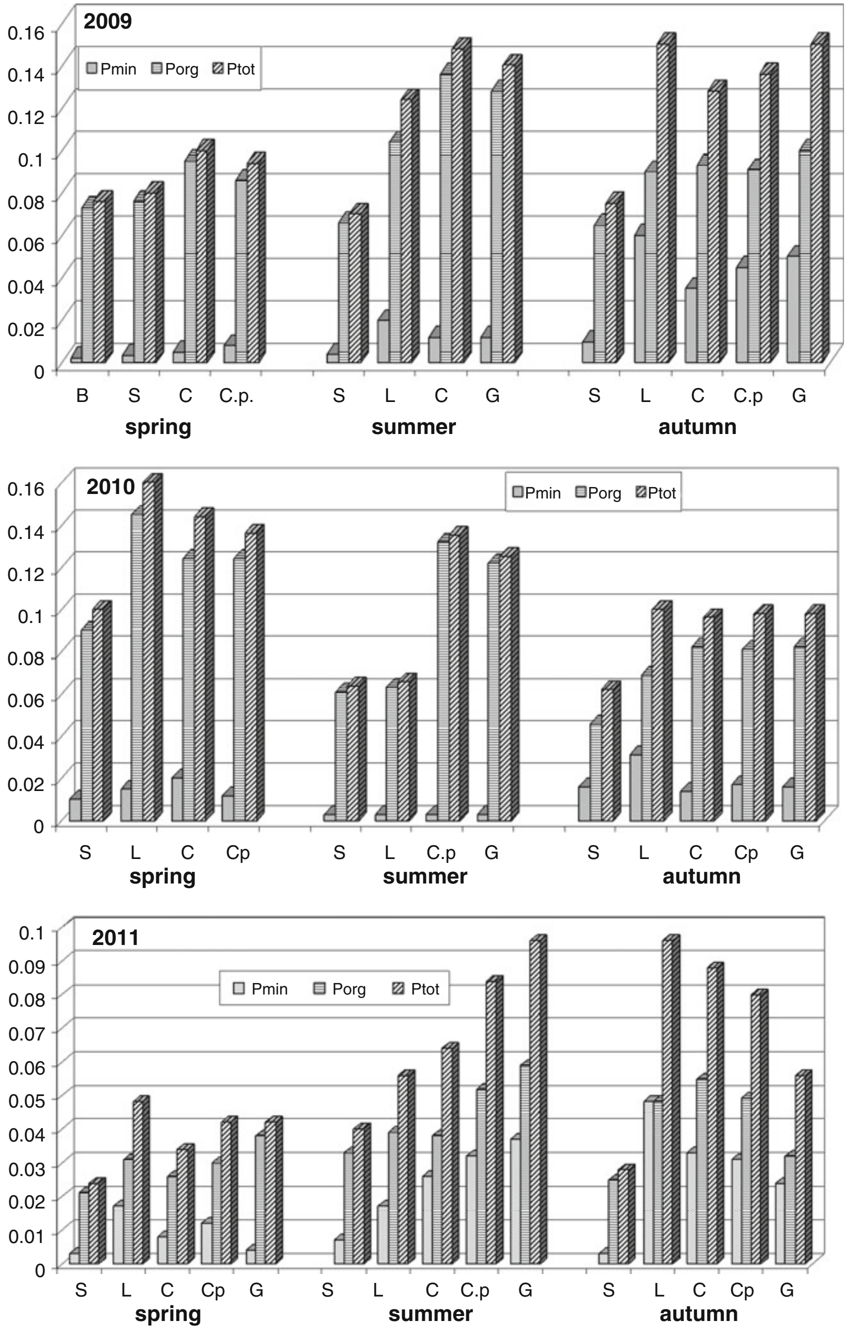


Fig. 7.8 Dynamics of mineral (Pmin), organic (Porg) and total (Ptot) phosphorus in Prut (*B* Braniste, *S* Sculeni, *L* Leuseni, *C* Cahul, *Cp* Cislita-Prut, *G* Giurgiulesti), 2009–2010, mg/l

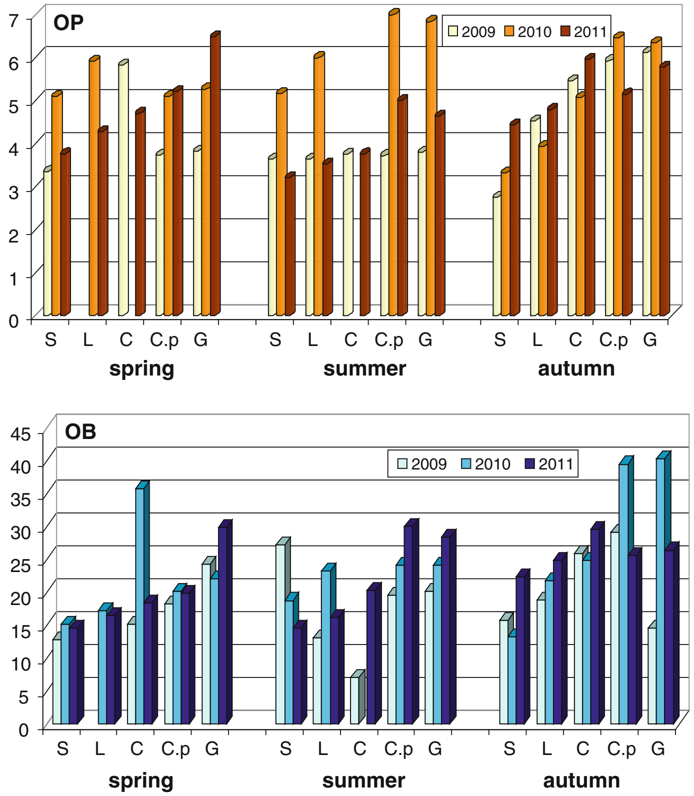


Fig. 7.9 Dynamics of permanganate (*OP*) and dichromate (*OB*) oxidability in Prut (*B* Braniste, *S* Sculeni, *L* Leuseni, *C* Cahul, *Cp* Cislita-Prut, *G* Giurgiulesti), mgO/l

of dichromate oxidability. For example, the concentration of organic substances in 2009 increased from 6.8 mg/l at Sculeni station to 21.2 mg/l at Giurgiulesti station, and in 2010—from 11.0 to 30.2 mg/l, respectively.

Usually, the values of permanganate oxidability increase to autumn, when some aquatic plants are under the process of decomposition, but in summer of 2010, during floods, big amounts of allochthonous organic matter penetrated into the river waters and this has led to increase of permanganate oxidability, by reaching the peak values (Fig. 7.9).

Thus, most often the Prut waters were satisfactory for hydrobiont development, but the suspension content, as well as the deficit of dissolved oxygen negatively influenced on some groups of aquatic organisms. Metamorphosis of chemical composition of Lower Prut water demonstrates a strong anthropogenic influence, but overall, the Prut waters corresponded to the requirements for multifunctional aquatic ecosystems (which may serve both as source of drinking water and water sources for irrigation, fisheries and aquaculture).

7.3 Bacterioplankton

In all aquatic ecosystems density is one of the most variable indices of bacterioplankton state (both density of total bacterioplankton and that of separate bacterioplankton physiological group), whose values can vary by 10 times or even more in multiannual aspect. In particular, this is typical for water bodies, which are subject to human impact.

The density of total bacterioplankton in investigated sector of Prut River varied in wide limits—from 0.5 to 32.2 million cells/ml—in the vegetative periods of 2009–2011 (Fig. 7.10). The highest annual mean value was recorded in 2009 and it was equal to 8.87 ± 1.13 million cells/ml, and the lowest-in 2011—2.5 ± 0.12 million cells/ml. In seasonal aspect, the highest density values were recorded in spring. To note that in 2010 the increase of density of total bacterioplankton occurred after floods, that means already in autumn period.

Saprophytic bacteria are the most widespread and numerous group of microorganisms, actively participating in primary destruction of easily degradable organic substances. Usually, their density is the highest in summer. It was similar in the case of Prut River: the saprophytes density was the highest in the summer of 2009 and 2011 and the mean value was 18.80 ± 3.7 and, respectively, 16.3 ± 6 240 thousand cells/ml. However, during the floods of summer 2010, there was low saprophytes density in water of Prut River, which is not typical for summer periods (Fig. 7.11).

Although bacterial biomass production varied in a large range (from 0 to 9.96 cal/l in 24 h) during study period, however, there has been a clear trend of decrease of this index from 2009 until 2011 (Fig. 7.12). The perishing of bacteria was recorded in the spring and summer of 2011, which can be explained by allochthonous microflora domination, as well as unfavorable influence of environmental factors. At some separate stations was not detected an obvious seasonal dynamics of bacterial production, but overall for 2009–2011 a trend of its

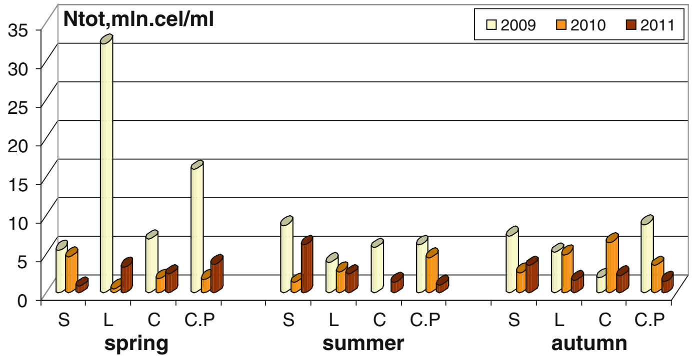


Fig. 7.10 The dynamics of density of total bacterioplankton (Ntot, million cells/ml) in Prut waters, 2009–2011 (*S* Sculeni, *L* Leuşeni, *C* Cahul, *C.P* Cislita Prut)

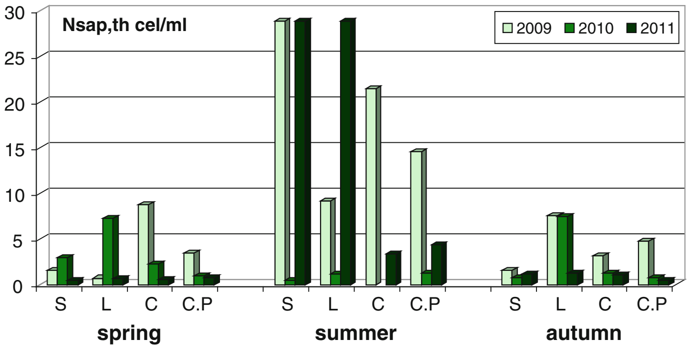


Fig. 7.11 The dynamics of density of total saprophytes (Nsap, thousand cells/ml) in Prut waters, 2009–2011 (*S* Sculeni, *L* Leuseni, *C* Cahul, *CP* Cislita Prut)

increasing has been observed from spring (1.15 ± 0.07 cal/l in 24 h) to autumn (2.03 ± 1.07 cal/l in 24 h).

Unlike the bacterioplankton production processes, in the case of bacterial destruction it is observed a more or less obvious dependency on the season and water temperature. In summer time the destruction intensity increases significantly and it decreases sharply to autumn. Obvious differences between years taken into account were not found. On average, for the period under observation it was revealed the growth of bacterial destruction intensity from spring (8.96 ± 0.91 cal/l in 24 h) to summer (16.09 ± 5.9 ca l in 24 h) and it decrease to autumn (4.86 ± 2.58 cal/l in 24 h) (Fig. 7.13).

One of the indicators of water quality is bacterial index, which is calculated as the ratio between density of saprophytes bacteria and density of total bacterioplankton and it is expressed as a percentage. As lower are the values of this index, as better is the water quality. Analysis of the results revealed that there is a permanent bacterial pollution of the river at Leuseni station, but the water is

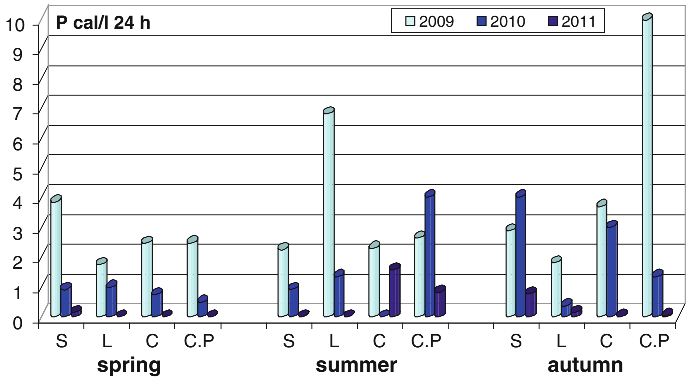


Fig. 7.12 Dynamics of bacterioplankton production (P, cal/l in 24 h) in Prut waters, 2009–2011 (*S* Sculeni, *L* Leuseni, *C* Cahul, *CP* Cislita Prut)

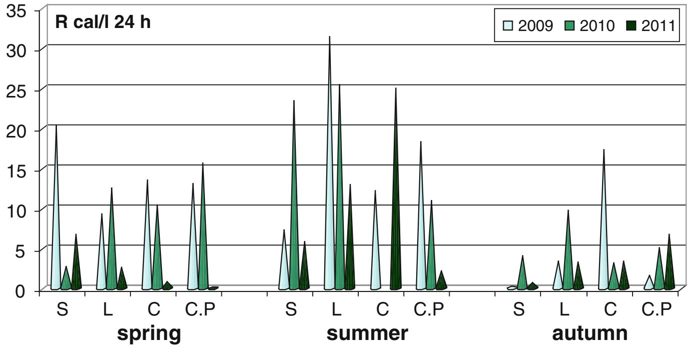


Fig. 7.13 Dynamics of bacterioplankton destruction processes (R, cal/l in 24 h) in Prut waters, 2009–2011 (*S* Sculeni, *L* Leuseni, *C* Cahul, *CP* Cislita Prut)

obviously cleaner at Sculeni station. From seasonal point of view, bacterial pollution is higher in summer, but it is less obvious in spring and autumn, this phenomenon being determined primarily by water temperature.

According to the classification of Ambrazene [3], Kireeva [28], Sculeni and Cislita-Prut stations were the cleanest from sanitary-microbiological point of view—there bacterial index was on average 0.12 % and, respectively, 0.10 % for the 2009–2010 vegetation seasons, the water being characterized as low-polluted. At the same time, the most polluted was Leuseni station, where bacterial index was equal to 0.41 %, the water being considered as heavily polluted (Fig. 7.14). On average for Lower Prut, bacterial index proved to be equal to 0.20 %, which characterized the water as moderately polluted.

The same general characteristic of Lower Prut water—low-polluted (3b)—is obtained and by applying the ecological-sanitary classification developed by [44]. However, in spring and autumn periods (except of Leuseni station) the water quality was oscillating between "clean" and "low-polluted" and in the summer of 2009 and 2011, at most stations, the water pollution level was oscillating from "moderately polluted" to "strongly polluted". It is difficult to explain, but during

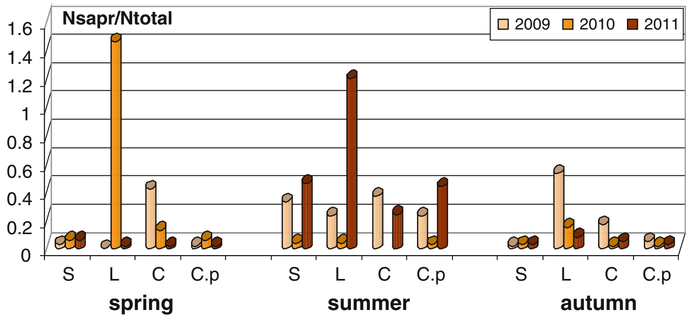


Fig. 7.14 Bacterial index value (Nsap/Ntot) in Prut River waters, 2009–2011

Table 7.2 Dynamics of ammonifying, nitrifying and denitrifying bacteria in Prut waters, 2009–2011, cells/ml

Year	Season	Station			
		Sculeni	Leuseni	Cahul	Cislita-Prut
Ammonifying bacteria					
2009	Spring	900	–	20,000	4000
	Summer	1840	980	400	1,200
	Autumn	750	500	4,200	6,800
2010	Spring	1,500	1,800	2,900	1,400
	Summer	1,400	2,500	–	4,000
	Autumn	800	2,200	900	500
2011	Spring	400	800	600	500
	Summer	1,700	1,550	1,800	2,500
	Autumn	300	320	620	1,200
Nitrifying bacteria					
2009	Spring	5	–	15	4
	Summer	7	5	2	5
	Autumn	10	15	8	12
2010	Spring	2	4	3	4
	Summer	7	6	10	5
	Autumn	18	17	–	12
2011	Spring	0.1	0.3	0.2	0.2
	Summer	15	18	20	30
	Autumn	5	7	9	11
Denitrifying bacteria					
2009	Spring	420	–	5,000	580
	Summer	4,400	750	800	500
	Autumn	150	500	160	90
2010	Spring	315	400	500	150
	Summer	260	210	–	180
	Autumn	290	600	190	100
2011	Spring	60	170	85	80
	Summer	150	180	155	150
	Autumn	200	250	300	100

floods in the summer of 2010, according to the bacterial index, river water was characterized as low-polluted.

Different eco-physiological groups of microorganisms are involved in the nitrogen, phosphorus and carbon cycle and by comparative analysis of these groups the pollution degree and nature of aquatic ecosystem can be found. Eco-physiological groups of microorganisms involved in free nitrogen fixation (aerobic and anaerobic), ammonification, nitrification, denitrification, phosphate mineralization, amylolysis, and cellulolysis were investigated.

Nitrogen cycle is carried out by many decomposition, mineralizing and autotrophic bacteria. Among the investigated bacteria, the group of ammonifying bacteria is the best represented numerically, their density ranging from 300 to 20,000 cells/ml (Table 7.2).

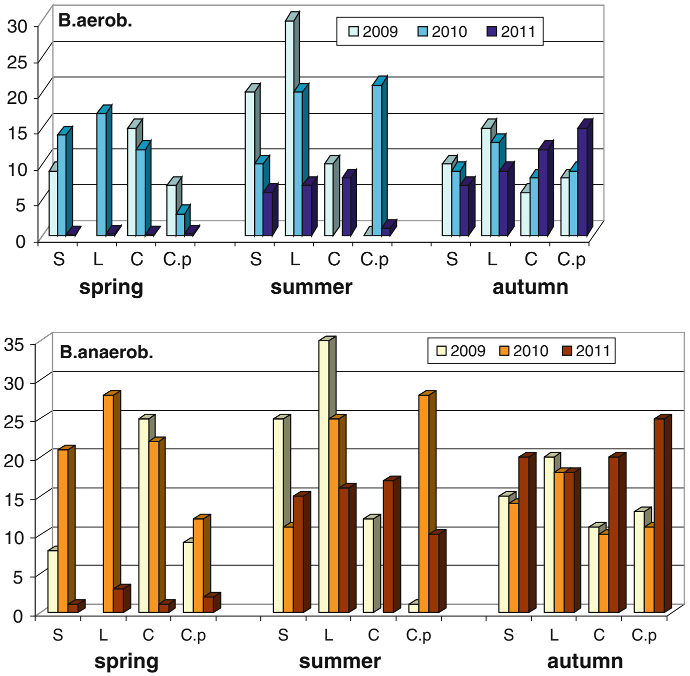


Fig. 7.15 Dynamics of density of aerobic and anaerobic nitrogen fixing microorganisms in Prut waters, 2009–2011, cel/ml (*S* Sculeni, *L* Leuseni, *C* Cahul, *CP* Cislita Prut)

The highest density of ammonifying bacteria was recorded at Cahul station, which shows an increased intensity of ammonification and denitrification processes in this sector of Prut River.

The density of nitrifying bacteria ranged from 0.1 to 30 cells/ml.

Free nitrogen fixation is a process that replaces the loss of nitrogen through denitrification. The density of microorganisms from the eco-physiological group of aerobic nitrogen fixing bacteria was low and ranged from 0.1 cells/ml to 30 cells/ml; anaerobic fixation was represented by a slightly higher density of bacteria—1–34 cells/ml (Fig. 7.15).

Thus, we can conclude that in the nitrogen microbial cycle the highest share is kept by ammonifying bacteria, while nitrifying bacteria and nitrogen fixing bacteria actually have the lowest density. Be noted that in previous years (up to 2009) the same situation was highlighted: the increased density of ammonifying and denitrifying bacteria, and low number of nitrifying and nitrogen fixing bacteria.

Although microbial processes have an important role in phosphorus cycle, few systematic investigations were performed on phosphate mineralizing bacteria [39, 40, 55, 56]. Mainly by low water temperature. Regarding the spatial distribution of these organisms, it was found that it is relatively consistent along the whole studied river segment (Table 7.3).

Table 7.3 The dynamics of density of phosphate mineralizing bacteria in Prut waters, 2009–2011, cells/ml

Year	Season	Station			
		Sculeni	Leuseni	Cahul	Cislita-Prut
2009	Spring	90	–	1,000	300
	Summer	400	1,400	550	5,500
	Autumn	11	100	25	30
2010	Spring	400	1,500	1,200	1,110
	Summer	250	270	–	980
	Autumn	15	110	35	30
2011	Spring	130	290	190	260
	Summer	100	200	500	545
	Autumn	50	60	70	90

As result of researches on this eco-physiological group was found that it is represented by a large number of microorganisms −11 to 5500 cells/ml. It turned out that in spring and summer the most favorable conditions for their development are created, while their density falls down sharply in autumn, a phenomenon caused

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Among the microorganisms involved in the carbon cycle the amylolytic, cellulosolytic, phenolytic and petrolytic bacteria were investigated.

The carried out investigations on eco-physiological group of amylolytic bacteria revealed a seasonal evolution of microorganisms density, the highest values being recorded in spring and summer—up to 24,000 cells/ml (Table 7.4). There was ascertained an increase of number of amylolytic bacteria along the river, the highest values being reached in the Cahul-Cislita-Prut sector.

Cellulosolytic bacteria are numerically underrepresented—from 3 cells/ml to 24 cells/ml (Fig. 7.16)

One of the indicators of intensifying human impact on ecosystems is the increase of amount of phenol compounds and petroleum products in natural

Table 7.4 The dynamics of density of amylolytic bacteria in Prut waters, 2009–2011, cells/ml

Year	Season	Station			
		Sculeni	Leuseni	Cahul	Cislita-Prut
2009	Spring	850	–	24,000	3,100
	Summer	2,400	1,400	1,280	1,600
	Autumn	5,400	5,000	3,200	4,100
2010	Spring	3,200	2,600	4,000	3,000
	Summer	3,200	3,800	–	4,100
	Autumn	1,100	2,000	900	700
2011	Spring	100	200	220	250
	Summer	10,000	12,000	14,000	18,000
	Autumn	900	1,100	1,000	1,080

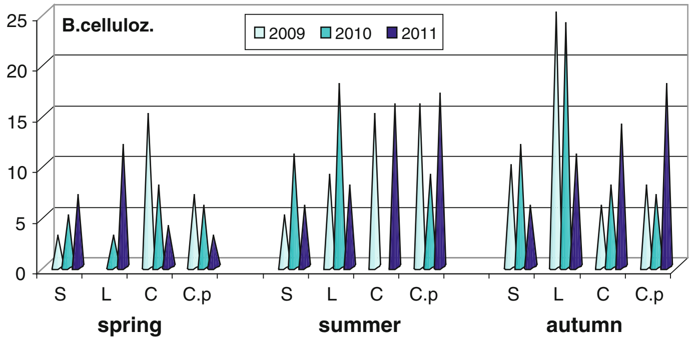


Fig. 7.16 The dynamics of density of cellulosolytic bacteria in Prut waters, 2009–2011, cells/ml (*S* Sculeni, *L* Leuseni, *C* Cahul, *CP* Cislita Prut)

waters. It is known that biological detoxification is essential in eradicating such substances in aquatic ecosystems and phenolytic bacteria and petroleum-oxidizing (petrolytic) bacteria, density and degree of activity of which indicate the ecosystem status, have the main role in this process. It is of interest to note that the density of these bacteria, which forms from 44 to 55 % of density of saprophytic bacteria is highly variable, this fact being rather explained by variation of human impact intensity on the ecosystem of Prut River, as of water temperature fluctuations during different seasons of the vegetation period (Figs. 7.11, 7.17, 7.18).

It is known that phenols are poorly degradable toxic substances. They penetrate into aquatic ecosystems as result of human activity, through waste waters and also, naturally, as result of biochemical decomposition of submerged vegetation and remains of hydrobionts. In the frame of investigations, which were carried out in 2010 on Prut River by the Department of Environmental Quality Monitoring of the State Hydrometeorological Service, in six cases were identified phenol concentrations, which exceeded the maximum admissible concentration in Prut.

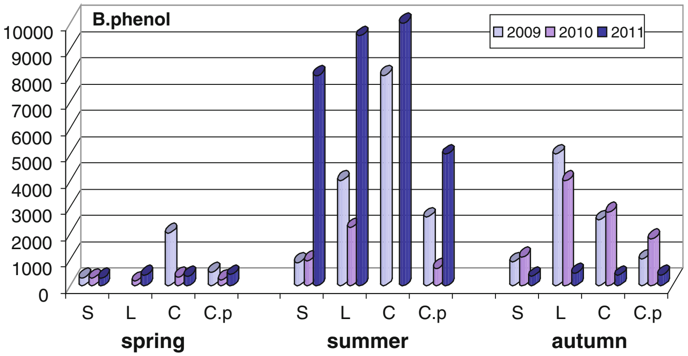


Fig. 7.17 The dynamics of density of phenolytic bacteria in Prut waters, 2009–2011, cells/ml (*S* Sculeni, *L* Leuseni, *C* Cahul, *CP* Cislita Prut)

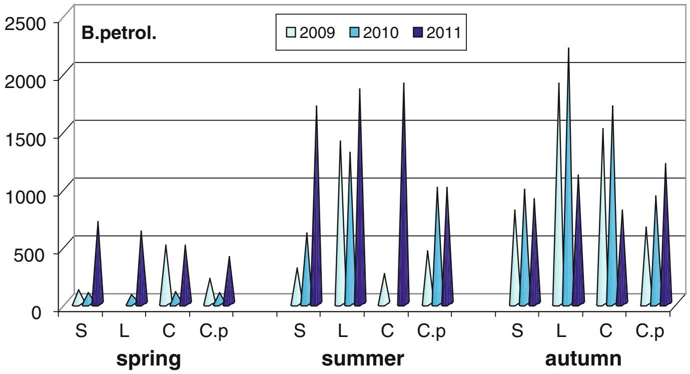


Fig. 7.18 The dynamics of density of petrolytic bacteria in Prut waters, 2009–2011 cells/ml (*S* Sculeni, *L* Leuseni, *C* Cahul, *CP* Cislita Prut)

The natural cycle of phenolic compounds includes several stages: accumulation of phenol complex compounds in hydrobionts, their decomposition up to simple phenols and then—up to carbon dioxide and water. Carbon of phenols is used by microorganisms as a source of nutrition and energy. Phenolytic bacteria were detected in all investigated water samples from Prut River (Fig. 7.17). It turned out that the density of phenolytic bacteria in Leuseni-Cahul sector (from 3.61 to 3.72 thousand cells/l) exceeded the density recorded for Sculeni (1.59 thousand cells/ ml) and Cislita-Prut (1.53 thousand cells/ml) stations more than two times. Under seasonal aspect, it was found that the most intense processes of phenol decomposition occurred in summer (Fig. 7.17).

The previous determinations carried out on Prut River [41, 60] revealed a higher number of phenolytic bacteria—up to 80 thousand cells/ml, which indirectly denotes significant water pollution by phenols in previous years.

Biodegradation of petroleum in Prut River takes place intensely with the involvement of fungi, yeasts and specialised bacteria called petrolytic, which are able to oxidize the petroleum, to use petroleum hydrocarbons as energy and carbon source. In the lower sector of Prut River the density of these organisms ranged from 70 to 2,200 cells/ml, constituting 11–15 % of the total heterotrophs (Fig. 7.18).

The most polluted stations with such bacteria are Leuseni station—on average 1,304 cells/ml and Cahul station—on average 1,013 cell/ml. These data denotes the constant existence of petroleum in Prut water. Penetration of petroleum in water bodies occurs by slow, weak, and chronic leakages from navigation vessels and also by sudden and massive discharges.

Thus, the functional state of bacterioplankton, regardless of its considerable changes over time, provides reliable information on status of Prut River ecosystem, but, however, for a relevant assessment of bacterioplankton, long-term observations are needed. Compared with the period 1993–2005, bacterial production and density of total bacterioplankton increased twice, simultaneously, the density of saprophytic microflora decreased and the mean values of bacterial destruction changed non-essentially.

Among the eco-physiological groups of bacteria, which take part in the cycle of main biogenic elements, the ammonifying (up to 20.0 thousand cells/ml), amylolytic (up to 24.0 thousand cells/ml) and denitrifying (up to 5.0 thousand cells/ml) bacteria dominated.

Phenolytic and petrolytic bacteria, with a density of 9.5 and 2.2 thousand cells/ml, respectively, are permanently identified in Prut water, which indirectly proves the existence of intensive anthropogenic impact. At the most stations of Prut River the water quality varied within “low- polluted”-“polluted”.

7.4 Phytoplankton

As result of investigations on phytoplankton of Prut River in the 2009–2011 period 106 species and intraspecific taxa were identified, which refer to 46 genera, 23 families, 12 orders, 7 classes and 4 phyla (Table 7.5). The base of floristic diversity consists of *Chlorophyta* and *Bacillariophyta* phyla, which recorded the highest number of taxa of different ranks. The share of *Chlorophyta* phylum makes 39.6 %

Table 7.5 Phytoplankton taxonomic spectrum of the Prut River in the 2009–2011 period

Phylum	Classes	Orders	Families	Genera	Species, varieties and forms
Cyanophyta	2	3	6	7	12
Bacillariophyta	2	5	6	16	39
Euglenophyta	1	1	1	4	13
Chlorophyta	2	3	10	19	42
Total	7	12	23	46	106

of total floristic diversity and 36.8 % are insured by *Bacillariophyta* phylum. *Euglenophyta* phylum constitutes 12.3 %, and *Cyanophyta* phylum—11 %.

In the composition of *Chlorophyta* phylum the main role in formation of taxonomic diversity belong to *Scenedesmus, Monoraphidium, Pediastrum* and *Tetraedron* genera, and in the composition of dominant complex the following species should be mentioned: *Actinastrum hantzschii* Lagerh. var. *hantzschii*, *Monoraphidium komarkovae* Nygaard, *M. contortum* Thur., *Tetrastrum triangulare* Chod.*, Scenedesmus quadricauda* Turp. *var. quadricauda* and *Coelastrum microporum Nageli.*

The most of identified *Bacilarophyta* algae were attributed to *Pennatophyceae* class, being represented mainly by *Navicula, Synedra, Nietzsche* and *Cymbella* genera, the dominant species being *Cyclotella Kuetzingiana Thw., Synedra acus Kutz. var. acus, Melosira granulata (Ehr.) Ralfs var. granulata, Nitzschia palea (Kutz.) W.Sm. var. palea şi Nitzschia sigmoidea (Ehr.) W.Sm. var.sigmoidea.*

In the composition of *Cyanophyta* phylum more representative was *Oscillatoria* genus, and the species *Synechocystis aquatilis* Sanv., *Aphanizomenon flos-aquae* (L.) Ralfs *f. flos-aquae, Oscillatoria planctonica* Wolosz.*, Merismopedia tenuissima* Lemm. and *Oscillatoria lacustris* (Kleb.) Geitl. builded the dominant complex.

According to species origin, the Prut River algal flora makes a very varied complex, the most species and intraspecific taxa of algae (75 %) assigning to group of cosmopolitans; to boreal group assigned only 11 % (Table 7.6).

Processes that occurred in Prut River as result of impact of anthropogenic factors significantly influenced the diversity and functioning of phytoplankton, which reacts quickly to changes in hydrological, hydrochemical and hydrobiological regimes of their living environment. The representatives of various algae phyla, which are present in the phytoplankton community composition, reacted differently, according to their specific features. Thus, in the last five to six decades Prut River suffered by habitat damages and species loss caused by the impact of a range of natural and anthropogenic factors. Of the total of 316 taxa certified in Prut during 1962–2008 [52, 68–70], recent investigations (2009–2011) revealed as mentioned above only 106 species and intraspecific taxa. For the majority of taxonomic groups the comparative analysis revealed a decrease of taxa number, which was known previously our researches, but taxa extinction is offset to some extent by continues identification of new species in Prut River. It should be noted that although there have been changes in taxonomic structure of phytoplankton, the ratio between the number of species of algae groups remained the same, but dominant and rare species differ from one period to another.

Chlorophyte algae were more diverse and reached higher values in 2009, particularly at Sculeni station, where also euglenophyte algae were growing more intense. But the average annual biomass values of these two groups of algae at all investigated stations did not exceed the biomass values of bacillariophyte algae, which are dominant in phytoplankton composition (Fig. 7.19).

Despite the increased values of density of cianophyte algae, the highest share in the formation of Prut River phytoplankton biomass belongs to bacillariophytes,

Table 7.6 List of algal species identified in Prut River during 2009–2011

Cyanophyta	Origin	Saprobity	Sculeni	Leuseni	Cahul	Cislita-Prut
Synechocystis aquatilis Sanv.	k		+	+	+	+
Merismopedia glauca (Ehr.) Nag f.glauca	k		–	–	–	+
Merismopedia tenuissima Lemm.	k	*β*- α	–	+	+	+
Gloeocapsa turgida (Kutz.) Hollerb. f.turgida	k	*o*	+	+	+	+
Oscillatoria kisselevii Anissim	–		+	+	+	+
Oscillatoria lacustris (Kleb.) Geitl.	k		+	+	+	+
Oscillatoria lauterbornii Schmidle	k	*ρ*	+	–	–	–
Oscillatoria planctonica Wolosz.	k		+	+	+	+
Oscillatoria subtilissima Kutz.	–	α	–	+	–	–
Romeria leopoliensis (Racib.) Koczw	–	*o-β*	–	+	+	+
Anabaena spiroides Kleb. f. spiroides	b	*o –β*	–	+	–	+
Aphanizomenon flos-aquae (L.)Ralfs f.flos-aquae	k	*β*	+	+	+	+
Bacillariophyta						
Melosira granulata (Ehr.) Ralfs var.granulata	k	*β*	–	+	+	+
Melosira italica (Ehr.) Kutz. var. italica	k	*o-β*	–	+	+	+
Cyclotella Kuetzingiana Thw.	k	*β*	+	+	+	+
Cyclotella meneghiniana Kutz var.meneghiniana	k	α-*β*	–	+	–	+
Diatoma vulgare Bory var.vulgare	k	*β*	+	+	+	–
Diatoma vulgare var. lineare Grun.	–		+	+	+	–
Fragillaria virescens Ralfs var. virescens	k	x	–	–	–	+
Synedra acus Kutz. var.acus	k	*β*	+	+	+	+
Synedra ulna var. amphirhynchus (Ehr.) Grun.	k		–	+	–	–
Synedra ulna (Nitzsch.) Ehr. var.ulna	k	*β*	–	–	+	+
Cocconeis placentula Ehr. var.placentula	b	*β*	+	+	+	+
Rhoicosphenia curvata (Kutz.) Grun. var. curvata	k	*β*	+	–	–	+
Navicula cincta (Ehr.) Kutz. var.cincta	k	*β*-α	+	+	–	+
Navicula cryptocephala Kutz. var.cryptocephala	k	α	+	+	+	+
Navicula cryptocephala var.intermedia Grun.	k	*β*	+	–	–	+
Navicula exigua (Greg.) O.Mul. var.exigua	k	*β*	+	+	–	–
Navicula grasilis Ehr.	b	*β-o*	+	+	–	+
Navicula placentula (Ehr.) Grun. f.placentula	k		–	–	+	–

(continued)

Table 7.6 (continued)

Cyanophyta	Origin	Saprobity	Sculeni	Leuseni	Cahul	Cislita-Prut
Navicula sp.			+	–	–	+
Navicula viridula Kutz. var.viridula	k	α	–	–	+	–
Pinnularia microstauron (Ehr.) Cl. var.microstauron	k	*o*	–	+	–	–
Gyrosigma acuminatum (Kutz.) Rabenh. var. acuminatum	b	*β*	+	+	+	+
Gyrosigma distortum (W.Sm.) Cl. var.distortum	–		–	+	–	+
Gyrosigma fasciola Ehr.	k		+	+	–	–
Amphora ovalis Kutz. var.ovalis	k	*o-β*	+	+	–	+
Cymbella lanceolata (Ehr.) V.H. var.lanceolata	b	*β*	+	+	–	–
Cymbella tumida (Breb.) V.H. var.tumida	k		+	+	+	–
Cymbella turgida (Greg.) Cl.	b		–	+	–	+
Cymbella ventricosa Kutz. var. ventricosa	k	*β*	+	–	+	–
Gomphonema olivaceum (Lyngb.) Kutz. var.olivaceum	b	*β*	+	+	+	+
Hantzschia amphioxys Grun. var.amphioxys	k	α	–	–	–	+
Nitzschia acicularis W.Sm. var. acicularis	k	α	+	+	+	+
Nitzschia kuetzingiana Hilse	b		+	+	+	+
Nitzschia longissima var.reversa (Breb.) Ralfs.W.Sm.	–		–	–	+	+
Nitzschia palea (Kutz.) W.Sm. var.palea	b	α	+	+	+	+
Nitzschia sigmoidea (Ehr.) W.Sm. var.sigmoidea	k	*β*	+	+	+	+
Nitzschia sublinearis Hust.	b		+	–	–	–
Cymatopleura eliptica (Breb.) W.Sm. var. eliptica	k	*β*	–	+	–	+
Cymatopleura solea (Breb.) W.Sm.var.solea	b	*β*-α	+	+	–	+
Euglenophyta						
Trachelomonas volvocina Ehr.	k	*β*	–	+	–	–
Trachelomonas verrucosa Stokes var.verrucosa	k		–	+	+	–
Trachelomonas oblonga Lemm. var.oblonga	k	*β*	–	–	+	+
Trachelomonas intermedia Dang. f.intermedia	k		+	+	–	+
Trachelomonas hispida (Perty) Stein. var. hispida	k	*β*	+	+	+	+
Trachelomonas hispida var. crenulatocollis (Maskell) Lemm.	k		–	–	+	–

(continued)

Table 7.6 (continued)

Cyanophyta	Origin	Saprobity	Sculeni	Leuseni	Cahul	Cislita-Prut
Strombomonas fluviatilis (Lemm.) Defl. var. fluviatilis	k	*β*	–	+	+	+
Euglena polymorpha Dang.	k	α	–	–	–	+
Euglena oxyuris Schmarda var. oxyuris	k	*β*-α	–	+	–	+
Euglena limnophila var. swirenkoi (Arnoldi) Popova	k		–	+	–	–
Euglena gracilis Klebs.	k	*o*	–	–	–	+
Euglena acus Ehr. var. acus	k	*β*	–	+	+	–
Phacus pleuronectes (Ehr.) Duj. var. pleuronectes	k	*β*	+	+	–	+
Chlorophyta						
Chlamydomonas globosa Snow.	k		+	+	+	+
Carteria pallida Korsch.	–		+	+	+	+
Ankyra ancora(G.M.Smith) Fott f. ancora	k		–	+	–	–
Schroederia setigera (Schroed.) Lemm.	k		–	+	–	+
Schroederia spiralis (Printz.)Korsch.	k		+	–	–	–
Pediastrum borianum var. longicorne Reinsch.	k		–	+	–	+
Pediastrum boryanum (Turp.) Menegh. var.boryanum	k	*β*	–	+	–	–
Pediastrum duplex Meyen. var. duplex	k	*β*	–	+	–	–
Pediastrum simplex Meyen	k		+	–	–	–
Dictyosphaerium pulchellum Wood.	k		–	+	–	–
Chlorella vulgaris Beier.	k	*ρ*-α	+	+	+	+
Tetraedron caudatum (Corda) Hansg. var. caudatum	b	*β*	–	–	+	–
Tetraedron minimum (A.Br.) Hansg. var. minimum	k	*β*	+	+	+	+
Tetraedron triangulare Korsch.	k		–	+	–	–
Lagerheimia genevensis Chod. var. genevensis	k	*β*	–	+	–	–
Lagerheimia wratislaviensis Schroed. var. wratislaviensis	k	*β*	+	+	+	+
Monoraphidium arcuatum (Korsch.)	k		+	+	+	+
Monoraphidium contortum Thur.	k		+	+	+	+
Monoraphidium griffithii (Berk.)	k		–	–	+	–
Monoraphidium komarkovae Nygaard	k		+	+	+	+
Monoraphidium minutum (Nag.)	k		+	+	+	+
Selenastrum gracile Reinsch.	k	*β*	+	–	–	–
Siderocelis ornata Fott.	k	*β*	+	–	–	–
Coelastrum microporum Nageli	k	*β*	–	+	+	+
Actinastrum hantzschii Lagerh. var.hantzschii	k	*β*	+	+	+	+
Crucigenia lauterbornei (Schmidle) Korsch.	k		–	+	+	–
Crucigenia tetrapedia (Kirchn.) W.et G.S.West	k	*o*-*β*	–	+	+	+

(continued)

Table 7.6 (continued)

Cyanophyta	Origin	Saprobity	Sculeni	Leuseni	Cahul	Cislita-Prut
Tetrastrum triacanthum Korschik.	k		–	–	+	–
Tetrastrum triangulare Chod.	k		+	+	+	+
Micractinium quadrisetum (Lemm.)G.S.Smith.	–		–	+	–	–
Scenedesmus apiculatus W.et G.S.West	k		–	–	+	–
Scenedesmus arcuatus Lemm.	k	*β*	–	+	–	+
Scenedesmus bicaudatus Dedussenko	k		–	+	+	+
Scenedesmus elipticus Corda	n-a		–	–	+	+
Scenedesmus falcatus Chodat.	k		+	+	+	+
Scenedesmus intermedius Chodat var.intermedius	k		+	+	–	–
Scenedesmus obtusus Meyen	k		–	+	+	+
Scenedesmus opoliensis Richt var. opoliensis	k	*β*	–	–	–	+
Scenedesmus protuberans Fritsch. var.protuberans	k		–	+	+	–
Scenedesmus quadricauda Turp. var. quadricauda	k	*β*	+	+	+	+
Scenedesmus spinosus Chodat	k		+	+	+	+
Closterium gracile Breb. f.gracile	k		+	+	–	–

Note k cosmopolitan, *b* boreal, *n-a* North Alpine, + present, − absent

due to their big sizes. In this way, the average annual biomass of bacillariophyte algae in Prut River varied from 1.39 to 3.95 g/m^3. The increased euglenophyte biomass at Cahul and Cislita-Prut stations certified a higher content of organic substances and excessive pollution of the river in this area.

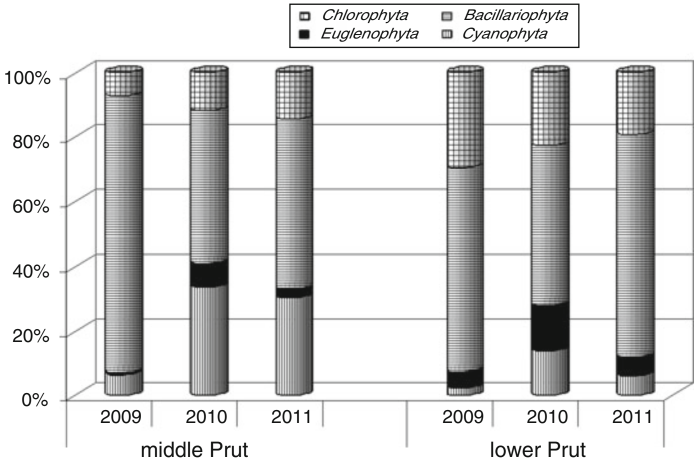


Fig. 7.19 The share of different algae groups in phytoplankton biomass in the Prut River within the Republic of Moldova in 2009–2011

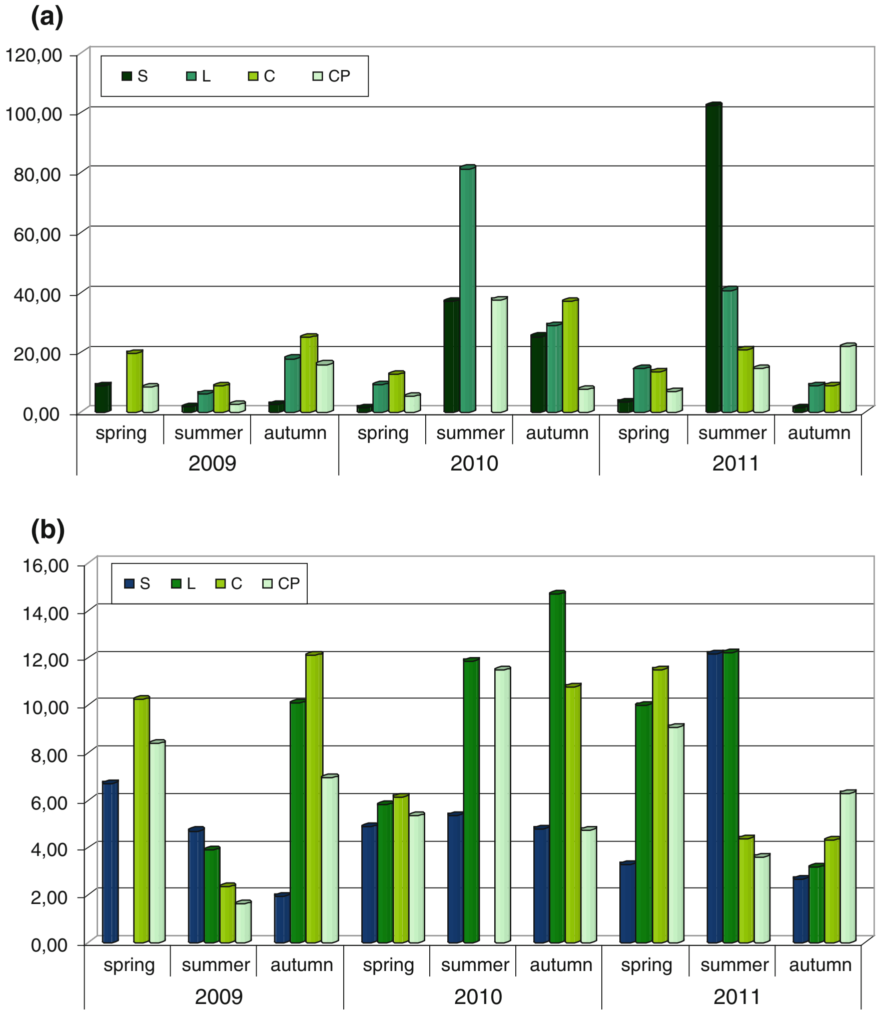


Fig. 7.20 Seasonal dynamics of density (million cells/l)—(**a**) and biomass (g/m^3)—(**b**) of phytoplankton in the Prut River (*S* Sculeni, *L* Leuseni, *C* Cahul, *CP* Cislita-Prut)

Cianophyte algae have formed larger quantities at Sculeni station, due to the penetration of species from Costesti-Stanca Lake, located upstream. But the role of cianophyte algae has diminished at Cahul and Cislita-Prut stations, where they recorded much lower biomass values.

In the quantitative dynamics of Prut River phytoplankton the increase of density values from Sculeni station to Cahul one was attested and then their decrease at Cislita-Prut station in all seasons (Fig. 7.20a).

In the summer and autumn of 2010, after floods, density values increased significantly at all investigated stations, the highest value being recorded in summer at Leuseni station (81.26 million cells/l). Increased values of phytoplankton density were recorded in summer of 2011 at Sculeni (102.2 million cells/l) and Leuseni (40.68 million cells/l) stations, when species of cianophyte algae *Synechocystis aquatilis* Sanv. and *Merismopedia tenuissima* Lemm. were growing in abundance in algal communities.

Biomass values of Prut River phytoplankton were much lower compared with density values and varied seasonally in wide limits. In spring, when phytoplankton was represented mainly by bacillariophyte algae, the biomass values ranged from 3.30 to 11.49 g/m^3 and positively correlated ($r = 0.75$) with density values, first increasing from Sculeni station to Cahul station, then decreasing somewhat at Cislita-Prut station (Fig. 7.20b).

Summer phytoplankton biomass values varied within the limits from 1.62 to 12.21 g/m^3 and were decreasing from Sculeni station to Cislita-Prut station. The composition of summer phytoplankton consisted mostly of chlorophytes (*Tetrastrum triangulare* Chod., *Scenedesmus quadricauda* Turp. *var. quadricauda*) and cianophytes (*Synechocystis aquatilis* Sanv., *Merismopedia tenuissima* Lemm., *Aphanizomenon flos-aquae* (L.) Ralfs *f. flos-aquae*).

In the autumn period the phytoplankton was represented mainly by species of *Bacillariophyta* phylum, of which only *Cyclotella Kuetzingiana* Thw. developed larger quantities. Phytoplankton biomass values ranged from 1.96 to 14.67 g/m^3 without presenting a well marked dynamics along the river. The values of autumnal phytoplankton biomass were higher in 2009 and 2010, but in autumn of 2011, although they were going up from Sculeni station to Cislita-Prut station, they did not exceed 6.28 g/m^3 (Fig. 7.20b).

In general, in Prut River the phytoplankton biomass values during the vegetation period were placed within 1.62 and 14.67 g/m^3, the highest value being recorded at Leuseni station in autumn of 2010 after summer floods.

7.5 Phytoplankton Primary Production and Destruction of Organic Substances

In Prut River the production of organic substances by phytoplankton depends not only on its quantity, but also by a range of biotic factors (taxonomic affiliation of algal species, their age and physiological state, cell size and concentration of pigments with an important role in the photosynthesis) and abiotic (solar radiation and water physico-chemical properties) [75, 76]. Thus, the dynamics of phytoplankton primary production in the Prut River is determined by seasonal and multiannual successions of planktonic algae communities.

For Prut River is characteristic a quite low water transparency—13–70 cm—in all seasons, and photosynthesis process occurs with a greater intensity to a depth of 25–30 cm. Specifically here were determined the highest values of primary production of phytoplankton. No big differences between values of phytoplankton primary production have been established in seasonal dynamics of production

Table 7.7 Values of biomass, primary production and destruction of organic matter in the Prut River during 2009–2011

Parameters		Spring n = 8	Summer n = 12	Autumn n = 8
$\sum A$ g $O_2/m^2 \cdot 24$ h	Min	0.59	0.38	0.04
	Max	5.43	8.16	4.39
	Mean	2.23 ± 0.55	2.20 ± 0,73	1.08 ± 0.19
$\sum R$ g $O_2/m^2 \cdot 24$ h	Min	1.21	0.12	0.42
	Max	12.48	49.92	9.24
	Mean	5.04 ± 1.18	16.7 ± 4.31	3.69 ± 0.33
A_{max} $mgO_2/l \cdot 24$ h	Min	0.39	0.33	0.06
	Max	7.63	3.01	2.24
	Mean	2.60 ± 0.96	1.35 ± 0.28	0.81 ± 0.10
R $mgO_2/l \cdot 24$ h	Min	0.80	0.08	0.21
	Max	6.24	24.96	4.62
	Mean	2.73 ± 0.58	8.55 ± 2.3	1.98 ± 0.17
B g/m^3	Min	3.30	1.62	1.96
	Max	11.49	12.21	14.67
	Mean	8.04 ± 0.98	6.69 ± 1.29	8.25 ± 0.54
$A_{max}/\sum A$	Min	0.30	0.19	0.01
	Max	2.5	3.38	2.76
	Mean	1.10 ± 0.30	1.06 ± 0.29	1.27 ± 0.14
A/R	Min	0.12	0.02	0.02
	Max	1.65	9.06	0.84
	Mean	0.59 ± 0.18	0.98 ± 0.81	0.29 ± 0.04

processes in Prut River, they being situated within the limits of 0.04–4.39 g O_2/m^2 24 h (Table 7.7).

Average values of primary production of phytoplankton, calculated for different seasons, demonstrated a decreasing intensity of photosynthesis process from spring (2.23 ± 0.55) to autumn (1.08 ± 0.19). An increasing trend from spring to autumn had also the values of Amax/ΣA ratio.

Despite expectations, the highest values of algal biomass did not correspond to highest values of primary production of phytoplankton, their correlation coefficient being higher only in the summer ($r = 0.68$). Direct correlation between the intensity of photosynthesis and biomass of phytoplankton was established at the depth of most intensive photosynthesis (25 cm), their correlation coefficient ranging within 0.66 and 0.72. The seasonal and spatial fluctuations of phytoplankton biomass in Prut River are not accompanied by corresponding fluctuations in primary production of phytoplankton. Thus, when phytoplankton biomass reaches a large quantities, the photosynthesis intensity is often lower (Fig. 7.21).

Prut River phytoplankton was more productive in the Leuseni-Cahul sector, photosynthesis intensity being characterized by well pronounced dynamics and significant spatial-temporal oscillations. The photosynthesis intensity of phytoplankton dominated by chlorophyte and bacillariophyte algae is higher than of phytoplankton dominated by cianophyte algae, due to photosynthetic peculiarities

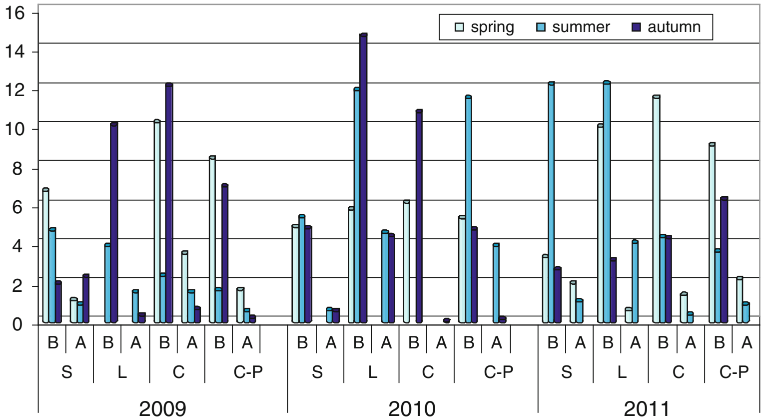


Fig. 7.21 Seasonal and multiannual dynamics of biomass (B, g/m^3) and primary production (A, g · O_2/m^2 · 24 h) of phytoplankton in the Prut River (*S* Sculeni, *L* Leuseni, *C* Cahul, *CP* Cislita-Prut)

of different species. Reduced development of phytoplankton is offset by increased photosynthetic activity of the species, which form its composition.

In general, high values of biomass have corresponded to low levels of primary production during spring and autumn. Reduction of the photosynthesis intensity with increase of phytoplankton biomass may be determined by a range of causes, among which it should be mention the diminishing of nutrient concentrations, decrease of transparency and, respectively, of euphotic layer, etc. In this way, there is a limit to the process of ecosystems eutrophication, beyond which nutrient intake will not contribute to increase of primary production. The decrease of primary production values with increasing phytoplankton biomass is an indicator of ecosystem balance disturbance.

The destruction of organic matter has taken place with the same intensity during spring and autumn, mean values ranging between 3.69 ± 0.33 and 5.04 ± 1.18 g·O_2/m^2·24 h, and they have notably increased up to 16.7 ± 4.31 g·O_2/m^2·24 h during summer (Table 7.3). So, in all seasons the values of destruction of organic substances were exceeding the values of phytoplankton production, the A/R ratio being, in most cases, less than 1.

Of the total of 106 species of algae identified in Prut River, 59 species are indicators of the degree of water saprobity. Among them β-mesosaprobic species formed 59 %, α-mesosaprobic species—11.9 % and oligosaprobic species—5.1 %.

During vernal period saprobic index values have ranged from 1.79 to 2.48, being lower at Cahul station. In spring the waters, which result by melting of accumulated snow from the adjacent territories, enter the Prut River; these waters have a high content of organic matter, mineralization of which at low temperatures (7.6–13.2 °C) is very slow. During this period, according to quantitative parameters of phytoplankton, river saprobity level corresponds to the β-mesosaprobic zone.

Summer gradual heating of water to 28 °C and favorable gaseous regime determines the intensification of water purification processes by the mineralization of organic substances and putting back to the circulation of mineral ones. In the summer saprobic index values ranged within 1.83 and 2.49, falling within the limits of the β-mesosaprobic zone and being higher in 2011.

During autumn saprobic index values have ranged from 1.76 to 3.04, in such way fitting in, the most often, with limits of β-mesosaprobic zone. Higher values of saprobic index, which fell within the limits of polysaprobic area, were recorded in autumn of 2011 at Sculeni (3.04) and Cahul (2.66) stations.

Among anthropogenic factors with major influence on the water quality of Prut River it should be mention the discharges of wastewaters and waste in its hydrographic basin, tributaries contribution in formation of suspensions content, construction and operation of Giurgiulesti terminal. Phytoplankton structure and water quality in Prut River downstream Costesti-Stinca Lake are influenced by water coming from the lower part of the lake. Prut River water quality downstream of Ungheni is influenced by discharges of insufficiently treated wastewater from facilities of Ungheni (Republic of Moldova) and Valea Mare (Romania), especially during the months of September and October, when the water flow of Prut River is very low.

Investigations conducted in the 2009–2011 period demonstrated that, in general, water quality in the Prut River was satisfactory for development of planktonic algae and other hydrobionts, with some exceptions, caused by increased concentrations of organic and mineral suspensions, as well as rather low values of water saturation with dissolved oxygen, especially during floods and after them.

In Prut River destruction processes overpower those of production in most cases, the self-purification index A/R ranging from 0.12 to 1.65 and the mean value being 0.59 ± 0.18 in spring, from 0.02 to 9.06 with a mean of 0.98 ± 0.81 in summer and from 0.02 to 0.84 with a mean of 0.29 ± 0.04 in autumn. This shows that, according to the average value of A/R index, the water quality of Prut River is of class 3–4 “moderately polluted”-“polluted”.

Investigations carried out on phytoplankton of Prut River in the 2009–2011 period revealed biomass values ranging from 3.30 to 11.49 g/m^3 during spring, from 1.62 to 12.21 g/m^3 during summer and 1.96–14.67 g/m^3 during autumn, which correspond basically to trophic categories “eutrophic” and “polytrophic” and rarely fits within the category of “mesotrophic”. Relatively low biomass of phytoplankton was typical for Cahul (2.35 g/m^3) and Cislita-Prut stations (1.62 g/m^3) in summer of 2009 and Sculeni station (1.96 g/m3) in autumn of 2009.

7.6 Zooplankton

Seventy four species and varieties of 3 taxonomic groups were identified (*Rotatoria, Copepoda, Cladocera*), the majority of species (67 % of total zooplankton) pertaining to *Rotatoria*. To *Copepoda* belong 13 species and varieties, or 18 % and to *Cladocera*—11 species or 15 % of the recorded species and varieties (Table 7.8). Despite the taxonomic dominance of rotifers, only two species (*Keratella quadrata,*

Table 7.8 List of species recorded for 2009–2011

Taxon	Saprobity	Presence in stations			
		Sculeni	Leuseni	Cahul	Cislita-Prut
Rotatoria					
Asplanchna herricki (Guerne)	o	+	+	+	–
Asplanchna priodonta (Gosse)	o-b	–	–	–	+
Brachionus angularis (Gosse)	b-α	+	+	+	+
Brachionus angularis bidens (Plate)	b	+	–	+	–
Brachionus bidentata (Anderson)	b	–	–	–	+
Brachionus bidentata inermis (Rousselet)	b	–	+	+	+
Brachionus budapestinensis budapestinensis (Daday)	b	+	–	+	+
Brachionus calyciflorus (Pallas)	b-α	+	+	+	+
Brachionus diversicornis (Daday)	b	+	+	–	–
Brachionus forficula (Wierzejski)	–	–	+	–	+
Brachionus leydigii (Cohn)	b	–	–	+	–
Brachionus leydigii leydigii (Cohn)	b	–	+	–	–
Brachionus leydigii rotundus (Rousselet)	b	+	+	+	–
Brachionus leydigii tridentatus (Zernov)	b	+	+	+	+
Brachionus nilsoni (Ahlstrom)	–	–	+	–	–
Brachionus quadridentatus ancylognathus (Schmarda)	b	–	+	–	+
Brachionus quadridentatus brevispinus (Ehrenberg)	b	–	+	–	+
Brachionus quadridentatus cluniorbicularis (Skoricov)	b	–	+	+	+
Brachionus quadridentatus quadridentatus (Hermann)	b	–	–	–	+
Brachionus rubens (Ehrenberg)	α-p	+	–	–	–
Brachionus urceus (Linnaeus)	b	+	–	–	+
Brachionus urceus urceus (Linnaeus)	b	–	–	–	+
Brachionus variabilis (Hempel)	–	–	–	+	–
Cephalodella hoodi (Gosse)	–	–	–	–	+
Eosphora ehrenbergi (Weber)	–	–	–	+	–
Epiphanes macroura (Barrois et Daday)	–	–	–	+	–
Euchlanis dilatata (Ehrenberg)	o-b	+	+	–	+
Filinia longiseta (Ehrenberg)	b-α	+	+	+	+
Filinia maior (Colditz)	b	–	–	–	+
Hexarthra oxyuris (Zernov)	–	–	–	–	+
Keratella cochlearis (Gosse)	b	–	+	+	+
Keratella cochlearis cochlearis (Gosse)	b	–	–	+	–
Keratella quadrata (Műller)	b	+	+	+	+
Keratella tropica reducta (Fadeev)	b	+	+	–	–
Keratella valga (Ehrenberg)	o-b	–	–	–	+
Keratella valga monospina (Klausener)	o-b	–	+	–	–

(continued)

Table 7.8 (continued)

Taxon	Saprobity	Presence in stations			
		Sculeni	Leuseni	Cahul	Cislita-Prut
Lecane luna (Műller)	o-b	–	–	–	+
Mytilina unquipes (Lucks)	–	+	–	–	–
Notholca acuminata (Ehrenberg)	o	+	+	+	+
Notholca acuminata acuminata (Ehrenberg)	o	–	+	–	–
Notholca squamula (Műller)	o-b	+	+	+	+
Polyarthra dolichoptera (Idelson)	o	+	+	+	+
Polyarthra minor (Voigt)	x-o	–	–	–	+
Synchaeta pectinata (Ehrenberg)	o-b	–	–	+	–
Testudinella mucronata (Gosse)	–	–	+	–	–
Testudinella patina (Hermann)	b	–	–	+	+
Testudinella truncata (Gosse)	–	–	+	–	–
Trichotria curta (Scorikov)	o	–	+	–	–
Trichotria pocillum bergi (Meissner)	o	–	–	–	+
Trichotria tetractis tetractis (Ehrenberg)	o	–	–	–	+
Copepoda					
Acanthocyclops gigas (Claus)	–	–	–	–	+
Acanthocyclops viridis (Jurine)	o-b	–	+	+	+
Acantocyclops abyssicola (Lilljeborg)	–	–	–	–	+
Canthocamptus bidens (Schmeil)	o	+	+	+	+
Cyclops strenuus strenuus (Fischer)	b-α	–	–	–	+
Cyclops vicinus (Uljanin)	b	–	–	–	+
Eucyclops serrulatus baicalocorrepus (Masepova)	o-b	+	–	–	–
Eucyclops serrulatus serrulatus (Fischer)	o-b	–	–	–	+
Eucyclops serrulatus speratus (Lilljeborg)	o-b	–	–	–	+
Eurytemora velox (Lilljeborg)	–	–	–	–	+
Macrocyclops albidus (Jurine)	b	+	+	–	–
Mesocyclops crassus (Fischer)	b	–	+	+	+
Microcyclops varicans (Sars)	–	+	+	+	+
Cladocera					
Alona rectangula (Sars)	o	+	+	+	+
Bosmina kessleri (Uljanin)	–	–	–	+	–
Bosmina longirostris (O. F. Műller)	o-b	–	+	+	+
Ceriodaphnia laticaudata (P.E. Műller)	o-b	–	+	–	–
Chydorus sphaericus (O. F. Műller)	o-b	+	–	+	+
Daphnia obtusa (Kurz)	o-b	–	+	–	+
Daphnia pulex (Leydig)	α	–	–	–	+
Macrothrix laticornis (Jurine)	b	+	–	–	–
Moina macrocopa (Straus)	α	–	–	–	+
Sida crystallina (O. F. Műller)	o	–	–	–	+
Simocephalus vetulus (O. F. Műller)	o-b	–	–	–	+

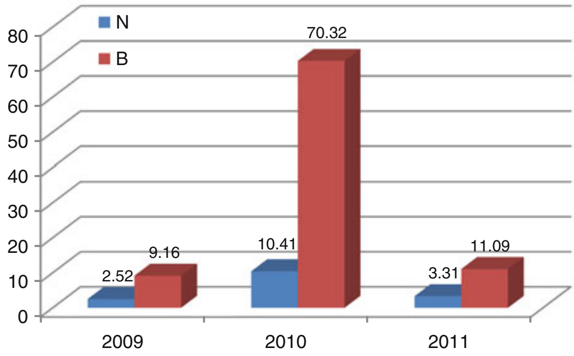


Fig. 7.22 Annual average values of zooplankton density (N, thousand ind./m^3) and biomass (B, mg/m^3) in Prut River, 2009–2011

Brachionus angularis) were recorded throughout the Lower Prut, in all seasons and years of study.

The richest in terms of taxonomic diversity was proved to be Cislita-Prut station, which is due, most likely, to lower speed of water.

Investigations revealed that the indicator species represented 80 % of the total number of species. More precisely, indicator species of β -mesosaprobity (34 % of the total number) and oligo- β -mesosaprobity (22 %) prevailed. It is of interest to note that the share of oligosaprobic indicator species was 14 %. Regarding the indicator species of a higher level of pollution (α- and β- α-mesosaprobic), it was found that their number was small and overall did not exceed 8 %. There have been registered only one indicator species of α-mesosaprobic-polysaprobic conditions and one indicator species of xeno-oligosaprobic conditions.

Hydrological regime of Prut River is quite unfavorable for the development of the majority of zooplankton groups. A negative impact on all groups of zooplankton has, primarily, the high content of suspended substances in water. Quantitative indices of Prut River zooplankton for 2009–2011 are relatively low, constituting on average 5410 ind./m^3 (density) and 30.19 mg/m^3 (biomass). Floods of 2008 and 2010 also reflected negatively on zooplankton development in Prut River, and their effect appeared to a greater extent in the following year (Fig. 7.22).

In spring the main role in the formation of zooplankton density is played by copepod crustaceans, and in summer-autumn—by rotifers. The biomass formation was determined, mainly, by copepods, due to their body size. Quantitative development of cladocera crustaceans was characterized by extremely low values up to their total absence, even in summer.

According to quantitative parameters, Cislita-Prut station has proven to be the most productive, with an average density of 7.51 ind./m^3 and biomass of 52.87 mg/m^3 (Table 7.9). Sculeni station has been noted by the lowest values of zooplankton quantitative indicators, as well, by their gradual decrease from 2009 to 2011.

The highest values of density were recorded in 2010—18,850 ind./m^3—at Leuseni station and of biomass—in the same year at Cislita-Prut station—118.9 mg/m^3.

Table 7.9 Annual average values of zooplankton density (N, thousand ind./m^3) and biomass (B, mg/m^3) in Prut River, depending on the station, 2009–2011

Year	Station			
	Sculeni	Leuseni	Cahul	Cislita-Prut
Density				
2009	0.83	1.36	5.01	2.56
2010	0.66	18.85	1.01	13.98
2011	0.62	1.34	5.31	5.99
Biomass				
2009	7.96	7.46	2.98	14.59
2010	3.54	106.99	7.97	118.9
2011	3.07	6.42	9.71	25.13

Table 7.10 Zooplankton saprobity index in Prut River

Year	Staţia			
	Sculeni	Leuseni	Cahul	Cislita-Prut
2009	2.04	1.46	1.65	1.81
2010	1.96	1.94	1.62	1.73
2011	1.76	1.91	1.86	1.91

Saprobity index, calculated based on indicator species of zooplankton, varied within 1.46 and 2.04 in 2009 (Table 7.10). Between 2010 and 2011 its variation limits were within 1.62 and 1.96 and, respectively, 1.76 and 1.91.

Saprobity index values were not too high and corresponded to β -mesosaprobic zone, with one exception—at Leuseni station in 2009 they corresponded to α-oligosaprobic zone. On average for investigated stations, the saprobity index, in dependence on the year, varied within a narrow range (1.74–1.86), falling within the limits of β-mesosaprobic zone, but however it was observed its increase from 2009 to 2011.

7.7 Zoobenthos

Monitoring of freshwater ecosystems mandatory include macrozoobenthonic animals as subject. This group of animals meets several requirements for indicator organisms: wide distribution, enough high density, relatively large size of the body, combination of populating certain biotopes and a certain degree of mobility [26]. Benthic organisms usually are not economically valuable or unique items, therefore their removal from water bodies for scientific purposes are not prejudice the given ecosystem [6]. Ninety seven species and taxonomical groups of macrozoobenthos have been founded and determined at Sculeni, Leuseni, Cahul, Cislita-Prut stations during 2009–2011 period (Table 7.11). Taxa were identified till the lowest possible rank. The most heterogeneous groups are *Insecta*—32 and

Table 7.11 The list of species of macrozoobenthos at Sculeni, Leuseni, Cahul, Cislita-Prut stations

	Sculeni	Leuseni	Cahul	Cislita-Prut
Nematomorpha				
1. *Gordius sp.*	+	+	–	+
2. *Nematoda*	+	–	+	+
Gastropoda				
3. *Physa acuta* (Draparnaud)	+	–	–	–
4. *Anisus (***Gyraulus)** *albus* (Müller)	–	–	–	+
5. *Ferrissia fragilis* (Tryon)	–	–	–	+
6. *Theodoxus danubialis* (Pfeiffer)	+	–	+	+
7. *Theodoxus fluviatilis* (Linne)	+	–	+	
8. *Viviparus viviparus* (Linne)	–	–	+	+
9. *Valvata piscinalis* (Müller)	+	+	–	–
10. *Lithoglyphus naticoides* (Pfeiffer)	+	+	+	+
11. *Fagotia esperi* (Ferrussas)	+	–	–	–
12. *Fagotia acicularis* (Ferrussas)	+	+	+	–
Bivalvia				
13. *Anodonta cygnea* (Linne)	–	–	–	+
14. *Anodonta piscinalis* (Nilsson)	–	–	–	+
15. *Anodonta anatina* (Linne)	–	–	–	+
16. *Pseudoanodonta complanata* (Rossmässler)	–	–	–	+
17. *Sinanodonta woodiana* (Lea)	–	+	+	+
18. *Unio pictorum* (Linne)	–	+	+	–
19. *Unio tumidus* (Philipsson, Retzius)	–	–	+	+
20. *Unio longirostris* (Rossmaessler)	–	–	–	+
21. *Crassiana crassa* (Philipsson)	+	–	+	–
22. *Sphaeriastrum rivicola* (Lamarck)	–	–	–	+
23. *Musculium creplini* (Dunker)	+	–	–	+
24. *Pisidium amnicum* (Müller)	+	–	–	+
25. *Dreissena polymorpha* (Pallas)	+	+	+	+
26. *Dreissena bugensis* (Andrusov)	+	+	+	+
27. *Corbicula fluminea* (Müller)	–	–	–	+
Polychaeta				
28. *Hypania invalida* (Grube)	–	+	–	–
Oligochaeta	+	+	+	+
29. *Branchiura sowerbyi* (Beddard)	+	–	+	+
30. *Eiseniella tetraedra* (Savigny)	–	–	–	+
31. *Lumbriculidae* Gen sp	–	+	–	–
32. *Lumbriculus variegatus* (Müller)	+	+	+	+
33. *Stylodrilus heringianus* (Claparede)	–	–	–	+
34. *Limnodrilus hoffmeisteri* (Claparede)	+	–	–	–
35. *Nais* spec. none	+	+	+	–
36. *Stylaria lacustris* (Linne)	+	+	–	–

(continued)

Table 7.11 (continued)

	Sculeni	Leuseni	Cahul	Cislita-Prut
37. *Pristina aequiseta* (Bourne)	–	+	–	–
38. *Dero dorsalis* (Ferroniere)	–	–	+	–
39. *Dero sp.*	+	–	–	–
40. *Tubifex* sp.div	+	+	+	+
41. *Tubifex tubifex* (Müller)	+	+	+	+
Crustacea				
42. *Pontastacus leptodactylus* (Karaman)	–	+	+	–
43. *Jaera sarsi* (Valkanov)	+	–	–	+
Conchostraca	–	–	–	+
Osrtacoda	–	–	–	+
44. *Cypridopsis vidua* (Müller)	–	–	–	+
Mysidacea				
45. *Limnomysis benedeni* (Czernavsky)	+	+	+	+
46. *Paramysis lacustris* (Czernavsky)	+	+	+	+
Amphipoda				
47. *Gammarus lacustris* (Sars)	–	–	+	+
48. *Dikerogammarus haemobaphes* (Eichwald)	+	+	+	+
49. *Dikerogammarus villosus* (Sowinsky).	+	–	–	+
50. *Pontogammarus robustoides* (Sars)	–	–	+	–
51. *Gammarus* sp	+	+	+	+
52. *Corophium curvispinum* (Sars)	–	–	+	+
53. *Corophium nobile* (Sars)	–	–	+	–
54. *Corophium robustrum* (Sars)	–	–	+	–
55. *Corophium* sp	+	+	+	+
Ephemeroptera				
56. *Caenis* sp.	+	–	+	–
57. *Caenis macrura* (Stephens)	–	+	–	–
58. *Palingenia longicauda* (Olivier)	+	+	+	–
59. *Heptagenia sulphurea* (Müller)	–	–	–	+
60. *Heptagenia flava* (Rostock)	+	+	+	–
61. *Potamanthus luteus* (Linnaeus)	+	–	–	–
62. *Baetis* sp	+	–	–	–
63. *Leptophlebia* sp.	–	–	+	–
Odonata				
64. *Coenagrion pulchellum* (Linden)	–	–	+	–
65. *Stylurus flavipes* (Charpentier)	+	–	–	–
66. *Platycnemis pennipes* (Pallas)	+	–	–	–
67. *Gomphus* sp.div none	+	+	+	+
68. *Gomphus vulgatisimus* (Linne)	+	+	–	–
69. *Gomphus flavipes* (Charpentier)	+	+	–	–
Heteroptera				
70. *Mesovelia furcata* (Mulsant and Rey)	–	–	+	–
71. *Gerris* sp.	–	–	+	–

(continued)

Table 7.11 (continued)

	Sculeni	Leuseni	Cahul	Cislita-Prut
Coleoptera				
72. *Haliplidae*	+	–	–	–
73. *Elmidae (Limnius)*	+	–	–	–
Collembola	–	+	–	–
74. *Podura aquatica* (Linne)	+	–	+	–
Arachnida	+	–	+	+
Hydracarina	–	–	+	–
Trichoptera				
75. Hidroptila sp.	+	–	–	–
76. Ecnomus tenellus (Rambur)	–	–	+	–
77. Polycentropidae	+	–	–	–
78. Philopotamidae sp.	+	–	+	–
79. Hydropsyche sp.	–	+	+	–
80. Hydropsyche ornatula (McLachlan)	+	–	–	+
Diptera				
Chironomidae	+	+	+	+
81. Chironomus plumosus (L.)	+	–	–	–
82. Chironomini Gen. sp.	+	+	+	+
83. Orthocladius sp.	+	+	+	–
Ceratopogonidae	+	+	–	+
84. Bezzia hydrophila (Kieffer)	+	+	–	–
Culicidae	–	–	+	+
Tipulidae	+	–	–	–
Simuliidae	–	+	–	–
Dolichopodidae	–	–	–	+
Tabanidae	+	–	–	–
Lepidoptera	+	–	–	–
Total	58	37	48	48

*Mollusc*a—25 species and taxonomical groups, which are followed by *Crustacea*—16 and *Annelida*—14 taxa.

The highest number of macrozoobenthos taxa in Prut River was recorded at Sculeni station (58 taxa) and fewest-at Leuseni station (37 taxa).

Both the total density of zoobenthos, as well as of zoobenthos without molluscs decreased along the river from Sculeni to Cislita-Prut (Fig. 7.23). The same trend was observed, also, for oligochaetes. The highest density of molluscs was found at Sculeni station, of chironomides—at Leuseni station and of crustaceans—at Cahul station. The remaining groups, taken together, registered the highest density at Leuseni station.

In fact, the biomass dynamics of zoobenthos without molluscs proved to be similar to that of its density (Figs. 7.23, 7.24) with one exception—in the summer of 2011 the largest biomass of *Unionidae* molluscs (5360 g/m^2) was detected at Cahul station.

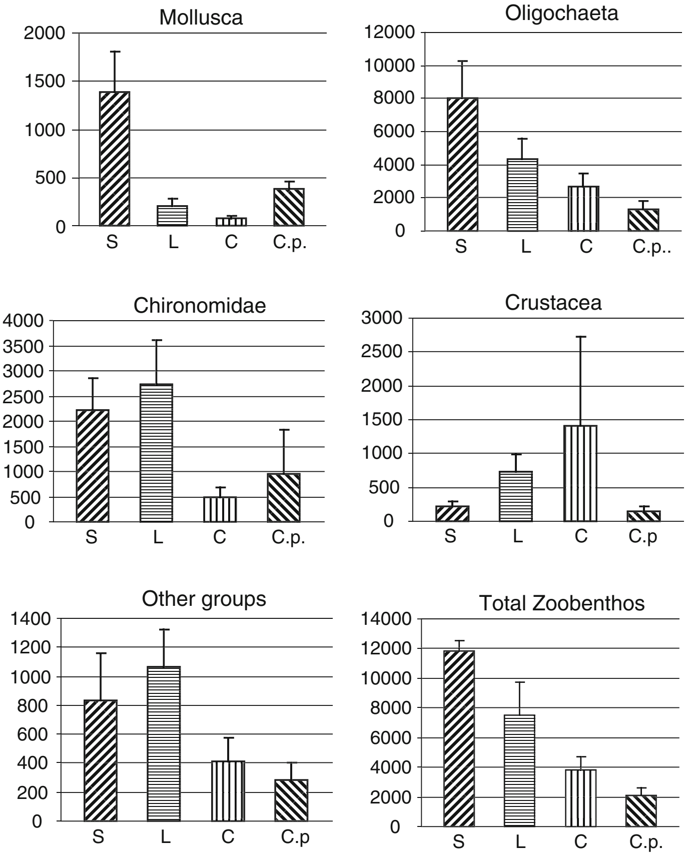


Fig. 7.23 Density (ind./m^2) of macrozoobenthos at Lower Prut sampling sites (Sculeni, Leuseni, Cahul, Cislita-Prut) in 2009–2011

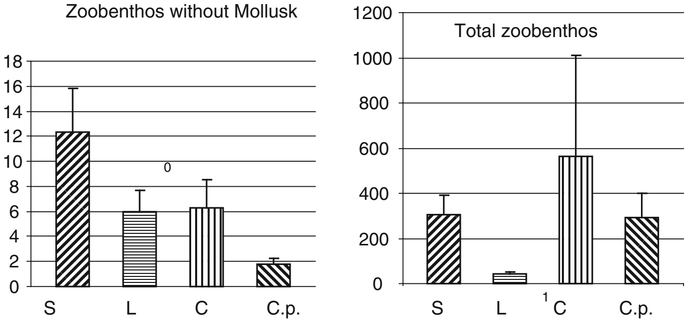


Fig. 7.24 Biomass (g/m^2) of macrozoobenthos at Lower Prut sampling sites in 2009–2011

Table 7.12 Density of macrozoobenthos (ind./m^2) in Lower Prut sampling sites, 2009–2011 (by seasons)

Sampling sites	2009			2010			2011		
	Spring	Summer	Autumn	Spring	Summer	Autumn	Spring	Summer	Autumn
Sculeni	8001	9960	28,954	32,559	–	2280	3,160	14,155	15,698
Leuseni	–	8,690	11,167	11,640	–	1,600	2,920	13,082	6,001
Cahul	3,129	9,609	1,405	2,760	–	7,322	3,761	4,396	4,685
Cislita-Prut	–	–	3,581		–		3,840	1,329	235

It is known that the type of substrate significantly influences the formation of benthic invertebrate communities. Usually on rocky substrates it is observed the highest diversity of benthic invertebrates and also the lowest saprobity values; on the silty substrates—opposite (Manual for the application of the AQEM system, [31]). At Sculeni station the river bottom is covered with gravel and sand, and also the stones are present, at Leuseni station—with strongly silty sand, at Cahul station—also, with strongly silty sand, but along the banks concrete boards are installed, and at Cislita-Prut station—with black mud which has a depth of over 30 cm. Substrate diversity, along with other environmental parameters influence the quantitative and the qualitative indices of zoobenthos.

There were observed significant differences in seasonal dynamics of macrozoobenthos depending on sampling site location (Tables 7.12, 7.13). Thus, at Sculeni station it was recorded a threefold increase of macrozoobenthos density from spring to autumn. At Leuseni station, where the biggest role in formation of macrozoobenthos density belongs to amphibiotic insects (Fig. 7.23. *Other groups, Chironomidae*), the highest density was observed in summer. Its abrupt decrease in autumn occurred as a result of insect metamorphosis (insect flight, at state of imago, from the water body).

Floods that occurred on Prut River in June 2010 greatly influenced the macrozoobenthos development. In that year it was observed a reduction of macrozoobenthos abundance—of density by about 10 times and a much higher reduction of biomass—in autumn samples compared with samples of spring.

In recent years, due to start of exploitation of Giurgiulesti terminal, new invasive species appeared in Prut River. At Leuseni station in 2009, for the first time for aquatic ecosystems of Moldova, it was found the Asian species of bivalves *Corbicula fluminea* [35], with a density of 6.23 ind./m^2 and biomass of 1.82 g/m^2 (Fig. 7.25). In 2011 these indices comprised up to 40 ind./m^2 and 91,456 g/m^2, respectively.

Invasive species of Asian bivalve molluscs *Sinanodonta woodiana*, which was originally discovered in Lake Beleu [36], in 2010 was encountered in Prut River at Cislita-Prut station (Fig. 7.26). It is worth to note that in 2011 shells of *S.woodiana* were found upstream—at Cahul and Leuseni stations.

In spring of 2011, for the first time for Prut River, at Cislita-Prut station was recorded the invasive species of gastropods *Ferrissia fragilis*, which has North American origin and morphologically resemble native species *Acroloxus lacustris*

Table 7.13 Biomass of macrozoobenthos (g/m^2) at Lower Prut sampling sites, 2009–2011 (by seasons)

Sampling sites	2009			2010			2011		
	Spring	Summer	Autumn	Spring	Summer	Autumn	Spring	Summer	Autumn
Sculeni	859.45	708.1	458.8	519.12	–	29.704	180.85	66.267	640.02
Leuseni	–	4.679	10.77	5.759	–	0.896	3.304	146.13	24.298
Cahul	0.4685	4.9427	1.004	1205.9	–	17.44	13.427	2719.5	47.423
Cislita-Prut	–	–	10.93	3041	–	395.81	823.54	38.824	362.2

Fig. 7.25 *Corbicula fluminea*

Fig. 7.26 *Sinanodonta woodiana* (Foto by Zubcov N.)

Fig. 7.27 *Ferrissia fragilis*

(Fig. 7.27). *F.fragilis* first appeared in the Dniester River delta and more specifically in the Turunciuc river arm [54].

The invasion species of oligochaetes *Branchiura sowerbyi*, originated from the Sino-Indian region and spread elsewhere due to human activity [38], has been identified for the first time in Moldova in 1989 [71], and during the 2009–2011 has been remarked at all stations, with the exception of Leuseni one.

7.8 Saprobic Index and Water Quality Classes

One and the same species of benthic invertebrates can be characterized in terms of saprobity in a wide range—from oligo- to polysaprobic [53], depending not only on the geographical region, type of ecosystem, but to a greater extent, on the ability of species to adapt to living conditions. For example, mollusc *Dreissena polymorpha*, previously considered an indicator of relatively clean water, today is found in many polluted biotopes. In this regard, saprobic index should be determined taking into account the specific conditions of the aquatic ecosystem [53].

Processes of pollution of water bodies and watercourses usually leads to decrease of total number of species in the community, but the total number of individuals remain at the same level, which is due to the decrease in the number of stenobiont oligosaprobic species and increase in the number of euribiont species and, later, of those saprobiont [26, 30, 50].

Thus, *Ephemeroptera* and *Trichoptera* groups, which are among the most sensitive to pollution zoobenthos groups, are met, de facto, everywhere in Prut River. The species *Palingenia longicauda*, previously widespread, it is now considered extinct in many European countries, but can be encountered in Serbia, Hungary—in Tisa River, in the Lower Danube basin, in Romania, Moldova and Ukraine [7]. In Prut River at Sculeni station in the summer of 2011 *Palingenia longicauda* actually reached the highest density of 440 ind./m^2 and the biomass of 10.744 g/m^2. At the same station can be detected a species of oxyphilic and reophylic bivalve molluscs *Crassiana crassa*, which is registered in the IUCN Red List of Threatened Species, version 2010.4 (www.iucnredlist.org) and, also, reophylic gastropod molluscs *Theodoxus danubialis*, *Theodoxus fluviatilis*, *Fagotia esperi*, *Fagotia acicularis*.

At Cislita-Prut station the highest diversity of bivalve molluscs was observed, 13 species as total and namely: *Anodonta cygnea*, *Anodonta piscinalis*, *Anodonta anatina*, *Pseudoanodonta complanata*, *Sinanodonta woodiana*, *Unio tumidus*, *Unio longirostris*, *Sphaeriastrum rivicola*, *Musculium creplini*, *Pisidium amnicum*, *Dreissena polymorpha*, *Dreissena bugensis*, *Corbicula fluminea*.

In order to assess the saprobity index and water quality class, data on macrozoobenthos status in the autumn of 2011 were used. Goodnight and Whitley index was calculated based on materials from 2009 to 2011.

The saprobic index of Pantle and Buck [46] in modifications made by [74], had the following values for the different sites on the Prut River: Sculeni—2.158, Leuseni—2.476, Cahul—2.26, Cislita-Prut—2.241 and, according to them, the water of Prut River referred to the 2nd–3rd classes of quality and it is assessed as moderate polluted.

In line with the oligochaete index of [9], the water of Prut River is characterized as polluted.

According to the Biological Monitoring Working Party index (BMWP), river water is characterized as moderately polluted or critically polluted.

According to River Trent Biotic Index (TBI) and modification of Extended Biotic Index (EBI), river is characterized as β-mesosaprobic water body and the water quality—as moderately polluted.

Thus, overall for investigated area of Prut River, the saprobity zones calculated based on macrozoobenthos varied within β-mesosaprobic and α-mesosaprobic and the water quality class—within the moderately polluted and critically polluted.

7.9 Relations Between Abiotic and Biotic Factors

Hydrobionts development and produced amount of organic matter in aquatic ecosystems depend on a range of environmental factors. Among them a special significance has nutrient content, the water brightness, transparency, and turbulence, the degree of pollution, etc. Based on various statistical evaluations, the analysis of relationship between abiotic factors, the number and biomass of aquatic organisms was performed.

Nutrients, especially compounds of nitrogen and phosphorus play the main role in the bacterioplankton and phytoplankton development. Dynamics and the relationship between ammonifying, nitrifying and denitrifying bacteria directly depend on the content of ammonium nitrate and nitrite ions in water ecosystems.

After analyzing the dynamics of concentrations of nitrogen and phosphorus compounds and the bacterioplankton density, a clear correlation has been established between these components in the Prut River waters. For instance, it was established that the density of ammonifying bacteria directly depends on the concentration of ammonium ions (Fig. 7.28). According to Fig. 7.28, it is obvious that in the summer and spring of 2010, when the water temperature ranged from 13 to 27 °C, the given correlation was almost linear, and in the autumn of 2010, 2011 and in spring of 2011, when the water temperature was equal to 4.8 °C, the correlation was less pronounced.

Regarding the dynamics of nitrifying bacteria throughout the course of Prut, a clear dependence on variations of nitrite nitrogen concentration was highlighted (Fig. 7.29).

The share of nitrates in composition of mineral nitrogen was about 85 % and namely the dynamics of nitrates was the dominant factor in the development of

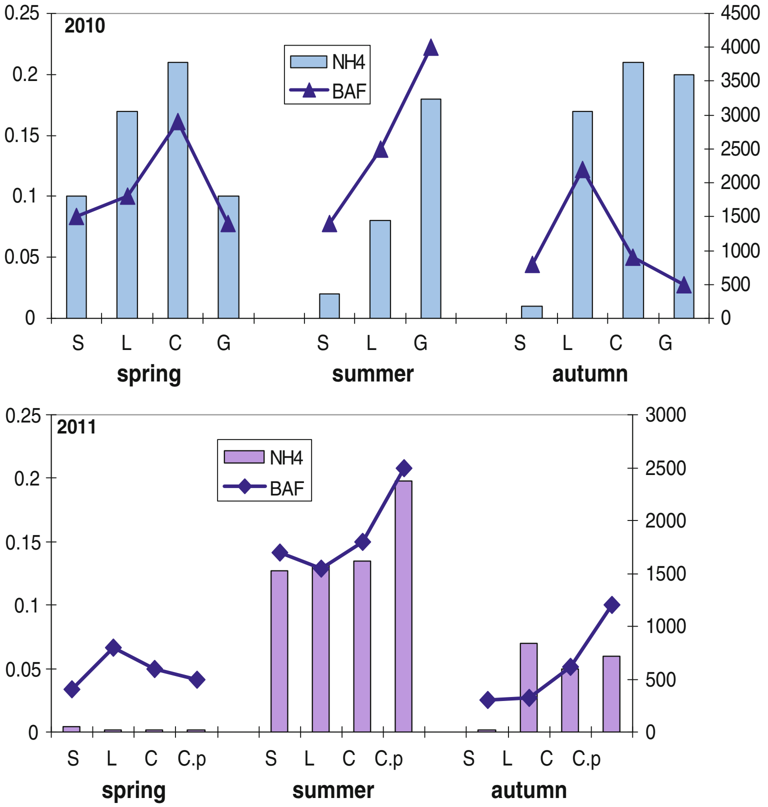


Fig. 7.28 The correlation between the concentration of ammonium ions (NH4, mgN/l) and the density of ammonifying bacteria (BAF, cells/ml) in Prut water in 2010 and 2011 (*S* Sculeni, *L* Leuseni, *C* Cahul, *Cp* Cislita-Prut, *G* Giurgiulesti)

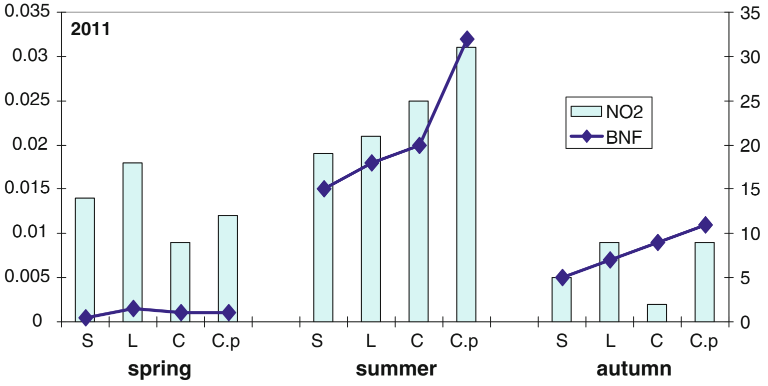


Fig. 7.29 The correlation between the concentration of nitrites (NO2, mgN/l) and density of nitrifying bacteria (BNF, cel/ml) in Prut water, 2011 (*S* Sculeni, *L* Leuseni, *C* Cahul, *Cp* Cislita-Prut, *G* Giurgiulesti)

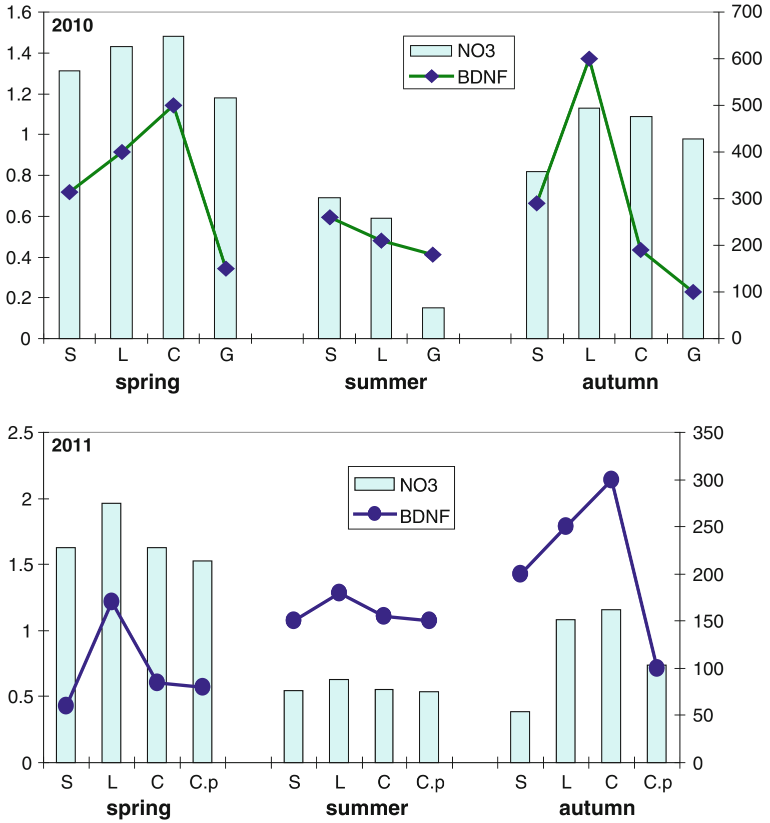


Fig. 7.30 The correlation between the concentration of nitrates (NO3, mgN/l) and density of denitrifying bacteria (BDNF, cells/ml) in Prut waters, 2010–2011 (*S* Sculeni, *L* Leuseni, *C* Cahul, *Cp* Cislita-Prut, *G* Giurgiulesti)

denitrifying microorganisms throughout the investigation period of Prut River (Fig. 7.30).

Planktonic algae, depending on their specific particularities, can use nutrients both as mineral compounds and organic [8, 27, 37, 47, 77]. Their presence in certain concentrations in aquatic ecosystems influences the quantitative parameters of phytoplankton, physiological state of algal cells and their photosynthetic activity, thus directly or indirectly influencing their productivity. Mineral nitrogen is used by algae, mainly, in the form of nitrates and ammonium salts. For cyanophyte algae both forms of nitrogen are equally accessible.

The analysis of multiannual and seasonal dynamics of nitrogen compounds concentrations and phytoplankton biomass allowed to determine that nitrates play a distinctive role in the development of phytoplankton, thus being attested to a positive correlation between nitrates dynamics and phytoplankton biomass (Figs. 7.31, 7.32).

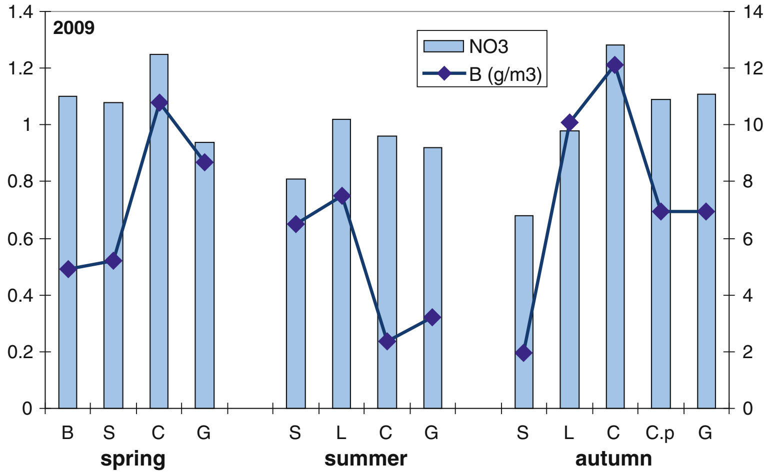


Fig. 7.31 The correlation between the concentration of nitrates (NO3, mgN/l) and biomass (B, g/m^3) of phytoplankton in Prut River in 2009 (*B* Braniste, *S* Sculeni *L* Leuseni, *C* Cahul, *Cp* Cislita-Prut, *G* Giurgiulesti)

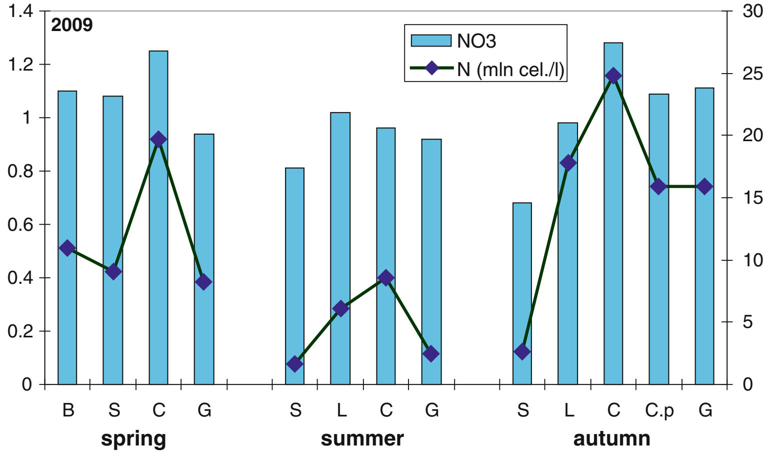


Fig. 7.32 Correlation between nitrates (NO3, mgN/l) and density (N, mln. cells/l) of phytoplankton in Prut River in 2009 (*B* Braniste, *S* Sculeni *L* Leuseni, *C* Cahul, *CP* Cislita-Prut, *G* Giurgiulesti)

Connection between the content of nitrates in the water and phytoplankton abundance stands out from the spring. With the start of the vegetation season, NO_3^- ions are actively assimilated by algal cells and, as higher is their concentration in water, as higher are the values of phytoplankton density and biomass.

Often mineral nitrogen (or sum of inorganic nitrogen compounds) is used as an integrated index of aquatic plant development. Mineral nitrogen concentration in

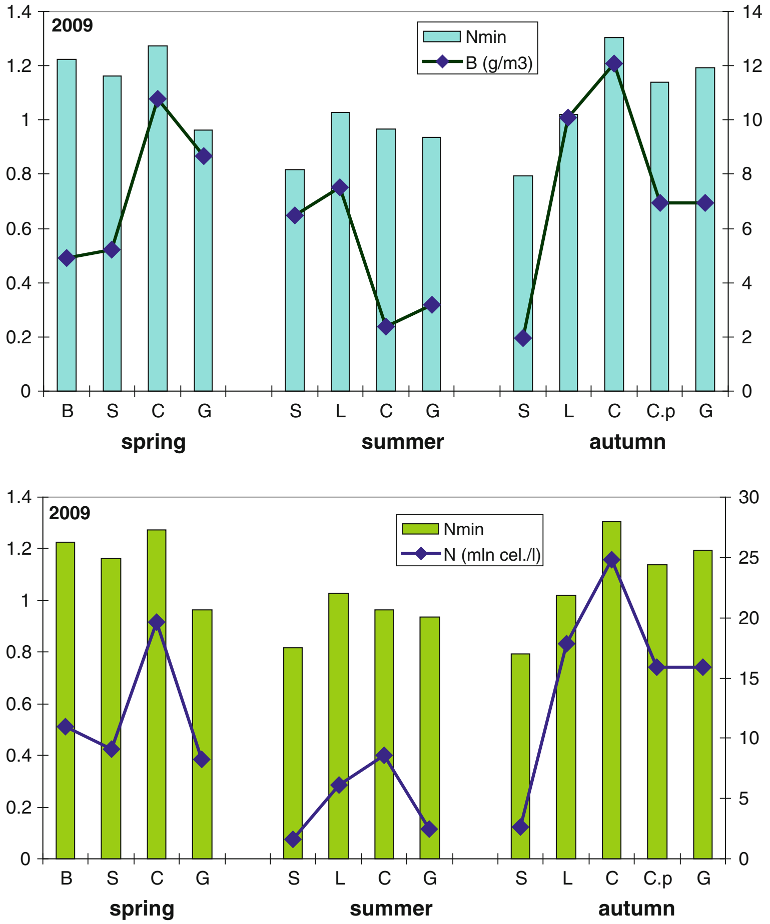


Fig. 7.33 The correlation between the concentration of mineral nitrogen (Nmin, mg/l), biomass (B, g/m^3) and density (N, million cells/l) of phytoplankton in Prut River in 2009 (*B* Braniste, *S* Sculeni *L* Leuseni, *C* Cahul, *Cp* Cislita-Prut, *G* Giurgiulesti)

Prut waters correlated positively with both the density and the biomass of phytoplankton during the vegetation season, despite the high variation of their values (Fig. 7.33).

Nitrogen inorganic compounds are substances, which are necessary for the growth of algae, and at their destruction a secondary pollution of water layers with organic nitrogen substances is observed. Thus, between mineral nitrogen concentration and phytoplankton biomass is established a positive linear dependence, and between organic nitrogen compounds and biomass of phytoplankton—on the contrary, negative. Such correlation between phytoplankton biomass and nitrogen compounds is characteristic for the ecosystems, in which the content of nitrogen compounds is satisfactory for processes of photosynthesis.

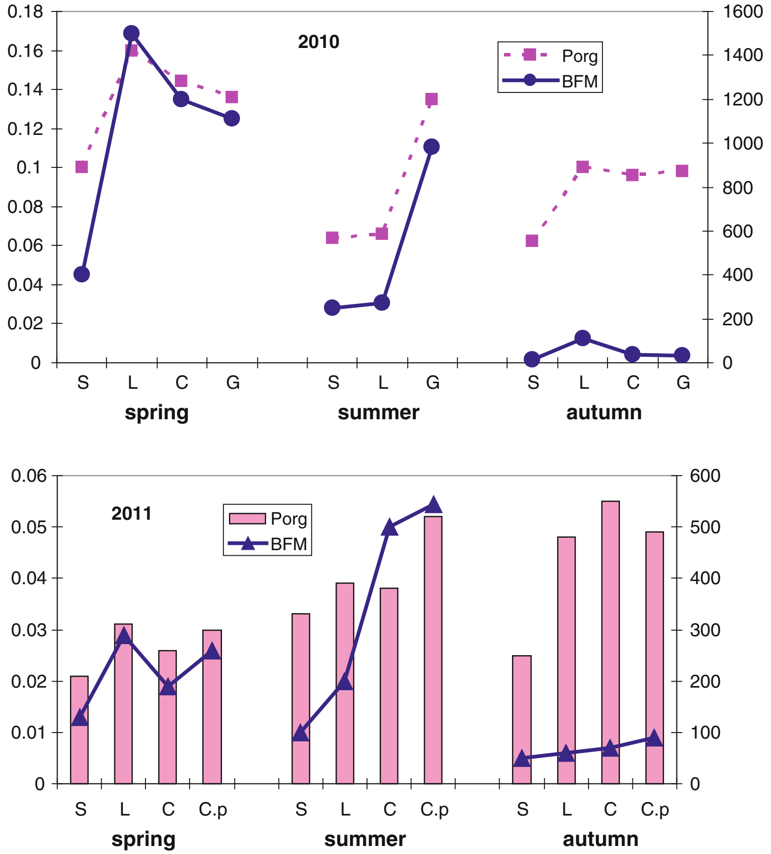
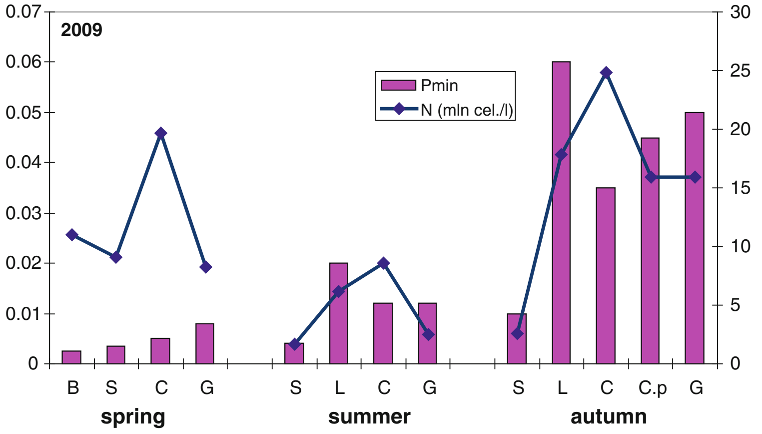


Fig. 7.34 The correlation between the concentration of organic phosphorus (Porg, mg/l) and density of phosphate mineralizing bacteria (BFM, cells/ml) in Prut waters, 2010–2011 (*S* Sculeni, *L* Leuseni, *C* Cahul, *Cp* Cislita-Prut, *G* Giurgiulesti)

The role of phosphorus in planktonic bacteria and algae consists of its participation in the processes of accumulation and transformation of energy in cells. Quantitative assessment of the intensity of reaction of planktonic bacteria and phytoplankton to changes in phosphorus concentration in water represents one of relevant methods of developing prognosis on aquatic ecosystem trophycity.

Last years mineral phosphorus concentration is often lower than that of organic phosphorus and namely phosphate mineralizing bacteria play an important role in establishing a balance between the organic and inorganic compounds of phosphorus. The number of phosphate mineralizing bacteria is in direct dependence with the organic phosphorus concentrations in Prut waters (Fig. 7.34).

However, during investigation period it has been noted a rather broad range of values of phytoplankton biomass and production at the same values of phosphorus concentration in water. This demonstrates that besides phosphorus concentration in



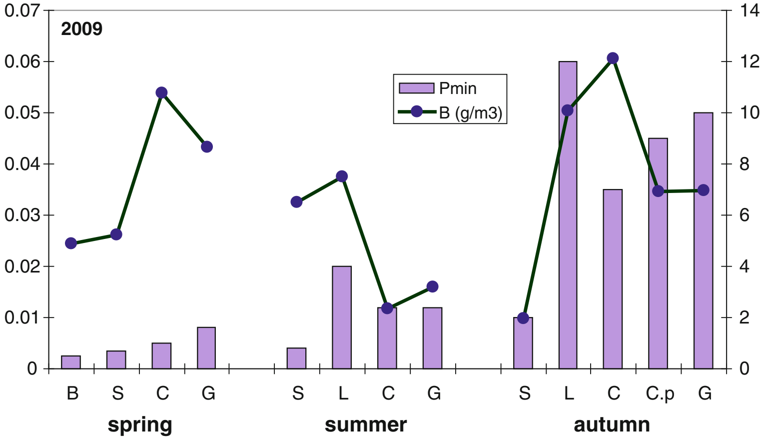


Fig. 7.35 The correlation between the concentration of mineral phosphorus (Pmin, mg/l), density (N, million cells/l) and biomass (B, g/m^3) of phytoplankton in Prut River (*B* Braniste, *S* Sculeni, *L* Leuseni, *C* Cahul, *Cp* Cislita-Prut, *G* Giurgiulesti) in 2009

water, the photosynthesis process and development of planktonic algae is influenced by an enough wide range of environmental factors, which act in complex and each—with a different intensity. It is important to mention that in 2009 a positive correlation or at least a trend towards a positive correlation between mineral phosphorus content and phytoplankton biomass and density was registered, with some exceptions in the autumn, when because of low water temperature bacterial production processes decrease in intensity (Fig. 7.35).

Dynamics of dissolved organic substances in Prut River water is a picture of destruction processes as organic substances are basic nutritional source for many groups of bacteria, especially, the amylolytic and cellulosolytic ones. It turned out that when the Prut water temperature is satisfactory for these groups of

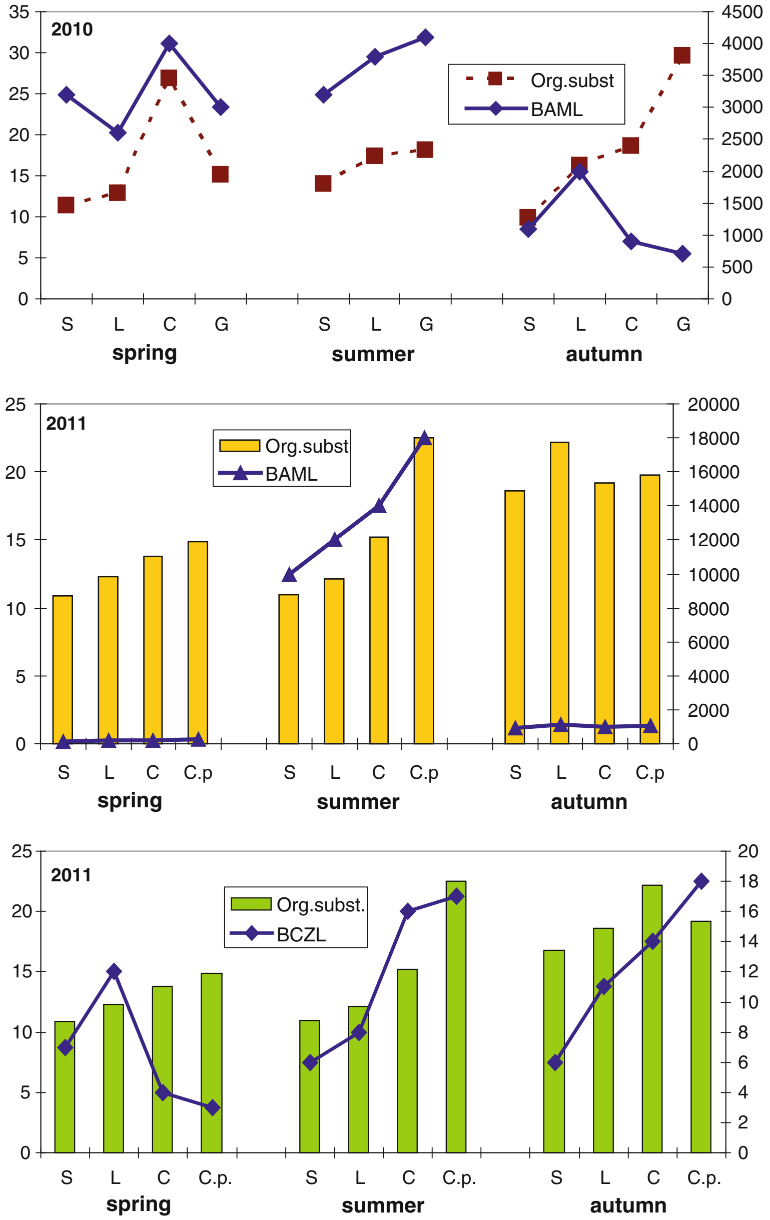


Fig. 7.36 The correlation between the concentration of organic substances (Org.subst., mg/l) and density of amylolytic bacteria (BAML, cells/ml), cellulosolytic bacteria (BCZL, cells/ml) in Prut waters, 2010–2011 (S-Sculeni, L-Leuseni, C-Cahul, Cp-Cislita-Prut, *G* Giurgiulesti)

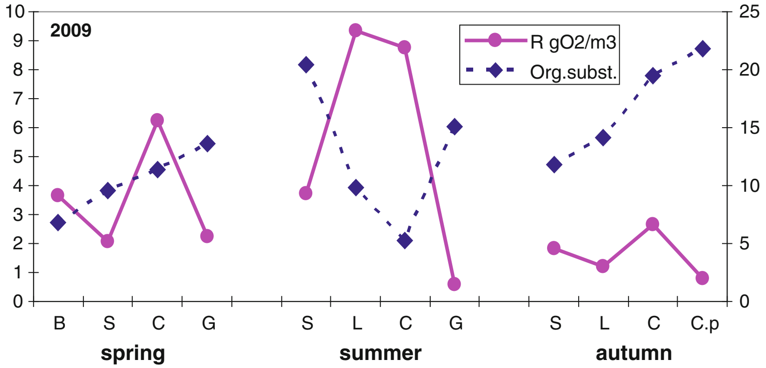


Fig. 7.37 Correlation between the content of dissolved organic matter (Org.subst., mg/l) and values of organic matter destruction (R, gO_2/m^3) in Prut River in 2009 (*B* Braniste, *S* Sculeni *L* Leuseni, *C* Cahul, *Cp* Cislita-Prut, *G* Giurgiulesti)

microorganisms, the dependence of the concentration of organic substances in water and number of these bacteria is almost linear (Fig. 7.36).

On the other hand, a negative correlation between the concentration of organic matter and values of organic matter destruction was established (Fig. 7.37).

The investigations established an evident negative correlation (r = −0.77 to 0.85) between the suspensions content and phytoplankton biomass. High content of suspensions significantly reduces the depth of euphotic layer and, respectively, the primary production values under 1 m^2 of aquatic surface and moreover, it often conditions high values of organic substance destruction. Correlation between suspensions content and phytoplankton biomass, which is typical for eutrophic aquatic ecosystems, is in line with regularities of functioning of continental aquatic

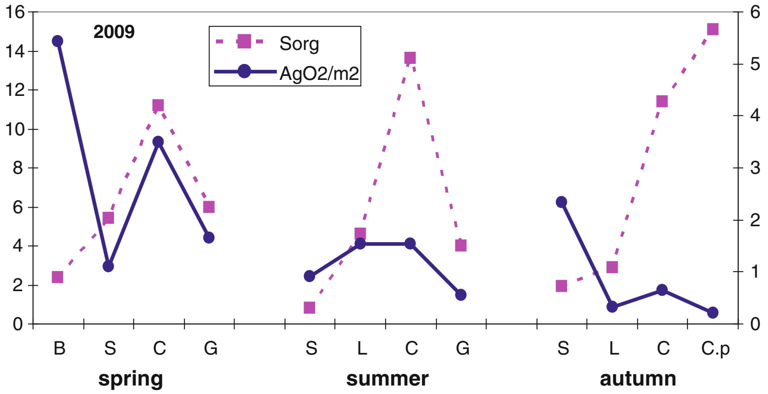


Fig. 7.38 Correlation between the content of organic suspensions (Sorg., mg/l) and values of phytoplankton primary production (A, gO_2/m^2) in Prut River waters in 2009 (*B* Braniste, *S* Sculeni, *L* Leuseni, *C* Cahul, *Cp* Cislita-Prut, *G* Giurgiulesti)

ecosystems concerning the influence of water transparency and turbidity on phytoplankton development and intensity of photosynthetic processes [76, 77, 78].

Regarding the dependence of intensity of phytoplankton primary production on the amount of organic suspensions, it was proved that given correlation has been direct and positive during the spring and summer of 2009 (Fig. 7.38).

In autumn, when a large part of planktonic algae, which are typical for warm periods of the year, complete their period of vegetation, perish and decompose, and the intensity of phytoplankton production processes is reduced, then an opposite correlation of these components of aquatic ecosystems becomes obvious.

7.10 Conclusion

In most cases, water quality was satisfactory for the development of bacteria, phytoplankton, zooplankton and benthic invertebrates, and fish, with some exceptions, caused by increased concentrations of suspended particles, organic matter and low values of amounts of water saturation with dissolved oxygen (during floods 2010 and the period after it).

The application of saprobic system allowed to conclude that investigated aquatic environments, in most cases, correspond to α-, β-mezosaprobic ecosystems, with water quality ranging from moderately polluted to polluted.

Prut River is a transboundary aquatic ecosystem, which has a critical role in the functioning of biosphere reservation of Lower Danube. In this context and based on several international treaties and conventions, EU directives on sustainable exploitation of aquatic resources from the Prut River hydrographical basin, it is necessary to restore the natural wetlands of the river, to clean the bed of several tributaries in order to prevent adverse consequences of floods and low flows.

It is necessary to review and restore the protection areas of Prut River and its tributaries, most of which are blocked by various hydraulic structures and on which banks are located numerous dumps.

It is important, also, to review the situation in the area of former Cahul fish farm, which can be transformed into a valuable wetland, maybe even in an area of ecological tourism.

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Chapter 8
Assessment of Flood Risk Areas in the Dniester River Basin (in the Limits of the Republic of Moldova)

Ana Jeleapov, Orest Melniciuc and Iurie Bejan

Abstract The most catastrophic floods on the territory of the Republic of Moldova are formed on its largest river: the Dniester River. Main measures implemented for flood protection are reservoirs and levees which were built in the middle of the last century. This paper contains first tentative of reevaluation of protection capacity of these measures basing on analysis of new database and modern methods and techniques. Flood hydrographs of different probabilities were calculated basing on new Standards of the Republic of Moldova. HEC-RAS model (USA) was implemented to simulate flood wave of different probabilities from Dubasari Reservoir to Slobazia Village and to evaluate flooded areas, water velocities and depths.

8.1 Introduction

Hydrometeorological disasters represent an integral part of the environment. They occur throughout the world and cause damaging consequences for economic activity. Globally, during the period 1980–2013, a half of total hydrometeorological disasters is formed by floods [1]. In the Republic of Moldova hydrometeorological disasters occur more intense and represent more than 90 % of all disasters. For the same period floods count 54 % of the total number of hydrometeorological disasters [1]. The greatest damage is caused by floods manifested on large rivers Dniester and Prut followed by small and medium-sized rivers. Particularly intense flooding occurred in July–August 2008 on the Dniester River which caused damage of 82.5 million lei and in 2010 on the Prut River which cost 84.2 million lei [2].

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In the Republic of Moldova the research in the field of flood risk is centered on collecting information about damages caused by floods and on development of local protection measures. Activities connected with flood researches are only starting. The first detailed research dedicated to development of "Scheme of flood protection of the Republic of Moldova settlements" was performed by the Institute ACVA-Proiect during 1996–1998 years [3]. However, the considerable number of calculations, included in 40 volumes, primarily refers only to assessment of potential flooded areas in case of 1 % probability, basing on old National Standards [4, 5]. In 2002, in Moldova, Associated European Centre for Flood Problems "CIAPI-Moldova" was created at the initiative of Council of Europe This organization existed only 2 years. During this time, the study with the theme "Problems of floods research in the Republic of Moldova" was performed [6]. This study presents the research results in the field of floods, flood generation factors and a summary of international experience on research and development of effective flood protection measures.

Application of modern hydrological and hydraulical software and GIS for flood wave modeling began in 2009 with the project "Elaboration of kinematical flood wave model and assessment of risk areas in case of floods on rivers of the Republic of Moldova" and continued with the second project "Development of geoinformational support for flood risk assessment in Prut River basin" [7, 8]. Main research activities of both projects were performed by Institute of Ecology and Geography of the Academy of Sciences of Moldova. The main purpose of the projects consisted of application of hydrodynamic software HEC-RAS (USA) [9, 10] for simulation of flood wave in case of dam break of Costesti-Stinca Reservoir situated on Prut River and of Dubasari Reservoir situated on the Dniester River.

In this context, we believe that the first tentative of using hydraulical modeling for flood risk assessment on the Dniester River in the limits of Moldova represents a great practical relevance and constitutes a big perspective for the future research.

8.2 Study Area

The Dniester River Basin is a transboundary river and spreads on the territory of three countries Poland, Ukraine and Republic of Moldova. Over 70 % of the basin is situated in limits of Ukraine and only 27 % belong to Republic of Moldova. The total area of the basin is approximately 72100 km^2 and the length is 1352 km. The basin is conventionally divided in three parts: the Upper Part represents the region from the Dniester spring to confluence with Zolota Lypa River (upstream Zalishchyky Village), the Middle Part is assigned to the region from Zolota Lypa River to Dubasari Town (generally characterized by a highland landscape) and Lower Part characterized by plain landscape (Fig. 8.1) [11]. The Upper part lays in Carpathians and represents only 30 % of the basin area but due to high amount of precipitations, 70 % of the Dniester runoff is generated in this area [11]. Average

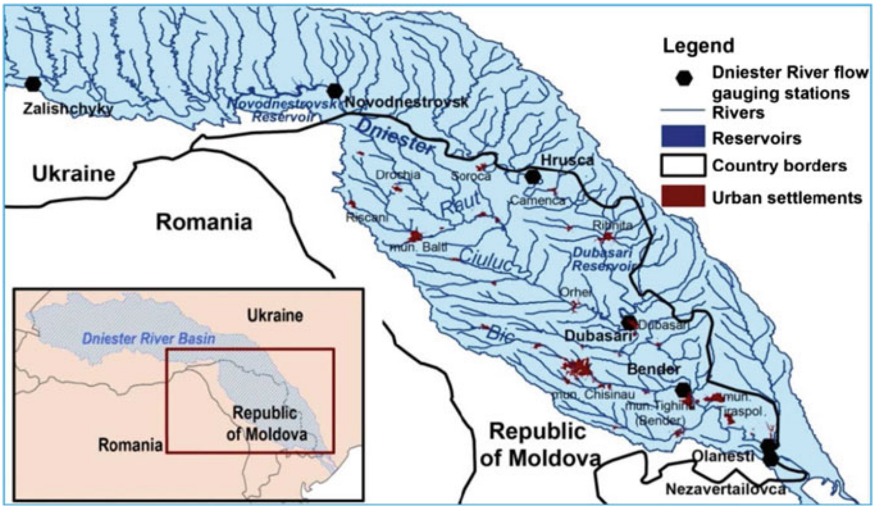

Fig. 8.1 Middle and lower part of the Dniester River Basin

amount of precipitations over basin area decreases constantly from 1300–1000 mm in the Upper part to 400–500 in the Lower Part [12, 13].

The Dniester River Basin forms 57 % (over 19000 km^2) of the territory of the Republic of Moldova and the length is 660 km. In the limits of Moldova, the Middle part of the basin is characterized by high land with the altitudes from 150 up to 400 m, the floodplain enlarges up to 3 km. The Lower Part of the basin differs from the other with a plain landscape lower 150 m. The floodplain extends from 4 to 6 km (on the region Dubasari- mun. Bender), up to 6–12 km till Turunchiuc branch, and up to 22 km near river mouth [13].

The Dniester River represents the main fresh water source of the country. In the limits of Moldova, the Dniester average discharge is 312 m^3/s, increasing up to 450–500 m^3/s in April and decreasing below 200 m^3/s during winter months. Total Dniester average volume is approximately 9.8 km^3. In years with humidity deficit Dniester water resources are estimated at 6 km^3, in years with high humidity the volume increases over 12 km^3, being 2 times higher than in dry periods. Being a transboundary river the Dniester water resources are equally divided by Ukraine and Republic of Moldova [2]. These water resources are considered as country propriety.

8.3 Methodology and Data Base

Basically, in the Republic of Moldova, HEC-RAS is the first and, for now, the main hydraulic model utilized for flood wave modeling in case of reservoirs dam break on big transboundary rivers [14, 15]. In this study HEC-RAS is also used to

Table 8.1 Characteristics of flow gauging stations of the Dniester River (in limits of Moldova territory)

River	Flow gauging station	Basin surface till gauging station, km^2	Mean maximal discharge, m^3/s	Distance to river mouth, km	Measurement period
Dniester	Hrusca	48700	1516	509	1968-present
Dniester	Dubasari	53600	1295	351	1956-present
Dniester	Bender	66100	1269	214	1881-1915; 1945-present
Dniester	Olanesti and	68900	1099	77	1959-present
	Nezavertailovca			69	1971-present

appreciate the potential flooded areas, water depth and water velocity. The main component used for this purpose is unsteady flow routing. Maximal discharges and flood hydrographs of different probabilities necessary as input data for unsteady flow routing were modeled basing on recommendations from National Standard of the Republic of Moldova [16].

Spatial data preprocessing and postprocessing was made using GIS and HEC-GeoRAS extension. Triangular irregular network (TIN) was generated in GIS basing on contour lines and elevation points extracted from topographic maps of scale 1:25000 [17]. The same maps were used for creation of levees, river banks, river centerline, obstructions and ineffective areas layers.

Main source of hydrological time series is the archives of State Hydrometeorological Service of the Republic of Moldova—organization responsible for stage and flow measurements. In limits of the Republic of Moldova territory the flow measurements are made at 5 from 11 gauging stations situated on the Dniester River: Hrusca, Dubasari, Bender, Olanesti and Nezavertailovca (Fig. 8.1). According to water cadastre [18], the time series of maximal discharges are available from 1881 to present (Table 8.1).

8.4 Results and Discussions

8.4.1 Flood Events and their Generating Factors

The general idea of the size and frequency of the Dniester floods can give instrumental observations, as well as historical and archival records which contain valuable information about the spontaneous nature of this phenomenon. The Dniester floods chronology covers a period of seven centuries (1146–1840 years) [19, 20]. First mention of the most powerful floods of the Dniester River is given in Hypatian chronicle in 1146. The Dniester floods, which took place in 1230, 1572, 1649, 1668, 1700, 1730, 1757, 1814, 1823, 1864 are described in details in

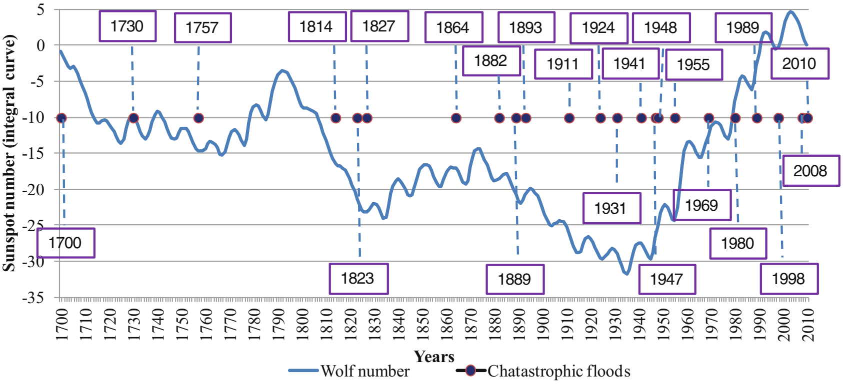

Fig. 8.2 Solar activity and the Dniester floods over the XVIII–XXI century

archival documents [21]. During instrumental observations the most powerful floods of the last century were reported in 1911, 1941, 1955, 1969, 1980, 1989, 2008 and 2010 [22]. The total damage from flooding in Moldova for the period from 1947 to 2000 amounts to 285.4 million lei [23].

The main climatic factor which generates the Dniester flood events is extreme meteorological conditions in Carpathian region, manifested especially in summer period. In this region rainfall intensity exceeds 250 mm/day and its spatial distribution spreads on a scale from 100 up to 3000 km^2 [24] .The effect of heavy rains is amplified by Carpathian steep slopes and as a consequence fast slope runoff, high debris flow and water levels are formed. The most dramatic flood of the last 20 years was observed in 2008. This flood was generated by stationary cyclonic activity over Western part of Ukraine, in Carpathians. At three gauging stations, located in the center of this cyclone, the total sum of rain exceeded 300 mm [25]. This resulted in the flooding of the territories and settlements along the river in both countries: Ukraine and Moldova. Generated discharges of the Dniester River exceeded 3400 m^3/s (at Hrusca gauging station) which is 10 times bigger than the average.

Atmospheric activity is driven mainly by the Sun. Analysis of Sun activity fluctuations [26] and flood time series can give an idea about a relationship between these phenomena (Fig. 8.2). Through, from XVII to XIX century, the flood appearance is equal to 1 in every 16 years. In period of decreasing solar activity (till 1935), one flood occurred every 12 years. In the period of increasing of solar activity: 1935–2010 the appearance of floods raised and 1 flood was observed in every 10 years already [21].

The comparison of these graphs shows that on the background of secular variations of solar activity there are complex flood events. Years, in which the disastrous floods are observed, in most cases, coincide with 11-year cycle of solar

Table 8.2 The main parameters of the biggest reservoirs located on the Dniester River [13, 27, 37]

Parameters	Novodnestrovsk	Dubasari (1956)
Country	Ukraine	Moldova
Distance to river mouth	677.7	351
Surface of the basin, km^2	40500	53600
Lengths, km	194	128
Year of construction	1982	1956
Levels		
Maximum water level (MWL), m	125	30.0
Full reservoir level (FRL), m	121	28.0
Minimum pool level (MPL), m	102.5	24.2
Volume, mln m^3/Surface, km^2		
at MWL	3600/160	633/80.0
at FRL	3000/142	485/67.5
at MPL	1000/75	272/46.8
Maximal discharge, m^3/s	8320	8200

activity. This fact should be taken into account when assessing the floods probability.

8.4.2 Flood Protection Measures: Reservoirs and Levees

Management of river floods becomes easier in comparison with other disasters because this disaster is manifested on river specific neighboring territories. In the Republic of Moldova flood protection measures are: reservoir operation, levees, channels, ponds, polders and others. The main measures taken to avoid the Dniester floods are dammed reservoirs and levees along the river. Two reservoirs are constructed on the Dniester River Bed: first is Novodnesrtovsk which is managed by Ukraine and second is Dubasari situated within the Republic of Moldova territory (Table 8.2). Both reservoirs are situated in the Middle Part of the basin and are constructed for multipurpose: water supply, irrigation, hydroelectric power generation, flow balancing, flood mitigation, fishery, recreation, navigation [13, 27].

Assessment of flood protection capacity of both reservoirs can be made basing on analysis of flood peaks changes along river bed for three time periods: 1st period 1981–1955 corresponds to natural flow, 2nd period 1956–1982 comprises the period of only Dubasari Reservoir operation, 3rd period from 1987 till present—covers the period of both reservoirs operation. For this purpose the most powerful floods were analyzed at the gauging station Zalishchyky situated upper Novodnestrovsk Reservoir and representing the unchanged flow by reservoirs and the gauging station Bender located in the Lower part of the basin, downstream Dubasari Reservoir (Table 8.3).

Table 8.3 Flood peak modifications for three periods of the Dniester flow measurements [38]

First period: 1887–1955				Second period: 1956–1982				Third period: 1987–2010			
Year	Zalishchyky	Bender	K	Year	Zalishchyky	Bender	K	Year	Zalishchyky	Bender	K
1900	3730	1270	0.34	1969	5970	3000	0.50	1989	2700	1510	0.56
1906	3070	1260	0.41	1970	2950	1730	0.59	1998	4080	1800	0.44
1913	4120	1400	0.34	1974	3300	1960	0.59	2008	5600	2610	0.46
1948	3420	1730	0.51	1980	3910	2490	0.64	2010	2765	1700	0.62
Average			0.40				0.58				0.52

Before reservoirs operation, spatial reduction of flood peaks was determined by growing area of the Dniester River Basin from 24600 km^2 (at Zalishchyky gauging station) to 72100 km^2 (at river mouth), and by enlarging of floodplain width. Coefficient of flood peak transformation (K) for this period is relatively constant, averaging 0.40. (Table 8.3). Reduction of flood peaks in Lower part of the Dniester River Basin increased in period of Dubasari reservoir operation. Regulation capacity of the reservoir was only 30 % of its full capacity (148 mln m^3), therefore, in the case of a rare probability flood with a maximum discharge greater than 3000 m^3/s, and a flood volume over 2000–3000 mln m^3, the flood peak reduction by reservoir was only on 10–15 % which means that flood wave passes through reservoir in transit. Operation period of both reservoirs changes the Dniester water flow regime during the phase of high flow. If prior to reservoirs peak flow transformation processes were associated with the distribution and accumulation of flow volumes in the natural river bed and floodplain, after the construction of reservoirs transformation of flood waves is carried out by their flood regulation capacity. This fact induced a better flood management in the region which is shown also by increasing K to 0.52–0.58. However, Dubasari Reservoir loses its capacity of flood protection because of significant decreasing of its parameters. Due to high silting processes useful storage volume was twice reduced, dead storage practically disappeared, decreasing from 272 to 80 mln m^3. [13]. Flood regulation capacity was also reduced because of decreasing of volume at MWL from 632.8 to 370 mln m^3. [13]. Thus, at present Dubasari Reservoir is not able to reduce the projected flood discharges without causing accident conditions and is operating in high-risk regime. For last 60 years of operation period no desilting activities were taken.

Besides reservoir, another method designed to protect agricultural areas and settlements against floods consists of a levees system built along river banks. Levees construction along the Dniester River began in the 50's of the last century. The total length of protection levees in the end of construction process was equal to 220 km along the Dniester River. [28] According to project calculation existing protection levees on the Dniester River in the limits of the Republic of Moldova are designed for ensuring a free-accident flow of 2600 m^3/s. However, flood events from 2008 and 2010 showed that the protection capacity of levees dramatically decreased. During 2008 flood the water level exceeded 6 m and over flooded constructed levees, also some part of levees were practically destroyed by high waters. In total, renovation together with elevation increasing activities must be taken for a length of 80 km of levees [28].

8.4.3 *Flood Wave Modeling*

Even if the last century was characterized by high flood protection activities like reservoir and levees building, at present these measures cannot show a high protection capacity. However, an illustrative approach about parameters of present or projected flood protection structures can be made by hydraulic model HEC-RAS. Evaluation of potential flooded regions was made on the sector situated downstream Dubasari Reservoir till Slobozia Village, the total length of the area is 185 km, landscape is characterized by a floodplain which enlarges from 3 km near Dubasari up to 8 km from Bender to Slobozia.

First phase of model development consisted of creation of geometry the Dniester floodplain [29, 30]. Automatic extraction of cross sections from TIN using HEC-GeoRAS gave a satisfactory result for river banks but not for river bed. Correction of cross section, especially of rived bed was made using cross sections database basing on field survey made in the 70–80' of last century [31]. Every cross section was manually corrected and adapted to reality in HEC-RAS environment, also appropriate Manning's value and contraction and expansion coefficients were chosen independently for the Dniester banks and bed [9].

After a detailed analysis and correction of river geometry model evaluation was made basing on simulation of real flood events from 1969, 1980, 2008, 2010 [32–35]. The pilot sector for model evaluation was considered region Dubasari Reservoir—mun. Bender. Observed runoff database is present at both points. Observed and modeled hydrographs are shown in Fig. 8.3. Simulation results of four flood events are shown in Table 8.4.

Assessment of modeled runoff quality was made by using four efficiency criteria: coefficient of determination (R^2), Nash–Sutcliffe efficiency (E), logarithmic Nash–Sutcliffe efficiency (ln E) and percent BIAS (PBIAS) [36]. High R^2, E and ln E (Table 8.5) meet general quality requirements [36] but PBIAS is still low simulated, probably because of TIN and cross-sections precision.

Even if simulations (PBIAS) are at the limit of satisfactory results, the model was applied for assessment of potential flooded areas, water depth and velocity in case of flood wave of different probability. Hydrographs of different probabilities were constructed on example of a real hydrograph from a recent period (2008 flood) which represents the actual situation of the Dniester runoff and protection measures capacities.

The first flow gauging station which meets the Dniester River on the territory of the Republic of Moldova is situated at Hrusca Village, upper the Northern part of Dubasari Reservoir. Hydrological information on pluvial floods characteristics (flood peaks, maximal stages, total volumes) at Hrusca gauging station comprises 2 periods of time: before (1968–1982 years) and after Novodnestrovks reservoir construction. Due to this fact the homogeneity of Hrusca time series was analyzed. The results of this analysis show that statistical parameters calculated for flood peaks as well as for flood volumes estimated separately for both periods are close to each other. Basing on statistical parameters and theoretical ordinate of gamma-distribution, flood peaks and volumes of 0.1, 0.5, 1 and 5 % probabilities were estimated for the Dniester time series of Hrusca gauging station (Table 8.6). Hydrographs of different probability were modeled on example of real hydrograph of 2008 flood basing on recommendations outlined in National Standard of the Republic of Moldova [16].

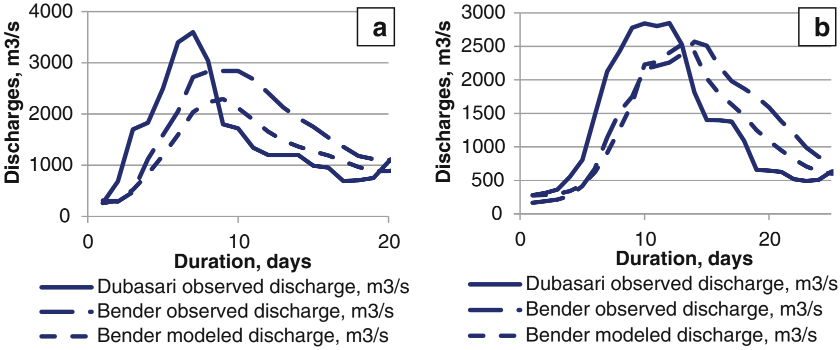

Fig. 8.3 Observed and modeled flood hydrographs of 1969 (**a**) and 2008 (**b**) floods

Table 8.4 Simulation results of the Dniester four flood events

Event	Hrusca observed flood peak, m^3/s	Dubasari observed flood peak, m^3/s	Bender observed flood peak, m^3/s	Bender modeled flood peak, m^3/s	Bender observed maximal stage, m	Bender modeled maximal stage, m
08.06.-02.07.1969	4430	3600	2840	2293	12.07	10.66
25.07-16.08.1980	3420	2630	2480	2284	12.33	11.11
21.07.-16.08.2008	3450	2847	2570	2528	12.75	11.19
18.05.-30.07.2010	1700	1600	1690	1423	10.85	10.50

Table 8.5 Performance statistics for the Dniester four flood events simulation

Event	R^2	E	Performance rating of E	ln E	PBIAS, %	Performance rating of PBIAS
08.06.-02.07.1969	0.99	0.70	Good	0.82	21.07	Satisfactory
25.07-16.08.1980	0.98	0.91	Very good	0.88	11.95	Good
21.07.-16.08.2008	0.96	0.88	Very good	0.90	13.43	Good
18.05.-30.07.2010	0.96	0.62	Satisfactory	0.70	19.41	Satisfactory

Hrusca hydrographs are considered as inflow hydrographs to Dubasari Reservoir. The reservoir outflow hydrographs were calculated basing on reservoir water balance approach, flood storage volume being considered as projected in 1956 equal to 148 mln m^3.

Basing on reservoir outflow hydrographs which are considered as input values, HEC-RAS modeled the hydrographs at Slobozia Village (Fig. 8.4). In the end potential flooded areas in case of flood wave of different probabilities as well as water velocity and water depth of the region Dubasari Reservoir—Slobozia Village were calculated and extracted to GIS environment (Figs. 8.5, 8.6, 8.7).

Table 8.6 Simulation results of the Dniester flood wave modeling of different probability

Exceedance probability, %	Hrusca modeled flood peak, m^3/s	Dubasari modeled flood peak, m^3/s	Slobozia modeled flood peak, m^3/s	Region Dubasari Reservoir – Slobozia Village				
				Total flooded area, km^2	Flooded settlements area, km^2	Maximal water velocity, m/s	Maximal water depth, m	Period between flood peaks, hours
0.1	7382	7108	6254	329	28.6	3.1	10.35	91
0.5	5712	5456	4653	315	23.0	3.5	9.43	105
1	5009	4760	4006	308	21.2	3.3	9.10	123
5	3442	3212	2849	200	13.4	2.6	8.23	129

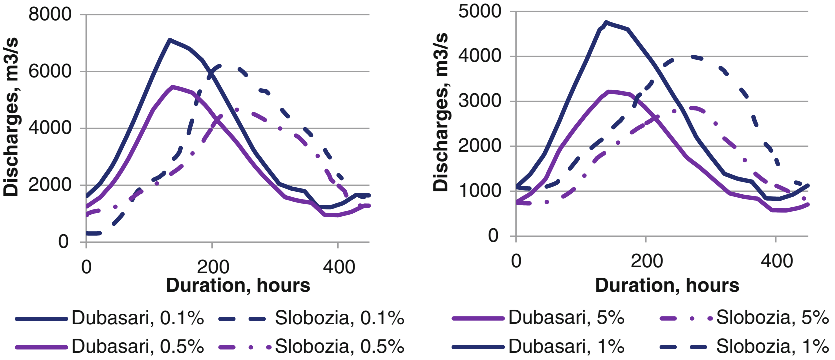

Fig. 8.4 Modeled hydrographs of different probablilities

The most vulnerable areas to floods are settlements as well as agriculture areas. Period between flood peaks from Dubasari Reservoir and Slobozia Village (Table 8.6) allows predicting the possible flood wave in the downstream part of the region and gives time to estimate the necessary flood protection measures. Adequate decisions on flood protection measures can prevent settlements from flooding and infrastructure damages, as well as decrease the number of affected people or victims.

Performed HEC-RAS model is capable to give an answer on protection capacity of levees as well as to show the impact of chances of levees positions and characteristics. Present levees system is capable to protect the area from flooding with a maximal discharge of 2600 m^3/s but modeled discharges exceed this value. Basing on these data a recalculation of levees characteristics can be made and modeled in HEC-RAS to understand the efficiency of their new measures.

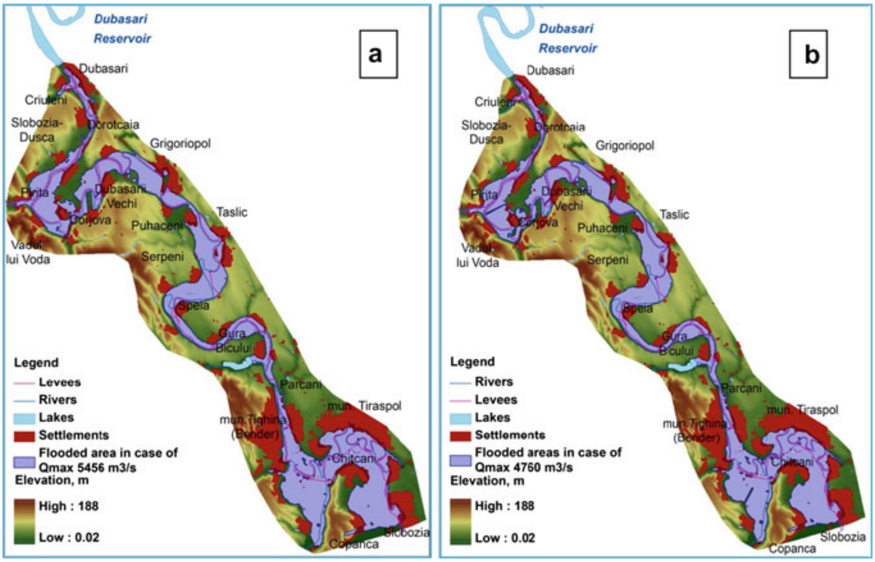

Fig. 8.5 Modeled flooded areas in case of floods of 0.5 % (**a**), 1 % (**b**) probability

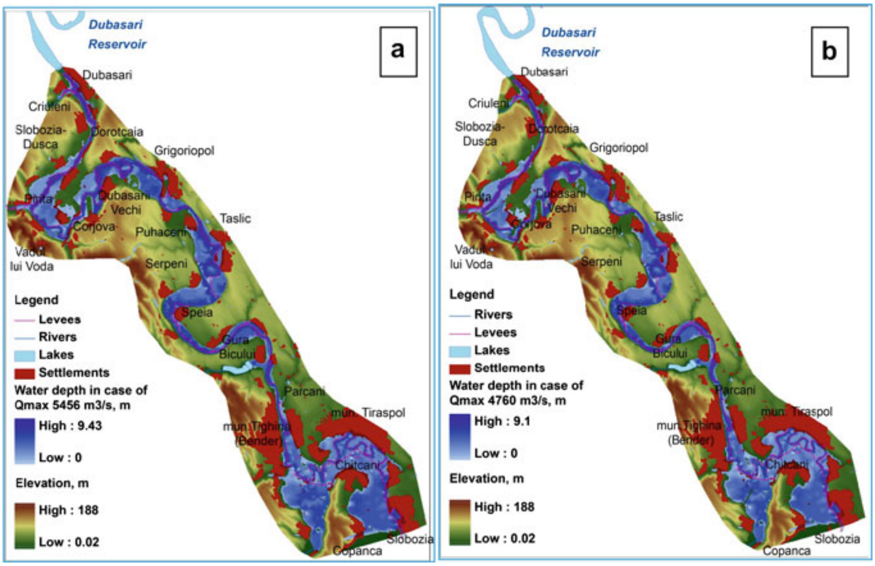

Fig. 8.6 Modeled water depth in case of floods of 0.5 % (**a**), 1 % (**b**) probability

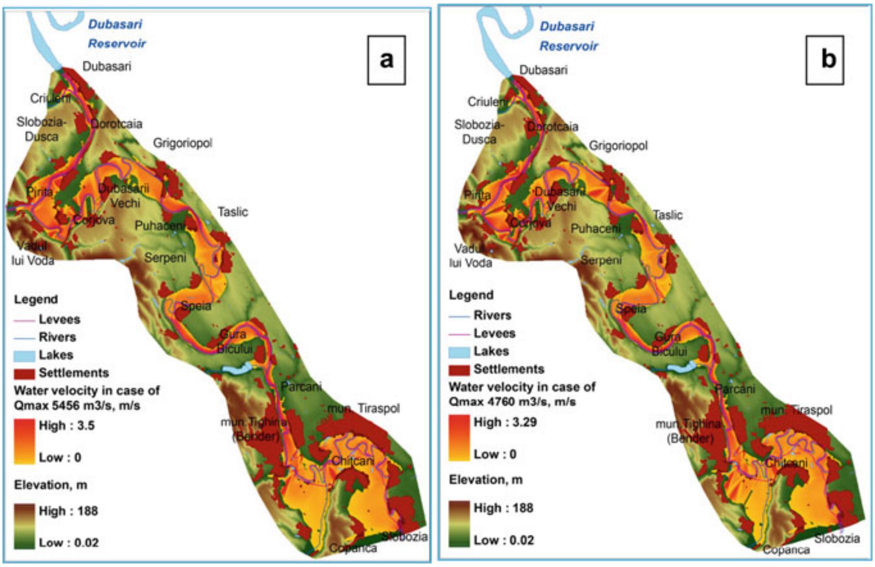

Fig. 8.7 Modeled water velocity in case of floods of 0.5 % (**a**), 1 % (**b**) probability

8.5 Conclusion and Recommendations

Instrumental observations of flood wave on the Dniester River began in 1881(Bender gauging station). The long range of observation dataset allows performing a detailed description and assessment of flood risk of the Dniester River during the time. Analysis of observed flood peaks and flood volumes showed that depending on flow regulation measures the coefficient of flood peaks changes along the river differs. A higher flood management capacity was achieved after construction of Novodnestrovsk and Dubasari reservoirs as well as levees system. However, due to reductions of protection structures characteristics during last 60 years, the flood risk increases.

The assessment of flood peaks and flood hydrographs of different probabilities for the Dniester River was performed basing on methods from new National Standards (at Hrusca) and also with consideration of low flood regulation capacity of Dubasari Reservoir (at Dubasari). Comparison of modeled and real hydrographs shows that the observed floods from 1969, 1980, 2008 are close to 3–8 % probabilities. Modeled hydrographs have a typical triangular shape and represent the input data for flood wave modeling in HEC-RAS environment.

The results of flood wave modelling in HEC-RAS can be considered reliable corresponding to input data set used in the study. Due to the inaccuracy of available elevation data used from topographic maps created in the 1980s of the last century, and their insufficient scale, modelled results cannot be considered sufficiently accurate. In other words, the elevation values, distances, data on riverbed and levees on these maps may not correspond exactly to reality. Model improvements can be done only in case of using modern elevation data or at least topographic maps with a scale of 1:10000 in combinations with actual data on the Dniester riverbed. It is imperative to make field survey and to obtain detailed information of river banks and adjacent territories and adequate and qualitative cross sections. All hydraulic structures located along the river and in the Dniester basin, such as pumping stations, reservoirs, irrigation channels and others and also the Dniester tributaries must be included in the model for more modern water management.

Also, a good water management of the Dniester River basin requires coordination and full cooperation between water management authorities of two bordering countries Ukraine and Moldova. For a better understanding of the processes which take place inside of the river basin and simulate the possible future environmental changes the Dniester River basin should be analyzed as a whole system which means that only basing on a common effort of Moldova and Ukraine the efficient measures a sustainable water use, flood mitigation and complex water management can be achieved.

A complex water management must also include hydraulic as well as hydrological modelling. A platform for this purpose can represent common implementation of HEC-HMS and HEC-RAS models.

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Part III
Groundwater

Chapter 9
Groundwater Quality in the Republic of Moldova

Constantin Moraru

Abstract Groundwater in the Republic of Moldova has a long history of usage as drinking and technical water. In rural areas they predominate (approximately 95 % of application) and in the urban territories water supply consists not less than 45 %. Over the last 100 years numerous investigators have contributed to the basic knowledge with respect to the Moldavian aquifer systems. A summary of previous studies, mainly limited to hydrogeology and ground water quality, is given by authors [6, 14, 15, 20]. Compared with other countries (territories) Republic of Moldova has enough reserves of groundwater potential (about 3.0 km^3/year of fresh water). Here, for applied hydrogeology quantity of water is secondary and quality of water is primary question. This is because territory of the country is highly populated and natural degree of ground water protection is low. Water quality is mainly affected by two categories of contaminates originated from (a) natural composition of water bearing rocks and (b) anthropogenic activities. Nowadays additional category is observed which is connected with multiseasonal fluctuation of climatic conditions (perhaps, global climate changes). The aim of this investigation was to examine present and main aspects of groundwater quality. Only aquifers containing potable water were studied.

Keywords Groundwater · Water quality · Hydrogeology · Aquifers

9.1 Materials and Methods

Hydrogeological data (water levels, well debit, etc.) were collected from geological archives, scientific reports, articles and directly during field survey. A considerable part of information was used from the data base of the Laboratory of

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Hydrogeology, Institute of Geology and Seismology, Academy of Sciences of Moldova. Initial hydrogeological data were checked for accuracy and geographical reference. SPSS-14 and Excel-2003, 2007 software are used for graphical and statistical analyses.

The sampling campaign included collection of data from shallow and deep wells. To identify the potential sources of pollution in the area of the wells, the relevant type of land use (built-up/urban, arable and nature) was also recorded, especially on the "upstream" side of the well. Also the products of arable lands were recorded.

In order to investigate nitrate pollution in the groundwater of the villages, sampling of shallow wells was done in two main directions, viz. (a) by following the direction of the slopes and (b) by following the contours of the hills. In this way maximum information was obtained with respect to topographical effects on nitrate levels and on nitrate variation on equal topographical level. For wells located near the village border with arable land, the term urban/arable was used. The topographical position of the wells in the cross-sections was roughly indicated by terms "high", "medium" and "low". These terms are qualitative indicators, with no absolute precision.

Based on the assumption that nitrate and bacteriological contamination in the shallow aquifers of the urban area originate from the same sources of pollution, *E-coli* bacteria were also sampled. Data about trace elements, organic pollutants in different media were used [9, 14, 15].

Analysis of electric conductivity (EC), pH, temperature and dissolved oxygen (DO) was done with the multiple purpose measuring instrument and different sounds of the field kit Multiline (Germany). Analysis of hardness, TDS and chemical elements was performed in the laboratory conditions using standardized methods. For the tests of total-coli and *E-coli* a special field set, including pipette, reaction devices and incubator was used. Because of lack of electricity in the field, the samples were temporarily stored in a cool place and by the end of the day they were placed in the incubator for the required period of time. However, the method will certainly prove the presence or absence of the bacteria and provide a relative indication regarding their number. Data form many sources were assessed as primary information [9, 14, 15, 18, 20].

9.2 Geological and Hydrogeological Setting

Geological structure is important for groundwater. It is like a matrix formed from different layers of rocks, which are united in permeable and impermeable strata. Permeable horizons (aquifers) are reservoirs for groundwater accumulation and impermeable ones (aquitards) serves as basis for water bearing horizons.

At present geology of the Moldova territory is studied well [1–3, 5, 6]. From the point of view of the authors [9] Moldova sits on a top of stable Pre-Cambrian (much older than 560 Ma years) crystalline shield, often denoted as the West - European

Platform. It follows that the crystalline basement of platform consists of highly metamorphic rocks that may have been subjected to several orogenic cycles. The literature on the geology of Moldova [5, 6] suggests that this crystalline platform has been reached in many exploration drillings throughout the country.

The rocks overlying the stable platform are nearly formless with regional sub-horizontal strata. Much of the stratigraphy overlying the crystalline basement is absent because of the lack of deposits or erosion afterwards. These stratigraphical gaps in sedimentation indicate that the area may have been a landmass for much of the time.

The Tertiary sediment pile is of paramount importance to groundwater and groundwater flow systems. Present-day Moldova is built up by the clayey and sandy marine rocks of the Neogene age. These rocks are exposed throughout the country; locally there are some thin veneers of Quaternary alluvial sediments. In terms of Alpine Geology (65.5–2.6 million years ago), this Middle to Late Miocene rocks (10–15 million years) represents the so-called Molasse deposits of the Eastern Carpathian mountain ranges.

The underlying rocks of the Paleozoic and Mesozoic ages (sandwiched between the crystalline basement and the Tertiary rocks) are much less important hydrogeologically. They are of interest for oil and gas exploration except for the northern part of Moldova where the top of the crystalline basement becomes shallow and is tapped by deep wells. The Paleozoic and Mesozoic rocks are exposed in the valley of the Rivers Nistru and Prut. As a result of geological development, different tectonic structures and faults were formed on the territory of the Republic of Moldova [1, 2, 10, 14, 15].

Fresh water containing aquifers, aquitards, their geological ages and regional distribution are shown in Table 9.1.

Table 9.1 Fresh water aquifers and aquitards distinguished in Moldova

Geological formation	Name/hydrogeological interpretation	Coverage of Moldova		
		South	Middle	North
Q	Quaternary/local aquifers	X	X	X
N_2P	Pontician/aquifer	X	–	–
$N_1S_3 + N_1m$	Upper Sarmatian-Meotician/aquifer	X	–	–
N_1S_3	Upper Sarmatian/aquitard	X	X	–
N_1S_2	Middle Sarmatian/aquitard	X	X	X
N_1S_2 – sand	Middle Sarmatian/aquifer	X	–	–
N_1S_2	Middle Sarmatian/aquitard	X	X	X
N_1S_2 – limestone	Middle Sarmatian/aquifer	X	X	–
N_1S_2 – clays	Middle Sarmatian/aquitard	X	X	X
N_1S_1	Lower Sarmatian/aquifer	X	X	X
$Cr_2S_2 + N_1b$	Cretaceous–Badenain/aquitard	X	X	X
$Cr_2S_1 + S$	Cretaceous–Silurian/aquifer	X[a]	X[a]	X

[a] Aquifer is present, but filled with brackish groundwater

All confined aquifers (from Miocene to Silurian) in Moldova's cross-section have sedimentation of marine origin. Unconfined Quaternary aquifer complex is of mixed marine and continental provenance. The oldest complex of aquifers belongs to Mesozoic and Paleozoic permeable deposits. In this geological periods water chemistry was predominately chloride and sodium. As the sea regressed, the northern part of the country was exposed to surface conditions while the southern part remained under a shallow sea. Infiltration of atmospheric precipitations and surface waters extruded saline water in the middle of Moldova where the Silurian horizon dips sharply under Mesozoic formations. Approximately 70–250 Ma years ago, Mesozoic aquifers filled with seawater. The Cretaceous aquifer in the northern part of Moldova changed the water chemistry analogically to the Silurian. A Jurassic complex of aquifers formed in the By Dobrudja depression, and its geochemistry remains the same. The TDS in these aquifers are between 60 and 300 g/l with high concentrations of trace elements, namely iodine, boron, rubidium, and bromine.

Tertiary aquifers formed under the influence of the Sarmatian paleosea. Initially, water in the Neogene water bearing rocks was middle saline corresponding to chloride sodium/calcium type. Flat sedimentation of deposits and its inclination from North to South provided good conditions to flush horizons by infiltrated surface and precipitated water. Until the Quaternary period, Neogene aquifer water chemistry drastically changed. Paleogeographical investigation indicates that water of Neogene horizons was brackish. The processes of flushing and water popping continue to the present time. Isotopic data show that the youngest water in Neogene aquifers is about 50 years (Northern part of Moldova) and the oldest is approximately 5000 years (Central part of Moldova). The water type is sodium bicarbonate to sodium chloride. The Black Sea is a regional area of ground water discharge.

Quaternary aquifers changed their chemical composition in the interval of TDS 1–6 mg/l. In the hot periods, the TDS increased and vice versa during humid periods. Atmospheric precipitations and ascending artesian water infiltrations are the main factors determining the history of shallow groundwater geochemistry. These mechanisms still function.

Some data used for the development of present results was described by authors [9, 11, 13, 17]. Variations of groundwater levels in time appear to be without much regularity. The changes of levels in the deep aquifers do not show a direct relation to variations in precipitation. Even in wells of shallow aquifers deeper than a few meters, the seasonal fluctuations may have been smoothened out because of the very low hydraulic conductivity of the upper layers. Representative relationship between ground water level and atmospheric precipitation are shown in the Fig. 9.1.

The situation of groundwater abstraction in Moldova has been quite complicated and is becoming increasingly obscure in recent time. The developments in the past can be relatively well reconstructed but that is not true for the present time. According to verbal information the regulations with respect to licenses for installation of water supply wells and the obligation to provide sufficient information,

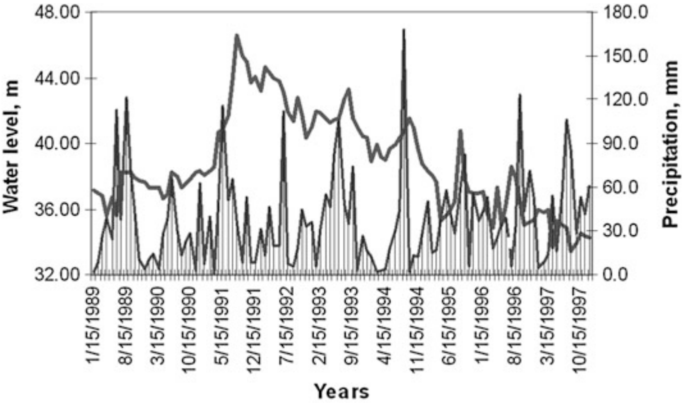

Fig. 9.1 Evolution of ground water level and atmospheric precipitation (*drop lines* are precipitation (mm) and above line are ground water level, absolute values, (m))

which were respected in the past, are now increasingly being violated. Information on the location and technical data of the larger well fields for water supply has been documented well. This also applies to most single deep wells for water abstraction installed before 1990. However, during the last 20 years many wells are being drilled without proper permission and the abstraction rates are unknown. This may become a problem for future water management, because the total production of these well cannot be neglected. Rough estimates show that the large numbers of these wells may withdraw much more water than the few major well fields. Water abstraction rate or debit is functionally dependent on water level decreasing in time or withdrawals (Fig. 9.2).

Dynamic of ground water abstraction analysis in Moldova clearly indicates that water consumption in the last 20 years is drastically reduced (Fig. 9.3) [17]. The same situation is characteristic for surface water abstraction too. This is because in Moldova economy was transformed from state to private form and many water consuming industrial objects were destroyed.

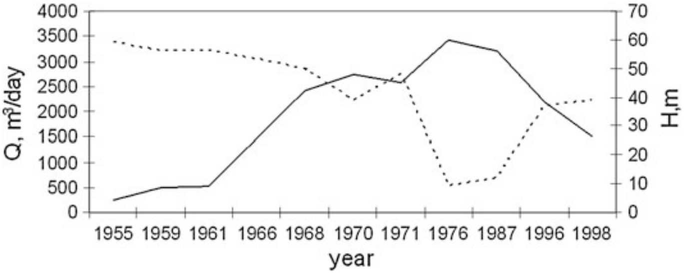

Fig. 9.2 Relationship of debit (Q) and water drawdown (H) in the deep well (*dot line* is H (m) and firm line is Q (m^3/day))

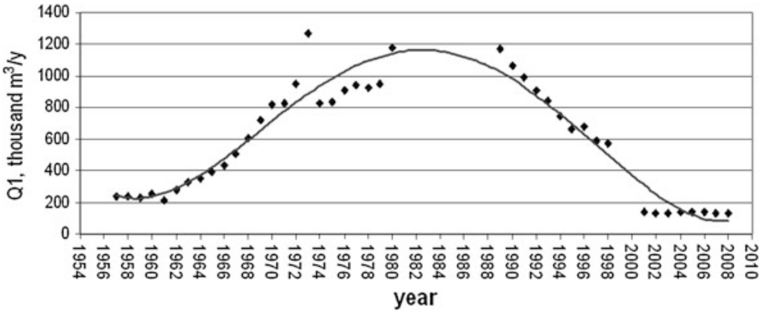

Fig. 9.3 Dynamic of ground water abstraction in Moldova

The relation between the production of larger well fields for water supply and the hydraulic heads in their surroundings was also analyzed. There only little relevant data regarding the water levels in and near the well fields, because of lack of monitoring wells. Water levels are occasionally (once a year or less frequently) collected from production wells after they have been stopped. This practice provided hard evidence of the relation between the depth of the depression cone and the production of the well field. However, it does provide only vague information about the development and size of the depression cone, which is a problem for applied hydrogeology and numerical modeling. At present depression cones are slowly recovered due to essential reduction of ground water extraction and water level rising. Direct data about this process are absent because no authentically information from production well fields.

Drinking water in the rural areas is mainly fetched from dug wells. These dug wells are tapping the Upper Neogen and Quaternary formations consisting of sedimentary rocks with high contents of clays and carbonate. Groundwater tables are reached mostly within 10 m and the wells rarely become dry. Practically every house has its own dug wells in the yard with a diameter ranging from 1 to 2 m. Apart from the numerous dug wells, deep wells can also be found recognizable by the typical steel water towers. However, most of the deep wells are out of order nowadays. Number of such well (abandoned) are only hypothetically known.

9.3 Groundwater Quality

Hydrogeochemistry of unconfined (shallow) and confined (deep) aquifers differs essentially. This is because thermodynamically and geologically these two types of aquifers have varied conditions of existence. In this context water quality of aquifers will be described apart.

Geochemical investigations and many field observations have revealed that considerable parts of the shallow aquifers (unconfined) in the rural areas of Moldova suffer from very high levels of nitrate, sulfate, chloride, selenium and total dissolved solids (TDS), etc. This contamination is caused to a large extent by the typical sources of domestic pollution such as manure heaps, household latrines on the farmyards, sewage from pigsties and poultry houses, household sewage, excessive use of fertilizers, etc. High TDS values countered the shape of villages and other man made territories [11]. Summarized data as relation spectra of detected concentration of chemical elements/parameters (C) and maximum admissible concentration (MAC) are presented in Fig. 9.4. This figure shown that shallow aquifer mostly contains high values of TDS and Hardness, and are polluted by Na, NO_3 and SO_4. Locally unconfined aquifer is polluted by Cl, NH_4, B, Br, F, Fe, Se, Mn and Sr.

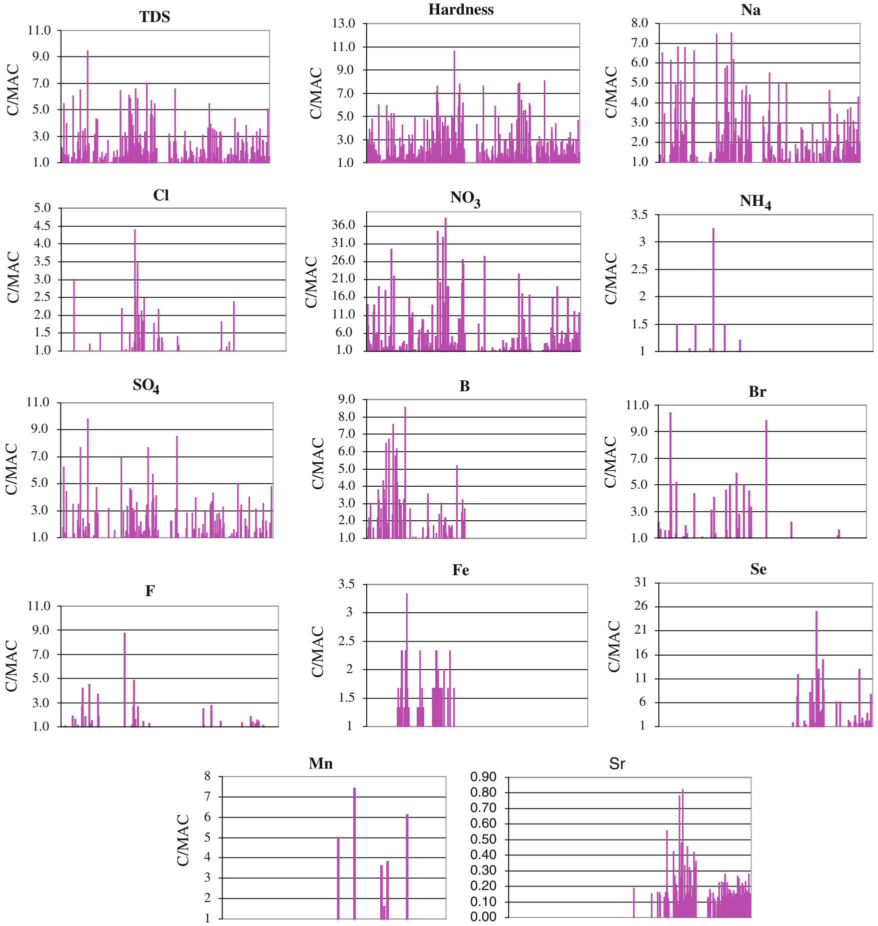

Fig. 9.4 Geochemical spectra of shallow groundwater (C is detected concentration, mg/l or mg—equivalent for hardness and MAC is maximum admissible concentration for the Republic of Moldova)

Authors [7, 9, 13–15] studied in details shallow groundwater quality of Moldova. Accordingly to these publication and new data the following is characteristic for shallow groundwater. The quality of the groundwater in the representative areas has been analyzed, taking into account the topographical situation of the wells, the groundwater flow direction in the shallow aquifers and the land use as indicative for the type of pollution.

The data have been combined for the analysis of the effects of land use. The differences in land use can be clearly distinguished from the water samples collected from dug wells and springs (Fig. 9.5). Analysis of this figure shows the following. Lowest values of nitrate were found in the *nature areas* (usually between 0.0 and 50.0 mg/l). In a few cases the water showed no nitrate at all. It was found that spring water from nature areas lacks nitrate if the area and the spring are well protected. However, the majority of springs discharge water from shallow aquifers affected by agriculture; in such cases the nitrate content showed the typical values for arable land. In *arable land* the nitrate content of dug wells and springs showed average nitrate contents of 50.0 mg/l and a 75-percentile of about 100.0 mg/l. However, the range of values is quite wide with maximum scores up to 250 mg/l. In the *built-up areas of the villages* (indicated as urban areas) nitrate contents from shallow wells show an average value of about 290.0 mg/l. The range of values is very wide with maximum values over 500.0 mg/l (see Fig. 9.5).

These high values can only be explained by local accumulation of nitrate from domestic pollution. Functionally, nitrate contents are supported by the data on electrical conductivity (EC values). EC values are high in the built-up areas of villages, because of its relation to nitrate pollution.

Unconfined groundwater level is correlative with topographical land surface [13]. For the purpose of investigating the pattern of nitrate levels in the villages in more detail, the data were regrouped with respect to the well location. With the direction of groundwater flow, the location of wells was indicated as high, medium or low, relative to their position in the sloping cross-sections. Locations up—hill have been called “high”, locations at the bottom of the valleys have been termed “low”, whereas locations half-way the slopes were classified as intermediate (“med”). The result of regrouping the data according to relative elevation of the wells proved to be very illustrative with respect to the general picture of nitrate concentration. Despite a large variation of nitrate concentrations on short distances, the average nitrate concentrations increase considerably in downward direction of the slopes (Fig. 9.6).

Analysis of data shows the following: (a) at the higher levels of slopes nitrate concentrations were found to be generally below 100.0 mg/l, with 40 % even below 50.0 mg/l; wherever a higher region of arable land borders the built-up area of a village, nitrate values adopt the values typical for those areas; (b) in the intermediate section of slopes the nitrate levels vary much more, values usually range from 50.0 to 300.0 mg/l, with maximum values up to 500.0 mg/l; (c) the highest values were found in the lower parts of villages. Nitrate contents frequently reached values up to 500.0–1000.0 mg/l and sometimes more. Values less

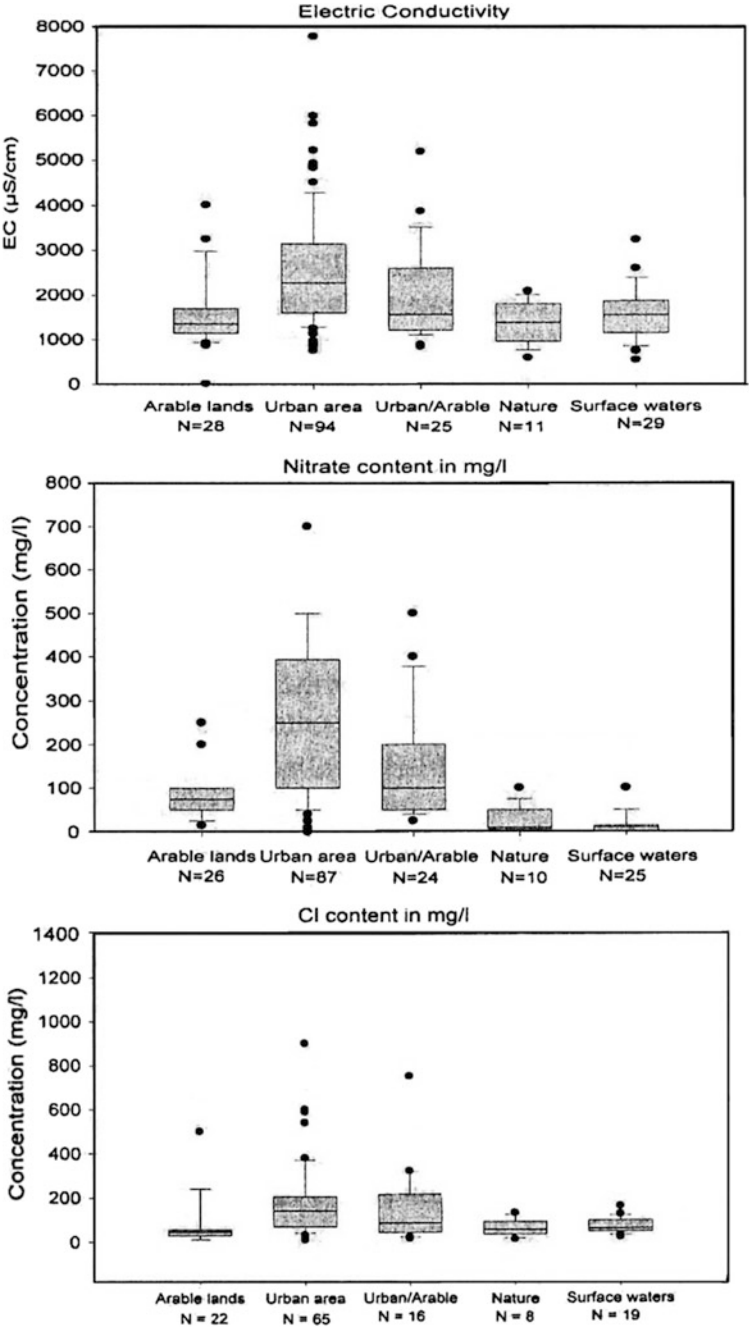

Fig. 9.5 Boxplots of EC, nitrate and chloride measured in shallow groundwater, grouped according to the land use type

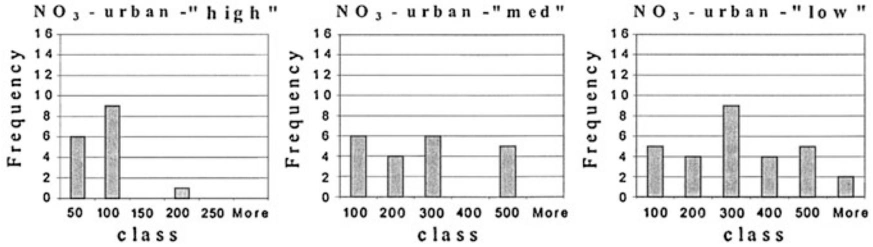

Fig. 9.6 Relationship between NO_3 in shallow wells and location in village

than 100 mg/l nitrate are very scarce and random in these lower parts. The increased nitrate levels observed in the groundwater of the middle and lower sectors of the villages can be explained from accumulation of nitrates in the direction of flow. This happens when the infiltrating water, after being polluted by sources at the ground surface is carried by the groundwater to lower places. The above situation is representative and it was found in the majority of the individual cross-sections. The local variation of the nitrate-concentration may be very strong as was observed from neighboring wells. Local differences up to 150.0 mg/l are no exception.

The relation between nitrate concentrations and the presence of *Escherichia coli* (*E.coli*) in the shallow groundwater was also studied [13]. From the results of the analysis it has to be concluded that the relation between nitrate concentrations and the presence of *E.coli* in the groundwater sampled from dug wells is not very strong. The reason for the absence of such relation is not very clear. Some very general findings are the following: (a) for nitrate concentrations below 250.0 mg/l no clear indication for the presence of *E-coli* and total-coli can be given. In many samples with nitrate concentrations up to 200.0 mg/l (and exceptionally up to 500.0 mg/l) bacteria were absent, while in some samples of only 70.0–80.0 mg/l nitrate the bacteria were found, (b) above the level of 200.0–250.0 mg/l nitrate the chances of also detecting *E-coli* or total-coli in the drinking water increase considerably, however again with some exceptions.

Nitrate and TDS are the most problematic for shallow ground water usage. Map of this parameters are presented in Fig. 9.7. At large scale shallow groundwater quality is under the influence of several mechanisms (Table 9.2) [14].

The quality of the confined aquifers differs strongly from that of shallow groundwater. The most striking difference is the much lower hardness, the higher pH and the total absence of NO_3 because of anoxic media. Hardness is usually much lower than 7 German degrees. This is typical for all deep aquifers containing fresh water. Aquifer of Lower Sarmatian age is the most used and characteristic for entire country. This aquifer is one of the Moldova’s main sources of fresh water. The geological position of the Lower Sarmatian horizon influences the distribution of major chemical elements. This occurs in the deep southwest. The Middle Sarmatian reef covers the Lower Sarmatian limestone on the large territory of

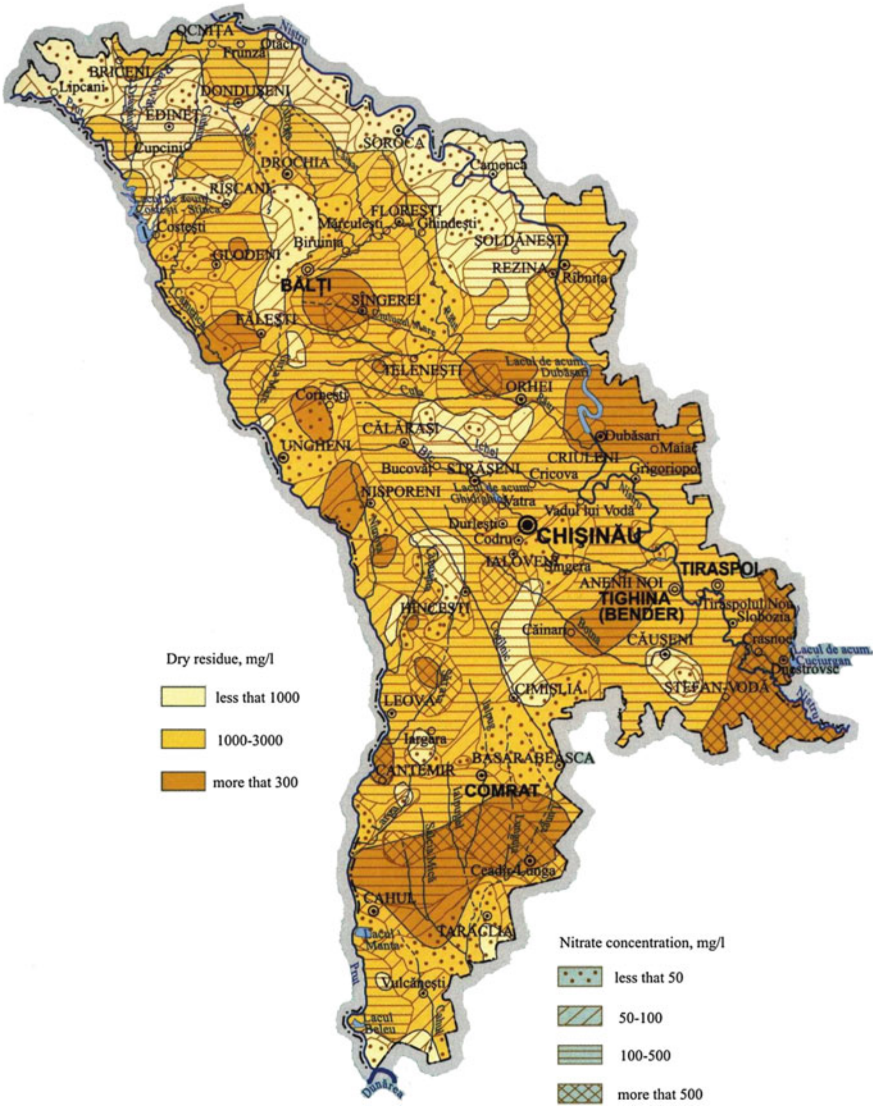

Fig. 9.7 Total dissolved solids and nitrate contents in shallow groundwater

southeast Moldova. The concentrations of TDS, Cl, Na, F, and NH_4 increase in the south–southwest direction. The reef area serves as a regional recharge zone, and this territory has elevated concentrations of Ca, Mg, NO_3, pH, hardness, and Sr.

Regionally groundwater quality of confined aquifers (including Lower Sarmatian one) is influenced by two major factors: rock geochemistry and tectonic faults. Summary of water–rock interaction is show in the Table 9.3 [14].

Table 9.2 Summary of plausible mechanisms controlling chemical composition of shallow water, Moldova

Mechanism	Resulting hydrochemistry
Infiltrating waters from precipitation, irrigation and stream flow	TDS is low, high concentration of bicarbonate, concentration of sodium in meq/l exceeds concentration of chloride
Reaction of infiltrating waters with soil and aquifer materials	Predominantly calcium, magnesium and bicarbonate; increases in sulphate
Infiltration of anthropogenic pollutants and contribution from organic materials	Concentration of nitrate is high, increasing of total hardness, chloride, sulphate

Table 9.3 Summary of plausible mechanisms controlling chemical composition of deep water, Moldova

Mechanism	Resulting Hydrochemistry
Dissolution of calcite and dolomite	Relatively small concentration of TDS and dominance of calcium, magnesium and bicarbonate in water
Dissolution of gypsum with carbonate equilibrium (dedolomitization)	Increase of TDS, mostly as increases in calcium and sulphate concentration. Bicarbonates concentrations are relatively constant
Cation exchange	Soft, high pH with $NaHCO_3$ type
Sulphate reduction	Increase in bicarbonate, decreasing sulphate contents with decrease in pH

Tectonic faults seem to have predominated role in the process of water mixing. For this purpose natural Helium (He) concentration was used to indicate a hydrodynamic connection between deep aquifers in Moldova. This method was proposed by Moraru [10] and widely used in many post-Soviet Union regions. Statistically helium content as 240×10^{-5} ml/l is considered the central value between background (<) and anomalous (>) detected concentrations. Chemically the helium-bearing waters of all productive aquifers of Moldavia have pronounced features, which distinguish them very strongly from the waters in which the helium content does not exceed the background level (Table 9.4). They have a sharply higher pH and increased concentrations of Na, K, CO_3, HCO_3, Cl, F, and dissolved aromatic organic matter, whereas the calcium and magnesium content fall to several milligrams per litter, and the redox potential is negative. Also H_2S gas is characteristic. We shall call these waters anomalous and the areas of their occurrence, hydrochemical anomalies. They include HCO_3–Cl–Na, Cl–HCO_3–Na, HCO_3–Na types. All have high helium concentrations, as can be seen by analyzing the data in the Table 9.4, which gives the mean concentrations of the chemical macro components, TDS, pH and helium concentration.

Waters with background or lower helium concentrations generally have low TDS, high carbonate hardness, neutral pH, positive redox potential and low fluorine concentrations. They are classified as HCO_3–SO_4–Mg–Ca–Na, and HCO_3–SO_4–Mg–Ca waters. They are found in the same productive aquifers, but in

Table 9.4 Mean concentrations of macro elements and helium in groundwater of Moldova

Age	Hydrochemical type of groundwater	Number of samples	Average concentrations of macro components in groundwater, mg/l								pH	Helium content, n x 10^{-5} ml/l
			Na^+	K^+	Ca^+	Mg^+	HCO_3^-	SO_4^-	Cl^-	TDS		
Late Cretace ous	HCO_3–SO_4–Na–Ca–Mg	24	157.0	9.9	83.8	44.6	548.54	164.5	40.6	775.0	7.3	116.8
	SO_4–HCO_3–Na–Ca–Mg	1	195.0	10.9	160.0	126.0	488.0	869.8	106.4	1712.0	7.8	9.9
	HCO_3–SO_4–Na	56	465.0	6.3	4.8	2.6	771.5	198.4	55.6	1118.0	8.3	975.6
	HCO_3–Cl–Na	6	546.0	5.8	6.9	5.9	765.6	168.0	417.0	1532.0	8.3	10000.0
Upper Sarmatian	HCO_3–Ca–Mg–Na	25	49.8	3.3	97.8	45.4	527.8	63.6	17.2	545.0	7.2	15.5
	HCO_3–SO_4–Ca–Mg	103	146.0	6.5	80.3	62.9	590.4	209.7	45.6	851.0	7.4	87.9
	SO_4–HCO_3–Na–Ca–Mg	18	286.0	8.3	153.8	135.9	627.0	739.0	101.5	1738.0	7.5	197.3
	HCO_3–SO_4–Na	90	410.1	8.9	6.4	4.2	733.8	185.7	53.7	1046.0	8.2	915.6
	HCO_3–Cl–Na	45	541.9	8.0	4.9	6.6	990.9	95.4	223.7	1376.0	8.3	1876.3
	HCO_3–Cl–Na–Ca	12	278.7	6.2	47.1	34.7	530.6	77.2	286.0	965.0	7.9	1619.4
	HCO_3–Na	20	481.1	8.3	3.5	3.1	1124.6	52.5	47.5	1168.0	8.1	961.8
Middle Sarmatian	HCO_3–SO_4–Ca–Mg	18	146.1	3.7	83.6	74.5	466.5	176.7	75.5	793.0	7.0	75.4
	SO_4–HCO_3–Na–Ca–Mg	5	316.2	2.9	76.2	78.5	476.8	349.2	113.0	1174.0	8.1	93.6
	HCO_3–Cl–Na	11	231.5	4.6	6.8	7.6	450.5	126.2	48.5	700.0	8.4	287.7
	Cl–HCO_3–Na	37	360.2	4.2	10.2	13.9	659.1	63.6	164.4	948.0	8.2	1739.8
	HCO_3–Na	5	526.6	2.4	7.7	1.8	564.8	3.7	429.8	1253.0	8.6	508.1
		4	447.5	6.1	4.6	5.7	1139.0	30.0	31.9	1034.0	8.0	370.8
Lower Sarmatian	HCO_3–SO_4–Cl–Ca–Mg	7	99.8	2.1	66.0	21.0	286.0	145.0	74.0	544.0	7.6	69.5
	SO_4–HCO_3–Cl–Ca–Mg	7	497.5	1.8	81.6	28.1	337.9	411.8	132.1	1271.0	7.6	69.5
	HCO_3–SO_4–Na	7	261.0	1.2	6.3	3.4	542.0	94.7	48.7	691.0	8.2	226.2
	HCO_3–Cl–Na	10	450.6	4.7	6.1	3.1	830.1	35.0	197.1	1111.0	8.4	1589.4
	Cl–HCO_3–Na	3	693.3	4.1	5.9	12.9	658.8	2.0	723.2	1770.0	8.3	728.6
	HCO_3–Na	5	353.4	0.9	3.6	2.1	770.9	38.9	41.0	824.0	8.1	913.3

areas of rigid stable blocks, and are typical leaching waters of carbonate and sulfate-bearing rocks.

The origin of the helium-bearing aquifers is complex. Because active tectonic faults drain the water-bearing rocks in the entire profile of the sedimentary cover, we may assume that the water quality in the cross-section is the product of deep waters mixing with leaching waters. This geological-structural and hydrodynamic situation produces various hard-to-interpret permanent geochemical processes such as the interaction of mixing waters in the water–rock system and their alteration at geochemical barriers.

Elementary chemical composition of confined aquifers (including Lower Sarmatian) is also composite. Statistical spectra as relation of detected concentration of chemical C and MAC are shown in Fig. 9.8. Analysis of these relations indicate that confined groundwater predominately suffer from high values of TDS, hardness, Na, SO_4 and F. In same places are detected very high concentrations of other chemical compounds, especially of Se and Sr.

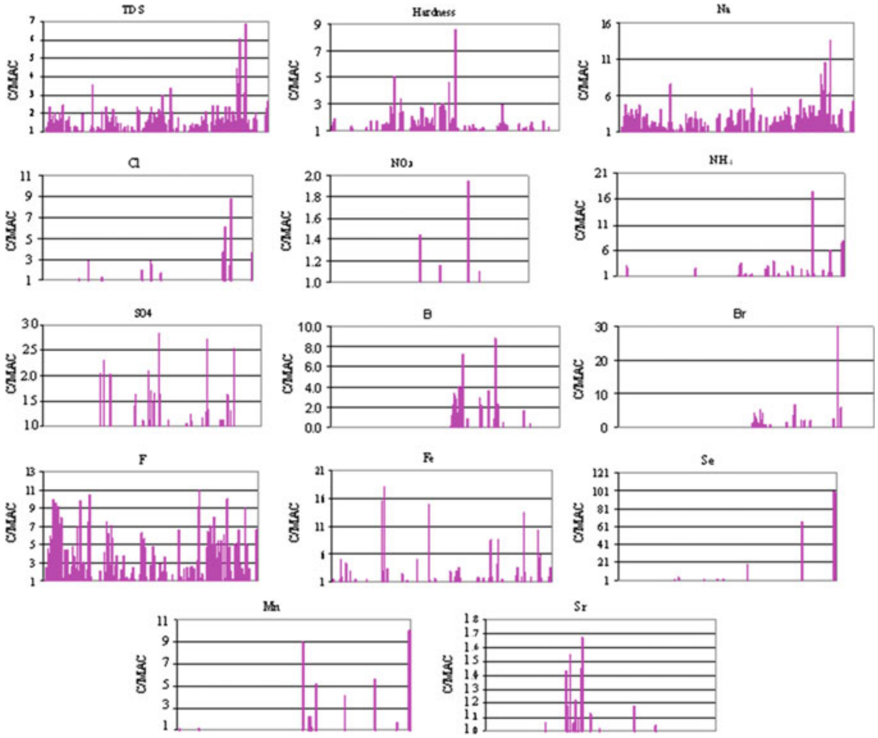

Fig. 9.8 Geochemical spectra of confined groundwater (Lower Sarmatian) (C is detected concentration, mg/l or mg –equivalent for hardness and MAC is maximum admissible concentration for the Republic of Moldova)

Map showing regional distribution of F, Se and Sr is presented in the Fig. 9.9. Fluoride is the most widespread element in Lower Sarmatian aquifer. Its high concentration (more than 1.2 mg/l) does not permit using of water without special treatment. Origin of fluoride in Moldova ground water was studied be many researchers [8, 18, 19]. Two provenance ways of fluoride are common for confined.

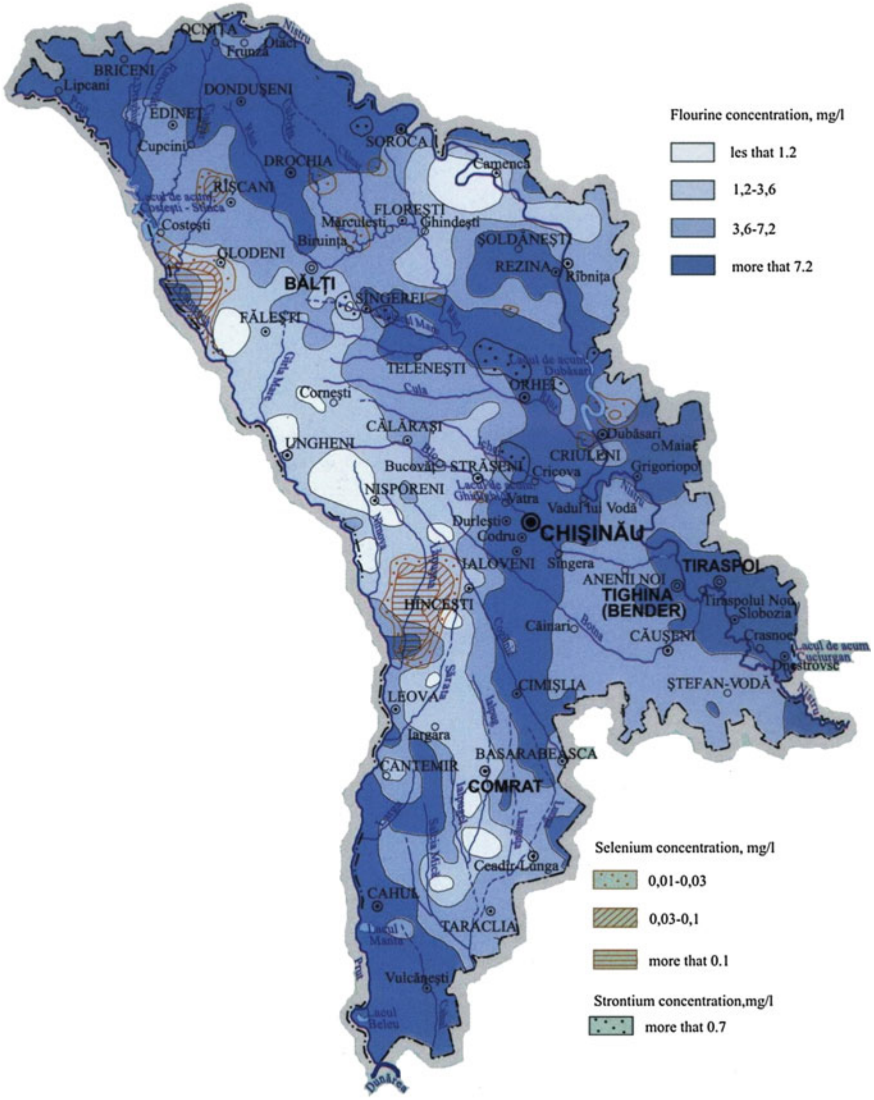

Fig. 9.9 Regional distribution of fluoride, selenium and strontium in the Lower Sarmatian aquifer groundwater

Table 9.5 Selenium concentration in deep Moldova's aquifers (mg/l)

Aquifer age	Number of well	Minimal content	Maximal content	Mean	Standard deviation
$N_1S_3 + N_1p$	42	0.0	0.0067	0.001	0.001
N_1S_2	76	0.0	0.0166	0.001	0.003
N_1S_1	311	0.0	0.6600	0.010	0.088
K_2	126	0.0	0.0415	0.001	0.003

Remark: zero values means that concentration is lover than analytical detection limit

One of them is connected with rock composition related to CaF_2 (fluorite). Dissolution of fluorite led to elevated concentration of F. For this case Ca concentration in water is a regulator of thermodynamic equilibrium between CaF_2 and F. Other provenance of F is its migration via tectonic faults from deep horizons [15]. In favor of this idea several features are important and namely: (a) concentration of Ca is decreasing with depth in a cross-section, (b) concentration of F in deeper saline aquifer is on several order more compared with freshwater containing horizons, (c) F is correlated with He which is a recognized tracer of tectonic faults.

Authors [4, 12, 16–18] studied regional distribution of selenium in the deep Neogen and Cretaceous—Silurian aquifers. It was make a point about high selenium concentrations in these aquifers. Also it is proposed that origin of selenium is connected with water bearing rocks. Other authors generalized selenium information for all ex-Soviet Union [19, 20]. It was revealed that only two hydrogeological provinces can be characterized with high selenium contents—Donetsk (coal basin, Ukraine) and Moldova.

For deep aquifers accordingly to recent investigation selenium content is shown in Table 9.5. Geostatistical analysis of selenium data indicates that about 90 % of concentrations are placed in the interval 0.0–0.01 mg/l. Only 10 % of wells can be characterized with high selenium concentration. Compared with shallow water analog similarly is characteristic for geochemistry of selenium in deep aquifers. Regional distribution is irregular and mostly separated anomalies are common. Selenium content functionally does not depend of water chemical composition. Only one positive correlation is found with sulfate. Authors [8, 19] remark that in deep aquifers, selenium distribution is controlled by redox potential (Eh).

9.4 Conclusions

At present in the Republic of Moldova groundwater abstraction is essentially reduced compared with the period of 1990 time. Approximately 200 thousands m^3/year of ground water is abstracted nowadays. This is about six times less than in 1990 and practically corresponds to 1960 period. In the same time groundwater recovery in confined aquifers is slow. Groundwater level variation for unconfined aquifers is not directly and well functionally dependent from atmospheric precipitation amount. Statistical trend of this dependence is finding only in the interval of ground water level between 0.0 and 3.0 m from land surface. Unconfined aquifers do not have a statistical dependence of water level from evolution of atmospheric precipitations.

Water quality in unconfined aquifers is controlled predominately by land use practices and position of water bearing strata in the geological cross-section. Fresh water well contains high values of TDS and temporal hardness, and in many cases they are polluted by Na, NO_3 and SO_4, and locally by Cl, NH_4, B, Br, F, Fe, Se, Mn and Sr. The most problematic is nitrogen pollution which is represented by nitrate. Rural areas used intensively shallow groundwater (about 95 % from total water supply) and TDS and NO_3 as a rule is detected inside of villages and others inhabitant's points.

Deep groundwater, stored in confined aquifers, is forming quality under the influence of two main factors: rock dissolution and mixing processes via tectonic faults. Rock-water processes lead to dissolution of calcite and dolomite, dissolution of gypsum with carbonate equilibrium (dedolomitization), cation exchange and sulphate reduction. Leakage from underlying aquifers results in big areas of mixing water types. Main constrains for fresh water supply is connected with high values of TDS, fluoride and locally of selenium and strontium. In the south and south–west part H_2S (hydrogen sulphide) is detected in many wells with concentration more than 100 ppm. Water has a specific odor and can not be used for fresh water supply.

Acknowledgments This study was carried out by the financial support of the State Program of the Academy of Sciences of Moldova "Scientific investigations and water quality management 2009–2012" (acad. Duca Gh). Author thanks collaborators of the Hydrogeology Lab. for their useful contributions and comments.

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Part IV
Water Treatment

Chapter 10
Textile Waste Water Treatment of Dyes by Combining the Coagulation and Catalytic Oxidation with Hydrogen Peroxide Methods

M. Gonta, Gh. Duca, V. Matveevici, V. Iambartv and L. Mocanu

Abstract The textile industry is one of the most polluting industries in terms of volumes and wastewater discharges in the environment. Textile wastewater contains high concentrations of colored substances and high color stability, a variation of pH and chemical oxygen demand (CCO). The average value of CCO and biochemical oxygen demand (CBO_5) is within the limits of 250–11700 mg O/l and 100–3500 mg O_2/l or [1], and the ratio CBO_5/CCO which is in the range 0.25–0.3 and shows the stability against biological treatment methods.

Keywords Dyes · Water treatment · Catalytic method · Coagulation method

Wastewater discharges from textile factories who were not effectively treated and have a small biological index (CBO/CCO < 0.25–0.3) [2] is inadmissible in water basins; due to the fact that they are quite toxic to living things of the water basins.

In practice traditional nondestructive methods are applied as ultrafiltration, reverse osmosis, ion exchange, adsorption of different adsorbent and coagulation with aluminum or iron coagulants. These physicochemical methods are destructive and lead to the transfer of organic dyes from water into solid matrix regeneration and require inevitable regeneration and post-treatment of solid and liquid remains, which are formed in the purge [3].

However coagulants application continues to be accepted as the reason that textile wastewater also contain various fibers and lint residue, which confers water a slurry aspect and can be removed more efficiently by coagulation method by applying coagulants [4]. Applying only the coagulation method for textile

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Water Science and Technology Library 69, DOI: 10.1007/978-3-319-02708-1_10,

wastewater leads to high coagulant consumption on one hand and on the other hand, not all textile dyes can be removed by this method [3].

Wastewater pretreatment methods are described and applied with the use of aluminum coagulant, followed by subsequent adsorption of dyes by remaining active coal. But the issues of active charcoal regeneration, which continue to remain unsettled technically and also due to high cost, make these methods replaceable by other more advanced and technological methods, which enable and lead to decrease not only of the dye concentration, but also reduce of waste and precipitates formed.

Recently, the application of advanced destructive methods leads to oxidation and mineralization of textile dyes. However these methods are applied effectively to solutions and dilute wastewater. Textile wastewater represent concentrated solutions (dye concentration reaches 200 mg/l or even more) and their treatment using only destructive methods is inefficient and leads only to a partial oxidation of the dye molecules, which can be further removed by adsorption with active charcoal. More so, that some of the compounds remaining after oxidation dye molecules are not effectively adsorbed and removed by adsorption with active charcoal [5].

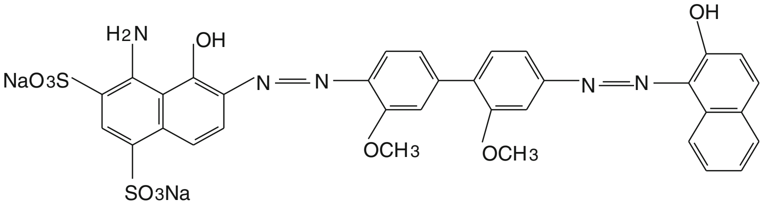
To this end, the present work was studied reduce the concentration of textile dyes and their mixture model solutions by combining the coagulation or electrocoagulation method with catalytic oxidation method with hydrogen peroxide catalyzed by FeII or ultraviolet (UV).

10.1 Experimental Part

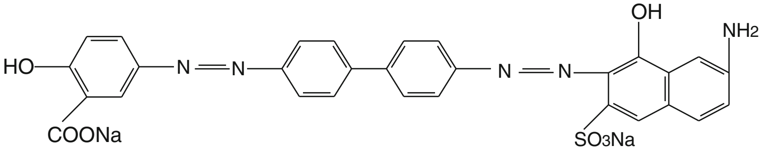
All research was performed in model systems prepared under direct dyes, active and acid dissolved in distilled water, initial concentration within limits which vary from 50 to 200 mg/l.

Direct dyes:

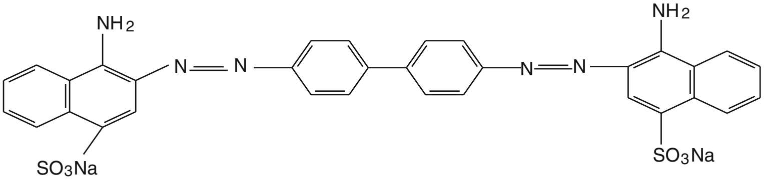
Direct blueK (AD): λ_{max} = 610 nm; M =683 g/mol



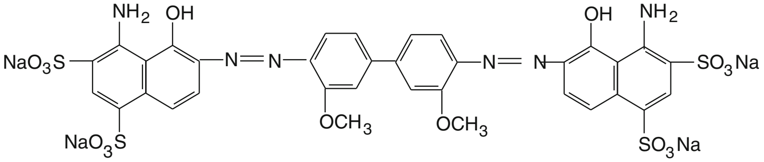
Direct brown (CD) (λ_{max}= 490 nm; M =595 g/mol)



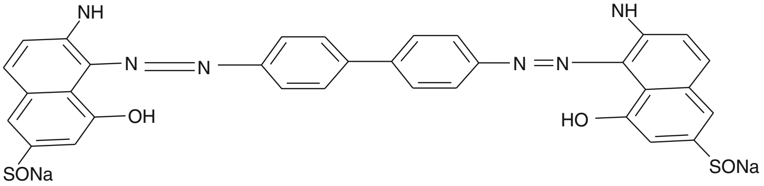
Direct bright red (RAD): λ_{max} = 540 nm; M =696 g/mol



Direct bright blue (AAD) : λ_{max} = 626 nm; M = 968 g/mol

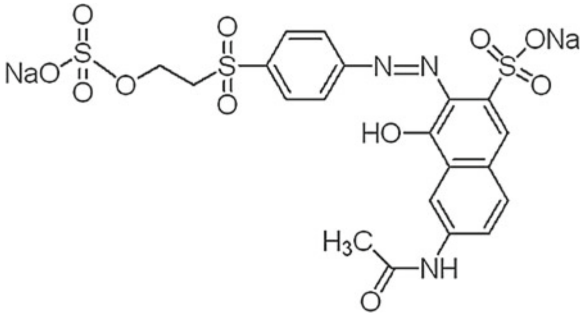


Direct violet (VD): λ = 540 nm. M = 696 g/mol

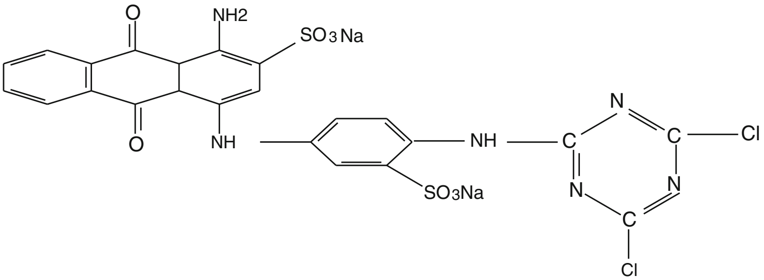


Group of active dyes, among them are listed the following:

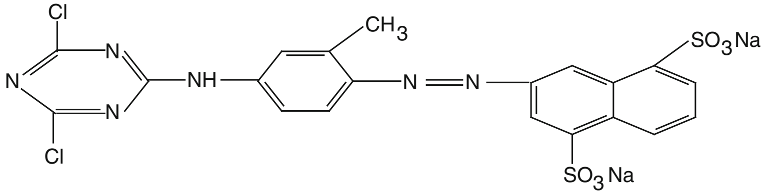
Active orange 16 (PA) : λ_{max} = 490 nm, M = 605 g/mol



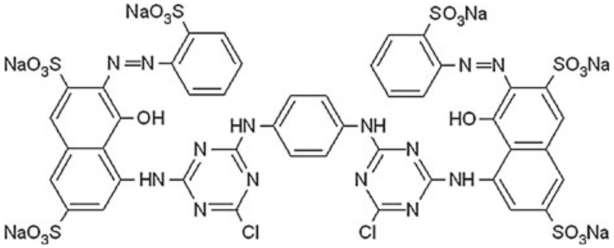
Active blue (AA): λ_{max} = 600 nm, M= 681 g/mol



Active golden yellow (GAA): λ_{max} = 370 nm, M= 613 g/mol

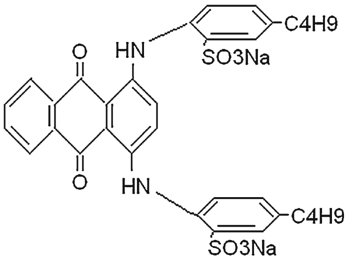


Active red (RA): λ_{max} = 510 nm, M= 1381 g/mol

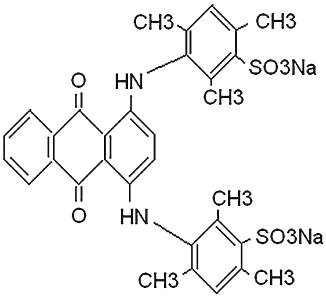


Group of acid anthra-chinonic dyes:

Acid green (VA): M = 706



Acid blue (A A) λ_{max} = 626 nm, M = 678



Concentration of textile dyes and their mixtures was determined from calibration curves modeled after the optical density of the solutions at that wavelength using spectrophotometer СФ-46.

Chemical treatment with aluminum coagulant chemical oxidation of textile dye solutions model was performed according to the method described in [5].

Based on the results obtained we calculated the effect of fading (E.dec. %) And degree of oxidation and mineralization (G.min. %) Of textile dyes and their mixtures at various conditions of catalytic oxidation with hydrogen peroxide in the presence of ions iron (II) and UV rays relations:

$$\text{E.dec.}\% = \ C_{0(\text{col})} - C_{\text{rem.(col)}} / C_{0(\text{col})} * 100\,\%$$

$$\text{Grad.min.}(\%) = \ CCO_0 - CCO_{\text{rem.}} / CCO_0 \ * 100\,\%$$

10.2 Results and Discussion

As a result of experimental research has established that. AAD and RAD colors are removed most efficiently at pH 5.3–5.5, CD at pH 5.5–6.0, and colors AD and VD at pH 6.0–6.2. The optimum pH depends on the nature of dyes and is subject to the load value colloidal aluminum hydroxide. Adding aluminum salts (aluminum sulphate) provides a very effective coagulation and remove all five colors indicate the model solutions with concentrations between 50–200 mg/l up to sanitary standards (1–3 MgO/l).

In their removal effectiveness depends on their initial concentration and chemical nature (Fig. 10.1). With increasing initial concentration of the specific consumption of aluminum direct dyes, dyes needed to eliminate the initial concentration remaining until the allowable discharge of treated water basins, decreases. This occurs due to regularity that with increasing initial concentration of dyes direct association intensifies processes of dye molecules that occur as a result of interaction of hydrogen bonds between polar groups –OH and $-NH_2$ molecules contained in dyes [1]. Effectiveness of the coagulation and removal of

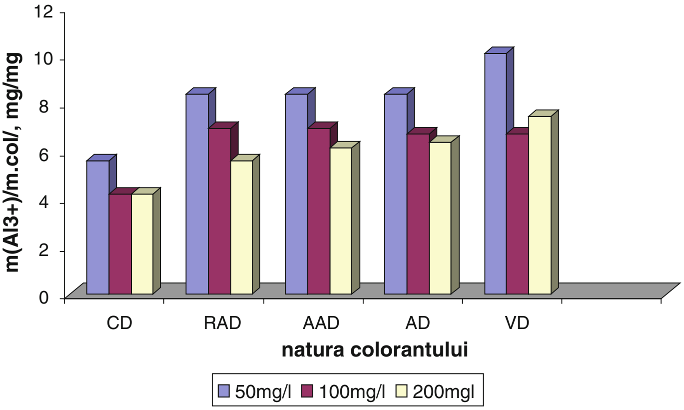


Fig. 10.1 Dependence of the specific consumption of aluminum coagulant necessary to remove direct dyes, their chemical nature and initial concentration

direct dyes depends on particle size associated (with as many polar groups containing dye molecule with both particle sizes are larger) and the negative charge of these particles (negative charge depends on the number of functional groups which can dissociate in aqueous solution) [2–4] (Fig. 10.1).

The associated particle size influences the process of oxidation dyes and destruction of hydrogen bonds in the electrochemical dissolution of aluminum anode electrochemical treatment of model solutions. As a result, the associated particle size decreases and the amount of aluminum coagulant required for treatment of model solutions (initial concentration of 200 mg/l) increases, leading to an increase in the specific consumption of aluminum and [6].

Amount of coagulant to neutralize and coagulation associated dye particles depends on the nature of the dye. Dye CD, which has the largest number of polar groups (3) and Nimai one anionic group clots most effective at low amounts of coagulant for forms associated with larger particles and the negative charge their lowest. With increasing electric charge (RAD has two anionic groups, VD-2, and AAD-4 groups) the amount of coagulant that is spent for their neutralization and coagulation that increases up to 4.32 and 9.72 mg/l (Table 10.1).

It was established that much more effective can be reduced by the amount of aluminum coagulant method combining coagulation and catalytic oxidation with H_2O_2 molecules of dye remaining in solution after coagulation, up to sanitary standards, which can be catalyzed by UV or by combining UV and Fe 2+ ions.

As a result of catalytic oxidation of dye molecules occurs converting them into CO_2 and H_2O and the products of oxidation, low molecular weight as aldehydes, ketones, acids. Degree of oxidation and degradation indicates how effective were oxidized and mineralized organic dye molecules.

We studied the dependence of the degree of oxidation and mineralization of direct dyes AAD, RAD, AD and CD depending on the concentration of hydrogen peroxide, which can be catalyzed decomposition to UV irradiation (Table 10.1) from which,

In the presence of H_2O_2 oxidant increases the degree of mineralization and the higher the peroxide concentration to $2–3 \times 10^{-3}$ mol/l (for coloring AD and CD) and peroxide concentration hydrogen of 5×10^{-3} mol/l (AAD colors and RAD). With further increase of hydrogen peroxide concentration degree of mineralization of dyes studied decreases (for colors CD and AD) and oxidation becomes less effective, and changes insignificantly (for colors AAD and RAD). This decrease may be due to the fact that the model solution is an excess of hydrogen peroxide and as a result some of the hydroxyl radicals are consumed according to the following equation [7].

$$H_2O_2 + HO^{\cdot} \rightarrow H_2O + HO_2$$

Therefore, increasing the concentration of hydrogen peroxide still does not lead to essential increase of the degree of oxidation and mineralization (for colors AAD and RAD) or even lead to the reduction of (for colors CD and AD) (Fig. 10.2).

Table 10.1 Dependence of the degree of oxidation and mineralization of direct dyes according to the concentration of hydrogen peroxide and UV irradiation time, pH 2.5, Co (col) = 50 mg/l

T, min	AAD Dye		RAD Dye		CD Dye		AD Dye	
	$CCO_{rem,}$ mgO/l	Gr.min. %	CCO_{rem}, mgO/l	Gr.min. %	CCO_{rem}, mgO/l	Gr.min. %	CCO_{rem}, mgO/l	Gr.min. %
$[H_2O_2] = 1 \times 10^{-3}$ mol/l								
20	15.3	62.68	40.62	28.73	27.0	22.86	26.70	40.7
40	13.3	67.99	40.00	29.82	26.6	24.00	24.80	44.9
60	9.69	71.32	34.37	39.69	25.0	28.60	23.76	47.2
$[H_2O_2] = 2 \times 10^{-3}$ mol/l								
20	4.70	88.52	15.34	73.09	16.44	53.14	12.50	72.2
40	4.37	89.34	13.87	75.67	15.12	56.80	11.75	73.9
60	3.87	90.56	7.87	86.19	12.50	64.28	8.91	80.2
$[H_2O_2] = 3 \times 10^{-3}$ mol/l								
20	5.30	87.04	18.12	68.20	21.88	37.5	7.63	83,0
40	4.69	88.52	15.62	72.60	21.25	39.3	6.47	85.6
60	4.06	90.10	9.32	83.65	18.44	47.31	4.89	89.1
$[H_2O_2] = 5 \times 10^{-3}$ mol/l								
20	4.69	88.37	16.25	71.5	25.00	28.6	12.50	72.2
40	3.75	90.65	20.63	63.80	22.50	35.7	11.25	75.0
60	2.81	93.15	8.12	85.75	19.40	47.43	9.95	77.8
$[H_2O_2] = 7 \times 10^{-3}$ mol/l								
20	3.75	90.25	33.12	41.89	28.00	20.0	16.87	62.5
40	3.70	90.97	45.00	21.00	26.6	24.0	13.12	70.8
60	2.80	93.10	30.94	45.72	25.6	28	11.45	74.5

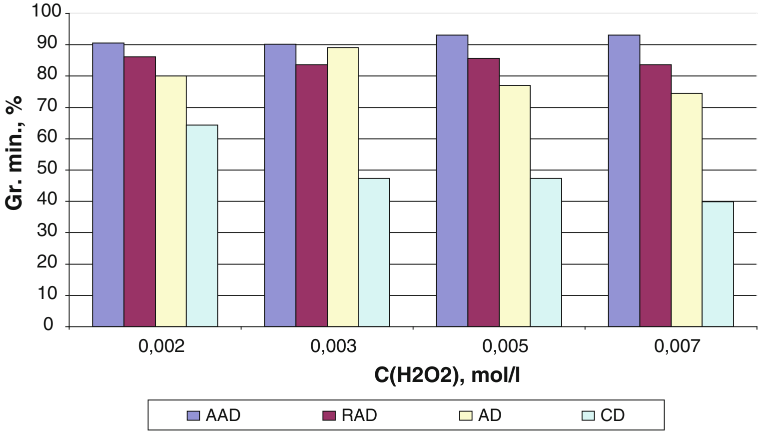


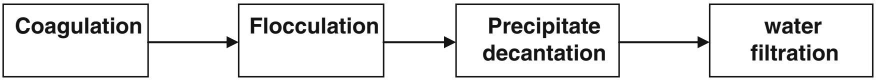
Fig. 10.2 Dependence of the degree of oxidation and mineralization of direct dyes AAD, RAD, AD and CD according to the concentration of hydrogen peroxide at UV irradiation. pH = 2.5, C0 (col) = 50 mg/l, Toxid. = 60 min

UV irradiation oxidation depends on the chemical composition and stability of dye molecules. The greatest degree of oxidation and mineralization plays AAD dye, then the dye RAD and AD and the lowest it has dye mineralization CD. (Fig. 10.2). But to reduce the dye concentration CD of concentrated solutions may recommend a reduction of the initial concentration of dye in the clotting process I step up to a residual concentration of 20–30 mg/l, then the catalytic oxidation can already reduce to sanitary standards.

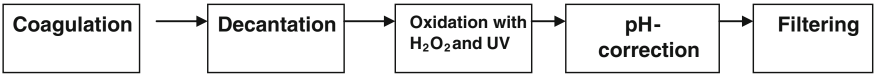
Therefore, to decrease the concentration of aluminum coagulant treatment was studied combined approach, which consists of treating the aluminum coagulant solutions I stage treatment model, followed by catalytic oxidation with hydrogen peroxide catalyzed by UV light at stage II treatment up to reduce direct dye concentration sanitary rules. With aluminum coagulant effectively remove direct dyes concentrated solutions (C = 200 mg/l) until all sanitary rules, but with increasing initial concentration increases the amount of aluminum coagulants necessary to reduce direct dye concentration up to sanitary standards. If direct coagulants concentration decreases from the initial 200 mg/l until the remaining 50 mg/l, which then can be reduced by catalytic oxidation method with hydrogen peroxide, then aluminum coagulant consumption is reduced by 20.0 to 2,5 times for all direct dyes studied.

Therefore, to reduce and remove direct dyes from model solutions with dye concentration in the range of 150–200 mg/l can recommend the following treatment methods:

1. For direct dyes (CD and RAD), which have large numbers of association of molecules and their concentrations decrease consume small amounts of aluminum coagulant treatment is recommended following scheme:



2. For direct dyes (AD, VD and AAD), with a smaller number of molecules of association and consumes a larger amount of aluminum coagulant to reduce their concentration, treatment is recommended following scheme: To reduce direct dye concentration treatment can recommend the following scheme:



Was studied further decrease the concentration of active dyes as active blue (AA), active red (IR), active orange (PA) and golden yellow active (GAA) and fatty acid as blue (Aacid) and acid green (Vacid) by combining the methods of coagulation and catalytic oxidation with hydrogen peroxide at UV irradiation. As a result of the research was obtained, that the treatment model solutions containing acid dyes or aluminum coagulant consumption, much depends on the initial concentration of dyes and their chemical nature (Fig. 10.3).

It was found that the effectiveness of reducing the concentration of active dyes and acids depends on particle size associated dyes, namely: the more the degree of association of molecules is lower specific consumption of aluminum coagulant increases and at increase awareness of association of molecules—specifically aluminum consumption decreases (Table 10.2). However some active colors (GAA, PA) and acid dyes (VA and AA) can be removed from solution focused until the rules permitted only with aluminum coagulant or their catalytic oxidation with hydrogen peroxide at UV irradiation (Fig. 10.4).

It was established that advanced oxidation method with photocatalytic hydrogen peroxide can oxidize and mineralization active dyes and acids to sanitary solutions only model remaining dye concentration up to 50 mg/l And by combining chemical the coagulation method and photocatalytic oxidation with hydrogen peroxide can purge solutions with initial concentration of active dyes and acid 200 mg/l, decreasing aluminum coagulant consumption of 2.5–3 times.

Based on experimental data obtained was found that all studied textile dyes are removed from the solution model combined method (chemical coagulation and catalytic oxidation with hydrogen peroxide (Table 10.2).

The lowest consumption of aluminum coagulant is for direct dyes, which have the highest degree of association of molecules. Among the most effective direct dyes clots and remove dye CD, then the RAD and AAD dye colors. To dye CD can only be applied chemical method of treatment with aluminum coagulant and colors for RAD and AAD may recommend treatment combined approach, which leads to lower costs 2.5–5.0 times respectively coagulant. Then comes the acid anthra-

Table 10.2 Dependence on specific expenses aluminum coagulant to reduce textile dyes concentration, depending on the nature and methods of treating dye solution model to Co = 200 mg/l

Nature of the dye	Electrochemical method			Combined method		
	$[Al^{3+}]$, mg/l	Crem. mg/l	mAl^{3+}/m col.	$[Al^{3+}]$, mg/l	Crem. mg/l	mAl^{3+}/m col.
Active dyes						
AA	14.00	1.90	0.071	6.48	50.00	0.043
	14.00	1.90	0.071	5.94	75.00	0.047
RA	18.64	2.00	0.094	8.64	50.00	0.058
	18.64	2.00	0.094	6.48	75.00	0.052
GAA	189.00	2.00	0.954	43.00	50.00	0.287
	189.00	2.00	0.954	36.00	75.00	0.288
PA	290.00	2.00	1.460	135.00	50.00	0.900
	290.00	2.00	1.460	109.00	75.00	0.960
Direct dyes						
RAD	5.40	1.50	0.027	0.54	50	0.004
	5.40	1.50	0.027	0.54	75	0.004
AAD	10.80	1.50	0.054	3.24	50	0.022
	10.80	1.50	0.054	1.62	75	0.013
CD	1.80	1.50	0.009	–	–	–
	1.80	1.50	0.009	–	–	–
Acid anthrax-chinonic dyes						
VA	7.56	1.50	0.038	3.24	50	0.022
	7.56	1.50	0.038	2.70	75	0.022
AA	7.56	1.50	0.038	2.16	50	0.014
	7.56	1.50	0.038	1.08	75	0.009

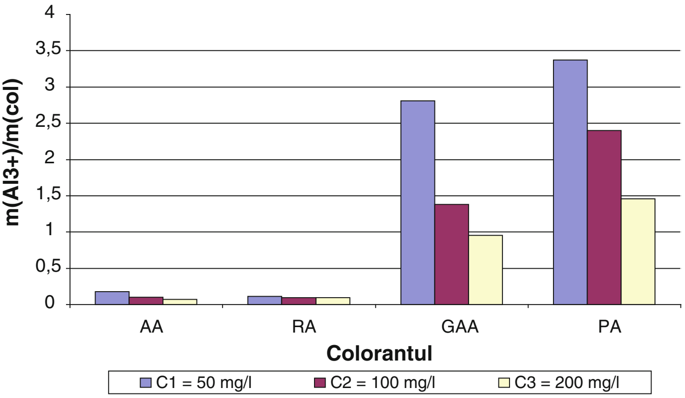


Fig. 10.3 Aluminum coagulant consumption dependency to reduce active dye concentration according to their initial concentration

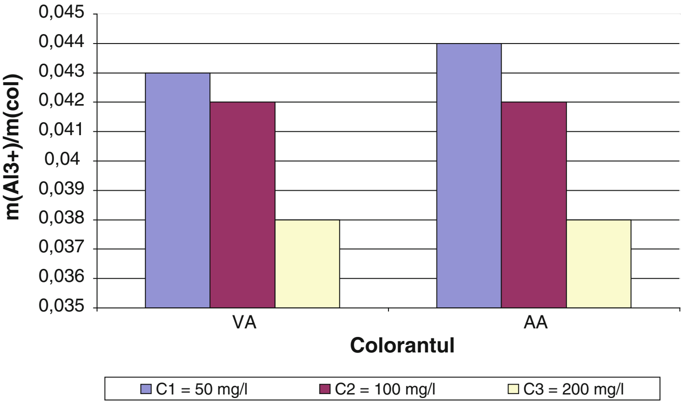


Fig. 10.4 Aluminum coagulant consumption dependency according to initial concentration and nature of acid dyes

chinonic dyes, which combined treat specific coagulant consumption is reduced by 1.7–2.7 times AA and RA active colors that have a lesser degree of association of molecules, for which specific consumption of aluminum decreases from 1.65 to 1.62 times respectively. Removing active dyes GAA and PA, which practically do not associate in aqueous solutions takes place with the largest aluminum coagulant expenses and combined treat them equally, we obtain a reduction of aluminum coagulant and reduce their concentration achieved with the coagulant costs of 3.3–1.62 times less.

10.3 Conclusions

1. Direct, active and acids dyes are removed from model solutions using aluminum coagulant, but the effectiveness of removal using aluminum consumption depends on the chemical nature and initial concentration of dyes.
2. It was established that direct, acid active dyes are oxidizes and mineralized in optimal conditions with catalytic decomposition of hydrogen peroxide in the presence of iron ions Co(II) and UV irradiation of the model solutions with initial concentration up to 50 mg/l and degree of mineralization for GAA colors and mixture of dyes PA and RA intensifies as can be purified and mixed solutions with concentration of 75 mg/l.
3. By combining the coagulation and catalytic oxidation method with hydrogen peroxide treatment model solutions containing direct, active and acid dyes specific consumption of aluminum is reduced from 1.6 to 3.5 times.

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Chapter 11
Treatment of Sulfurous Waters Using Activated Carbons

Tudor Lupascu, Raisa Nastas and Vasile Rusu

Abstract Efficient catalysts in the oxidation of hydrogen sulfide oxygen species are activated carbons. Activated carbon research highlights the important role of surface functional groups as a source for free radicals and initiate steps in catalytic activation of oxygen on the surface of activated carbon. Studies show that with increasing oxygen content on the surface of carbon, the concentration of functional groups increases the adsorption capacity of sulfur (II) species and their oxidation to higher degrees of oxidation. Is noted the important role of acid–base properties of activated carbons and their surface pH in suspension, influencing dissociation and oxidation of hydrogen sulfide to different species of sulfur. Oxidized active carbon is rich in acidic functional groups on the surface, has a higher catalytic activity and is more efficient compared to commercial activated carbon BAU-A, which is poor in functional groups and has an alkaline surface pH. Oxidized active carbon produced from peach stones and impregnated with ions Fe^{3+} and Cu^{2+} shows increased catalytic activity in the oxidation of sulfur species in reduced form, compared to adsorbents before impregnation with metals. Oxidation products generated in the presence of catalysts obtained by impregnation with metals are thiosulfates, sulfites and sulfates, without the formation of colloidal sulfur. The state or form of immobilized metals on the surface of activated carbon influences significantly the selectivity of formation of sulfur species. Impregnated metals present on the surface of activated carbon in the form of ions, favor the formation of sulfur in high oxidation degree of S^{4+} and S^{6+}, while impregnated metals present as oxides, favor the oxidation of ion sulfide to elementary sulfur. Comparative analysis of the catalytic activity of obtained catalysts shows that the most effective catalyst is obtained from oxidized activated carbon from peach stones and impregnated with Cu^{2+}ions. The catalyst shows pronounced catalytic activity at higher pH values of the solutions, which is important from the practical point of view, ensuring efficient catalytic activity under to near natural groundwater

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alkaline pH. The catalyst can be re-used for a long time, keeping the pores unclogged and maintaining the porous structure at the characteristic parameters of this adsorbent, being recommended for practical purposes to remove hydrogen sulfide species from sulfurous groundwater.

11.1 Introduction

Various methods have been proposed for the oxidation of hydrogen sulfide in aqueous medium, using different oxidizing agents, such as potassium permanganate, sodium or potassium dichromate, chlorine, ozone, hydrogen peroxide [1, 2]. Such methods have serious drawbacks, being uneconomical due to high reagents prices and also disadvantageous in terms of possible environmental pollution by oxidizing agents. H_2S oxidation with oxygen in the absence of catalysts is very slow, due to different electronic configurations of reactants [3–12].

Oxidation of sulfur (II) species, such as H_2S, $HS^-$and S^{2-}, has a complex stoichiometry because of the broad spectrum of products and meta-stable intermediates produced during the reaction, including colloidal sulfur S_n, octarhombic elemental sulfur S_8, thiosulfate ions $S_2O_3^{2-}$, sulfite ions SO_3^{2-}, poly-sulfides S_4^{2-}, S_5^{2-}, tetrathionate ions $S_4O_6^{2-}$, sulfate ions $SO_4{}^{2-}$ [3–10].

Efficient catalysts for the oxidation of hydrogen sulfide species are transition metals [2, 4, 5, 11, 13–20] and their complexes [3, 8, 9, 20–22], activated carbons [4, 10, 13, 23–40], being able to change the electronic configuration of the reactants (H_2S or O_2).

The type of the products and intermediates formed during the oxidation process with oxygen depends largely on pH, reagents concentrations (S(II), oxygen), and the type of the catalyst [3, 5]. In the presence of activated carbons as catalysts, the sulfur is frequently shown as the major product [4, 10, 25–28, 33, 35, 41, 43, 48], while the sulfur species S^{4+} and $S^{6+}$are recorded in smaller amounts (about 30 %) [26, 27, 33, 42].

The mechanism of formation of elemental sulfur and SO_x species is determined largely by the acid–base properties of activated carbon and their surface pH in suspension [26, 32, 42]. It is considered that the first step is the catalytic activation of oxygen on the surface of activated carbon. The sources of active oxygen on the surface or its forms of existence are not clear yet, considering the source of free radicals is either the air oxygen [43], the functional groups on the surface [27] or the chemisorbed oxygen [27, 42].

The pH value influences the type and quantities of sulfur species formed during oxidation with oxygen in aqueous media [4]. In the pH range 7–14 the main oxidation product is thiosulfate, up to 45–60 %. At low pH values poly-thionic acids are formed in small quantities and their content decreases with increasing pH, lacking in solution at pH 8.9. Sulfite ions are formed at pH higher than 8. Overall, it appears that sulfite ions, thiosulfate and sulfate ions are formed in significant quantities at pH $>$ 10–11.

Catalytic processes for removal of hydrogen sulfide are also affected by the matrix composition of activated carbon [44]. Inorganic substances (ash) and present metals [31] have catalytic effects. Impregnation of activated carbon with transition metals modifies catalytic properties of activated carbons [13, 27, 36, 39, 40, 45–47, 61, 62]. Important oxidative properties for removing aqueous sulfides are shown by active carbon impregnated with oxides of transition metal NiO, CoO, CuO, MnO, Cr_2O_3, Fe_2O_3, TiO_2, V_2O_5, MoO_2, and oxide mixes [13]. The oxides of transition metals are used in industry as adsorbents and/or catalysts to remove hydrogen sulfide from different media [14–18, 20, 33]. At low temperatures the reaction takes place on the hydrated surface of oxides. This process leads to the formation of sulfides and sulfur precipitation. There are two possible mechanisms of catalytic oxidation of sulfur species (II) via transition metal ions, either by the formation of free radicals by electron transfer or by forming metal-sulfide complexes and sulfur precipitation [4, 8].

Hydrophilic properties of carbons are also important, favoring the formation of a water film adsorbed on their surface, which facilitates oxidation of hydrogen sulfide. However, the interpretations of oxidation mechanisms are still quite controversial in the literature, among the factors which may influence the catalytic activity of carbons being mentioned the influence of volume and pore radius [41], surface functional groups [27], surface pH [26, 42, 49] and affinity for water [26, 28].

Summarizing all mentioned above, it can be stated that interpretations of catalytic action of activated carbons during the oxidation with oxygen of hydrogen sulfide species in aqueous solutions are still quite controversial in the literature, one of the reasons being insufficient study of their surface chemistry.

One of the technology that needs improvement is application of activated carbons at various stages of water treatments. Annually, Moldova imports significant amounts of activated carbons for different purposes. On the other hand, canning and wine plants annually store important quantities of stones of different garden-plants and fruit, and grape seeds. These agricultural wastes can be used as raw materials to obtain activated carbons.

The purpose of this work was to develop catalysts based on new carbonaceous adsorbents derived from fruit stone, and to further apply them for removal of species of hydrogen sulfide from model solutions and underground waters.

11.2 Results and Discussions

11.2.1 Characterization of Carbonaceous Adsorbents

Table 11.1 shows the adsorption capacity and structural parameters determined from nitrogen adsorption isotherms (77 K) for active carbons obtained by physical–chemical activation with water vapor from peach stones (CAP23), after oxidation with nitric acid (CAPO23), and after impregnation with metals through

Table 11.1 Surface area and pore structure parameters for unmodified, oxidized and impregnated carbonaceous adsorbents, obtained from nitrogen sorption isotherms (77 K)

Sample	S^{a}_{BET}, (m^2/g)	S^{b}_{meso}, (m^2/g)	V^{c}_{total}, (cm^3/g)	V^{d}_{meso}, (cm^3/g)	V^{e}_{micro}, (cm^3/g)	R^{f}, Å
CAP23, initial	957	110	0.57	0.15	0.42	11.9
CAPO23, oxidized	869	130	0.52	0.17	0.35	11.9
CAPO23Cu (0.4 meq Cu^{2+}/g)	811	120	0.48	0.11	0.37	11.8
CAPO23Fe (0.8 meq Fe^{3+}/g)	839	110	0.50	0.16	0.34	11.9
BAU-A, commercial	480	–	0.36	0.11	0.25	6.0

[a] S_{BET}—surface area
[b] S_{meso}—mesopore surface area
[c] V_{total}—total pore volume
[d] V_{meso}—mesopore volume
[e] V_{micro}—micropore volume
[f] R-average pore radius

the “wet” method (CAPO23Cu and CAPO23Fe) [46, 52]. A procedure for impregnation with metal oxides (catalyst CAP23NiO) was previously described [63]. Adsorption isotherms were obtained using the volumetric gas adsorption analyzer (Autosorb-1, Quantachrome, USA). The total area by BET (S_{BET}) was calculated using the Brunauer-Emmett-Teller method. The *t*-method of de Boer variant was used for calculations of S_{meso} and V_{micro} [46, 50, 51]. These results show that the obtained adsorbents are mainly micro-porous adsorbents. The oxidation and metal impregnation lead to further changes in their porous structure, manifested by destruction of micro-pores and leading to an overall decrease of parameters by about 10–15 %. By comparison, the commercial carbonaceous adsorbent obtained from birch wood (BAU-A, Russia) is presented.

Developed carbonaceous adsorbents have been characterized by Boehm titration method in order to quantify surface chemistry properties [53]. In the Table 11.2 are presented quantities and character of the functional groups, and also the pH value of carbonaceous adsorbents suspension. Presented data demonstrate that the amount of strong carboxylic groups on the surface of oxidized activated

Table 11.2 Surface chemistry of activated carbons characterized by Boehm method and pH of suspension

Sample	pH of suspension	Quantity of the functional groups (Amount, meq/g)				Character of the functional groups (Amount, meq/g)			
		Titrant				Carboxylic		Phenolic	Basic
		0.05 N $NaHCO_3$	0.1 N Na_2CO_3	0.05 N NaOH	0.1 N HCl	Strong acidic	Weak acidic		
CAP23	5.2	0.10	0.29	0.58	0.59	0.10	0.19	0.29	0.59
CAPO23	4.6	1.4	1.65	2.71	0.35	1.34	0.31	1.06	0.35
BAU-A	10.0	0.1	0.1	0.2	0.35	0.1	0	0.1	0.35

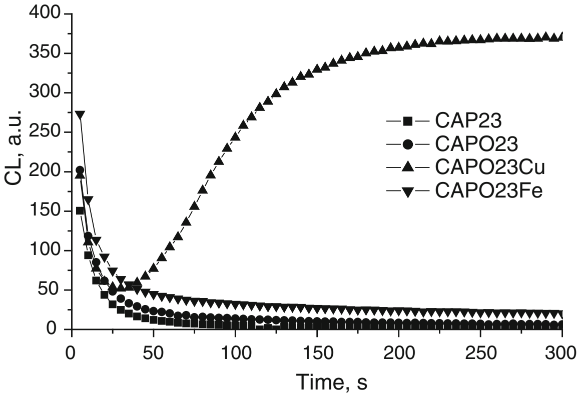


Fig. 11.1 Redox properties of carbonaceous adsorbents evaluated by chemiluminescence method

carbon CAPO23 increases by about 13 times, in comparison with un-oxidized activated carbon CAP23. Activated carbon BAU-A is poorer in functional groups and surface pH is alkaline (Table 11.2).

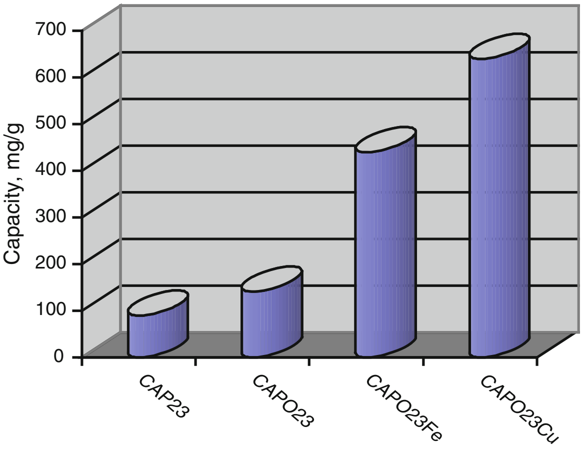
Redox properties of carbonaceous adsorbents were evaluated using chemiluminescence (CL) technique (system luminol-H_2O_2, in buffer TRIS–HCl, at pH 8.6) [54]. For chemiluminescence measurements a luminometer TD 20/20 (Turner Desing, USA) was used.

Kinetics curves of hydrogen peroxide decomposition show the same behavior for adsorbents CAP23, CAPO23 and CAPO23Fe (Fig. 11.1). Impregnation with copper ions considerably increased oxidative activity of the sample. After a period of induction (20 s) the oxidative activity of CAPO23Cu sample increased by about 25 times in comparison with CAPO23 and CAPO23Fe.

11.2.2 Hydrogen Sulfide Oxidation With Oxygen in the Presence of Activated Carbons

Testing of carbonaceous adsorbents for the elimination of hydrogen sulfide from model solutions was performed in static conditions with periodic stirring, by keeping solid/liquid ratio of 1:800, initial concentration of Na_2S 800 mg/L, and pH value of 8.5. The experiments were performed by using lab installation provided with an air bubbler and recovery flask for aerated hydrogen sulfide at appropriate parameters, i.e. solid/liquid ratio, aeration flow rate, pH of the medium, initial concentration of sulfur species [55]. Elemental sulfur, thiosulfate, sulfite and sulfate ions, and aerated hydrogen sulfide from recovery flask were determined in the equilibrium solutions after 24 h of contact with adsorbents by standard methods [56]. All sulfur species were recalculated as H_2S, and removal (R) of hydrogen sulfide from solutions expressed in %.

Fig. 11.2 Carbonaceous adsorbents capacity for adsorption/oxidation of sulfide ions



The results (Fig. 11.2) emphasize the high capacity of sulfide ions elimination for carbonaceous adsorbent obtained from peach stones modified with copper ions (CAPO23Cu). The rate of oxidation-aeration process increases considerably, by 14–16 times, and the amount of aerated H_2S decreases from 67 to 12 % in the presence of activated carbon obtained from peach stones (CAP23) and up to approx. 4 % in the presence of oxidized activated carbon CAPO23 (Fig. 11.3). Sulfur species with high oxidation degrees, S^{IV} and S^{VI}, prevail if the sulfide oxidation is carried out in the presence of oxidized activated carbon (CAPO23) obtained from peach stones (Table 11.3) [57]. More probably, oxygen atoms of COOR ester groups and/or lactone C–O–C groups on the surface of oxidized activated carbons participate in the oxidation of sulfides [27]. Data obtained previously [58] show that the amount of strong carboxyl groups increases by about 13 times on the surface of oxidized activated carbon CAPO23, compared to the

Fig. 11.3 Kinetics of sulfide ions elimination (R, %) in the absence *4* and in the presence of activated carbon obtained from peach stones CAP23 *1*, oxidized activated carbon CAPO23 *2*, and commercial activated carbon BAU-A made of birch wood *3*. Initial concentration of the solution $C_0 = 10$ mg/L, pH 8.5, mass ratio mg O_2 : mg H_2S ¾ in the presence of 1 g of catalyst

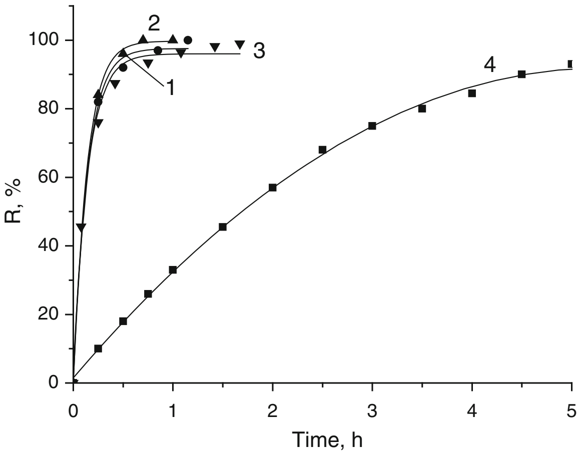


Table 11.3 Quantities of aerated and oxidized hydrogen sulfide in the absence and in the presence of activated carbon from peach stones CAP23, oxidized activated carbon CAPO23 and commercial activated carbon from birch wood BAU-A

Active carbon	Aerated content, %	Oxidized content, %	Sulfur species formed in the process of oxidation, %			
			S^0 colloidal	$S_2O_3^{2-}$	SO_3^{2-}	SO_4^{2-}
In the absence of carbon	67.0	33.0	–	–	–	–
CAP23	12.0	88.0	20.4	0	12.5	67.1
CAPO23	4.3	95.6	6.1	11.7	15.4	65.9
BAU-A	9.2	90.8	32.9	32.9	4.5	31.2

Initial concentration of the solution $C_0 = 10$ mg/L, pH 8.5, mass ratio mg O_2 : mg H_2S 3:4 in the presence of 1 g of catalyst

quantities of these groups on the surface of the un-oxidized carbon CAP23. In the FTIR spectrum of oxidized activated carbon (CAPO23) there is a new band at 1727 cm^{-1}, attributed to esters and lactones [59].

The relationship between the degree of removal of sulfide ions in the presence of carbonaceous adsorbents and the total content of acidic groups on the surface is shown in Fig. 11.4. It is considered that with increasing of oxygen content on the surface of carbon, both by the concentration functional groups and the chemisorbed oxygen, increases the adsorption capacity of hydrogen sulfide species and their oxidation to higher degrees of oxidation [23–27, 41, 60].

Different behavior of the investigated adsorbents in the oxidation-aeration of sulfide ions is also caused by acidic properties of their surfaces or by surface pH. For CAP23 and CAPO23 carbons the surface pH is acidic, 5.2 and 4.6 respectively, while the surface pH of BAU-A carbon is alkaline, reaching pH 10 (Table 11.2). The more acidic is the carbon surface, the greater is the proportion of

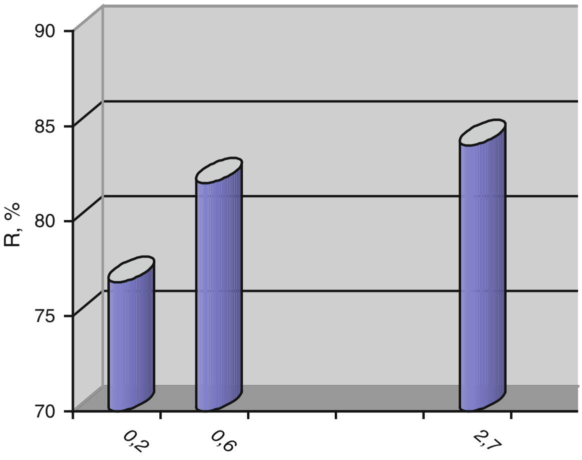


Fig. 11. 4 The degree of removal (R (%), determined in the first 15 min after the start of the experiment) of sulfide ions in the presence of carbonaceous adsorbents, as function of the total amount of surface acidic groups. Comparative analysis for the commercial activated carbon from birch wood BAU-A, activated carbon from peach stones CAP23 and oxidized activated carbon CAPO23

sulfur oxidized to S^{4+} and S^{6+} species, as pointed out also by [42]. It appears that S^{IV} and S^{VI} sulfur species prevail if the sulfide oxidation is carried out in the presence of oxidized activated carbon which contains significantly more carboxylic groups on the surface as compared to their quantities on the surface of unoxidized carbon (Table 11.2).

11.2.3 Oxidation of Hydrogen Sulfide Species in the Presence of Carbonaceous Adsorbents Impregnated With Metals

Table 11.4 shows the amounts of hydrogen sulfide aerated and oxidized in the presence of oxidized activated carbon obtained from stones of peaches and impregnated with metal ions (CAPO23Fe, CAPO23Cu) or with nickel oxide (CAP23NiO) [63, 64]. Active carbons impregnated with metals show a pronounced catalytic activity in the oxidation of sulfur species, as compared to the catalytic activity of those adsorbents before their impregnation with metals. The state or form of the immobilized metal on the surface of the carbons essentially influences the reaction speed of the process, with a noted increase of the oxidation rate in the presence of catalysts in the order CAPO23Fe < CAPO23Cu < - CAP23NiO (Fig. 11.5).

Oxidation rate of sulfur species the presence of CAP23-NiO catalyst is much higher, being by 2–2.5 times higher than in the presence of other catalysts. However, the major product of the oxidation in the presence of CAP23-NiO catalyst is colloid sulfur, constituting 95 % of the species formed. In the presence of catalysts CAPO23Fe or CAPO23Cu oxidation products are thiosulfates, sulfites and sulfates (Table 11.4). To be mentioned that in the presence of these catalysts colloidal sulfur is not formed during oxidation.

Table 11.5 shows the catalytic capacity under static conditions (expressed as the amount of hydrogen sulfide adsorbed/oxidized by 1 g of carbonaceous

Table 11.4 Quantities of aerated and oxidized hydrogen sulfide in the absence and in the presence of oxidized activated carbons from peach stones and impregnated with metal ions (CAPO23Fe, CAPO23Cu), and carbon impregnated with nickel oxide (CAP23-NiO)

Active carbon	Aerated content, %	Oxidized content, %	Sulfur species formed in the process of oxidation, %			
			S^0 colloidal	$S_2O_3^{2-}$	SO_3^{2-}	SO_4^{2-}
CAPO23Fe (0.8 meq Fe^{3+}/g)	33.5	66.5	0	16.1	17.7	66.2
CAPO23Cu (0.4 meq Cu^{2+}/g)	41.6	58.3	0	9.3	32.7	58.1
CAP23-NiO (0.5 meq Ni^{2+}/g)	5.3	94.7	95.5	4.8	0	0

Initial concentration of the solution $C_0 = 10$ mg/L, pH 8.5, mass ratio mg O_2 : mg H_2S 3:4 in the presence of 0.5 g of catalyst

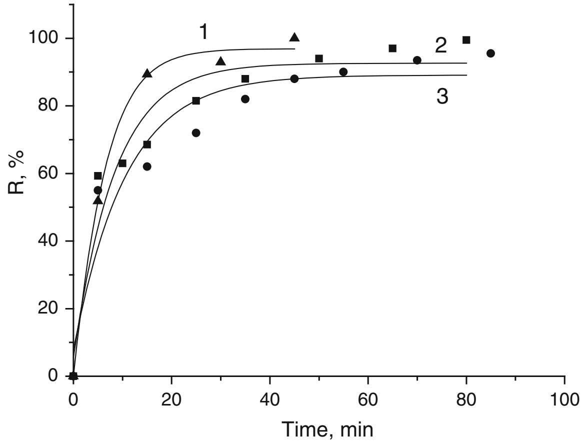


Fig. 11.5 Kinetics of sulfide ions removal (R, %) in the presence of activated carbons CAP23-NiO *1*, CAPO23Cu *2* and CAPO23Fe *3*. Initial solution concentration $C_0 = 10$ mg/L, pH 8.5, mass ratio mg O_2 : mg H_2S 3:4 in the presence of 0.5 g of catalyst

Table 11.5 Catalytic capacity of activated carbons CAPO23Fe and CAPO23Cu (oxidized activated carbons obtained from peach stones and metal impregnated) for oxidation/adsorption of hydrogen sulfide at various pH values of solutions under static conditions

Sample	Metal quantity	Catalytic capacity, mole H_2S/g	
		pH of solution 8.5	pH of solution 11.5
CAPO23Fe	0.8 meq Fe^{3+}/g	13×10^{-3}	8×10^{-3}
CAPO23Cu	0.4 meq Cu^{2+}/g	19×10^{-3}	46×10^{-3}

adsorbent) of adsorbents CAPO23Fe and CAPO23Cu at different pH values of solutions. The data show that the type of metal impregnated on the carbon surface also influences the catalytic activity of adsorbents. Oxidized activated carbons obtained from peach stones and impregnated with Fe^{3+} (CAPO23Fe), exhibit higher catalytic activity at low pH, while carbon impregnated with Cu^{2+} (CAPO23Cu) exhibits a more pronounced catalytic activity at higher pH values.

Comparative analysis of the catalytic activity of obtained catalysts shows that the most effective catalyst is CAPO23Cu obtained from oxidized activated carbon from peach stones and impregnated with Cu^{2+} ions. The catalyst shows pronounced catalytic activity at higher pH values of the solutions, which is important from the practical point of view, ensuring efficient catalytic activity under to near natural groundwater alkaline pH.

11.2.4 Oxidation of Hydrogen Sulfide Species Using Micro-Pilot Installation

Testing of carbonaceous adsorbents for the elimination of hydrogen sulfide from model solutions was performed using micro-pilot installation provided with an air bubbler and recovery flask for aerated hydrogen sulfide at appropriate parameters,

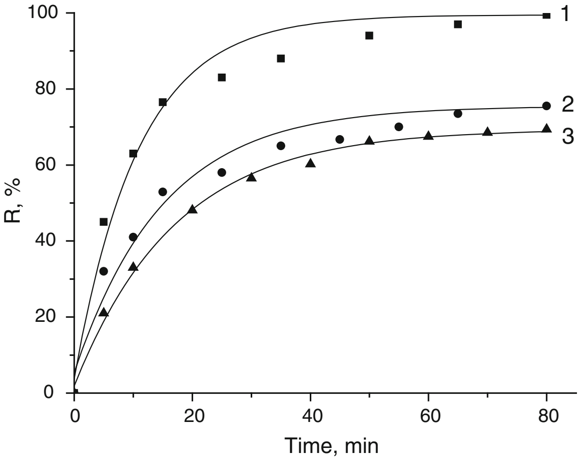


Fig. 11.6 Kinetics of hydrogen sulfide removal (R, %) in the presence of CAPO23Cu at various pH values of the solution: *1* pH 8.5; *2* pH 9.5; *3* pH 10.5

i.e. solid/liquid ratio, aeration flow rate, pH of the medium, initial concentration of sulfur species [3, 55, 56, 63].

Figure 11.6 presents the influence of the pH on the kinetics of hydrogen sulfide removal in the presence of the carbonaceous adsorbent CAPO23Cu. Increasing the pH from 8.5 to 10.5 leads to a slower rate of sulfide ions removal (R, %), while quantities (%) of oxidized H_2S and of formed SO_4^{2-} ions significantly increases (Table 11.6). From the chemical balance of hydrogen sulfide species $H_2S \leftrightarrow HS^- \leftrightarrow S^{2-}$, at low pH the chemical equilibrium is shifted to the left resulting in increased H_2S concentration in solution. Previous studies show that at pH values of 7.5–8.5 the removal of hydrogen sulfide from the solution by bubbling predominates [64]. At higher pH values chemical balance of hydrogen sulfide species is shifted to the right, and during aeration of the solution with air oxygen the oxidation of ionized species predominates.

Kinetics of sulfide ions elimination in the presence of adsorbents is influenced by the applied ratio of solid : liquid (adsorbent CAPO23Cu : model solution, Fig. 11.7). Increasing this ratio by 4 times leads to a higher rate of sulfide ions elimination, by about 3–4 times, while the amount of aerated products decreases by approx. 3 times, and the equilibrium is established after 20–60 min of contact.

Table 11.6 Quantities of H_2S aerated and oxidized to sulfur species in the presence of CAPO23Cu at various pH of the solutions (C_0 = 10 mg/L, pH = 8.5, ratio mgO_2/mgH_2S = 3:4, mass of catalyst 0.5 g)

pH of the medium	Quantity (%) of H_2S			Quantity (%) of H_2S oxidized to sulfur species:		
	Not removed	Aerated	Oxidized	S^0 colloidal	$\sum(S_2O_3^{2-}+SO_3^{2-})$	SO_4^{2-}
8.5	0.1	41.6	58.3	0	41.9	58.1
9.5	24.5	2.5	73.0	0	27.7	72.3
10.5	30.6	1.4	68.0	0	30.1	69.9

Fig. 11.7 Kinetics of hydrogen sulfide removal in the presence of the CAPO23Cu at various solid : liquid ratio values (S:L, g:mL). Initial concentration of sulfide ions 9.2 mg/L, pH = 8.5. *1*—S:L = 1:2000; *2*—S:L = 1:800; *3*—S:L = 1:500

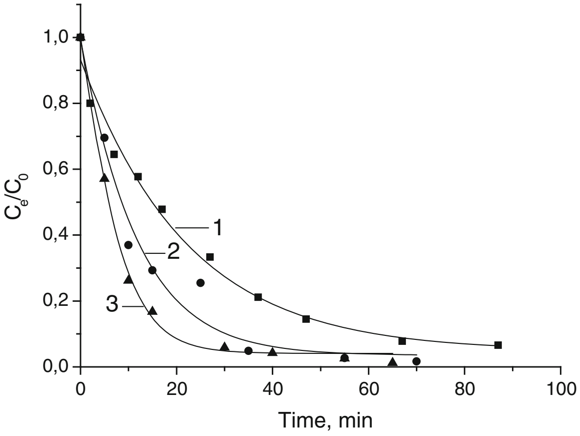
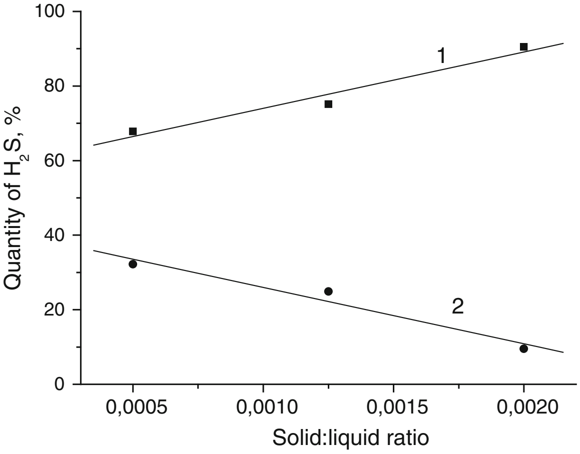


Fig. 11.8 Quantities of hydrogen sulfide species oxidized/adsorbed (*1*) or aerated (*2*) at different S:L ratio values



Total oxidation of thiosulfate and sulfite ions in the presence of adsorbent CAPO23Cu is reached after 50–60 min (Fig. 11.10). A linear dependence is found between the amount of removed hydrogen sulfide species (oxidized/adsorbed or aerated) and the ratio of solid : liquid (Fig. 11.8). The adsorbent CAPO23Cu can be re-used by recycling, and the results reveal a slight decrease of the rate of sulfide ions removal after three contact cycles (Fig. 11.9).

11.2.5 Application for Natural Groundwater

Figure 11.11 shows the kinetics of hydrogen sulfide removal from the natural groundwater (well No. 1, Hincesti locality of RM), and from the model solution at concentration and pH close to natural conditions. The kinetics of these processes is

Fig. 11.9 Kinetics of hydrogen sulfide removal by recycling of the adsorbent CAPO23Cu. The solid : liquid ratio (g:mL) 1:800. Initial concentration of sulfide ions 3.0 mg/L, pH = 8.5. *1*—first cycle; *2*—second cycle; *3*—third cycle

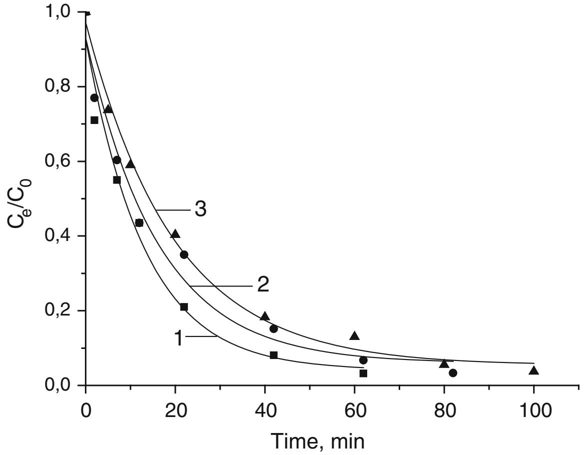


Fig. 11.10 Kinetics of oxidation of thiosulfate and sulfite ions in the presence of the adsorbent CAPO23Cu. The solid : liquid ratio (g:mL) 1:800, pH = 8.5. Initial concentrations of model solutions: *1*—3 mg/L, *2*—7 mg/L; *3*—9 mg/L; *4*—14 mg/L; *5*—17 mg/L Na_2S

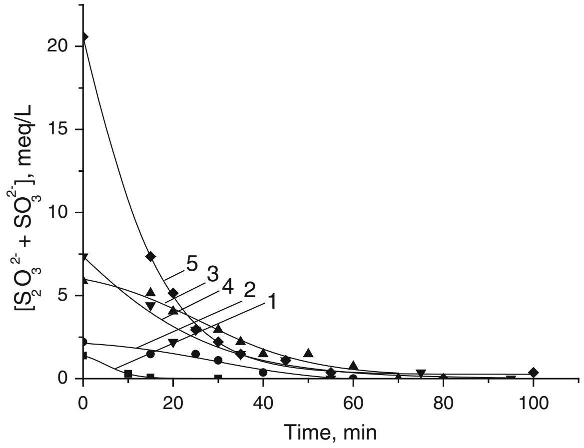


Fig. 11.11 Kinetics of hydrogen sulfide removal in the presence of the adsorbent CAPO23Cu (0.5 g) for the model solution (*1*, C_0 = 10 mg/L, pH 8.5) and groundwater (*2*, C_0 = 6.7 mg/L, pH 8.6) Mass ratio mg O_2 : mg H_2S 3:4

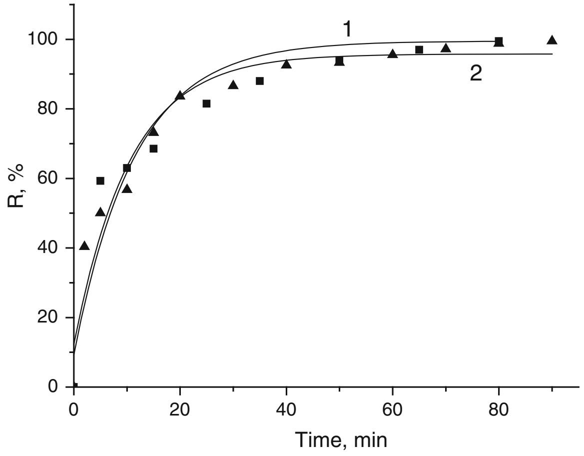


Table 11.7 Quantity of H_2S aerated and oxidized in the presence of CAPO23Cu. Mass ratio mg O_2 : mg H_2S 3:4 in the presence of 0.5 g of catalyst

Catalyst	Aerated amount, %	Oxidized amount, %	Sulfur species formed during oxidation, %			
			S^0 colloidal	$S_2O_3^{2-}$	SO_3^{2-}	SO_4^{2-}
CAPO23Cu	Model solution. Initial solution concentration $C_0 = 10$ mg/L, pH 8.5					
	41.6	58.3	0	9.3	32.7	58.1
	Groundwater. Initial concentration $C_0 = 6.7$ mg/L, pH 8.6					
	16.4	83.6	0	0.2	51.8	48.0

the same and colloidal sulfur is not formed (Table 11.7). The catalyst can be used for a long time, keeping the pores unclogged and maintaining the porous structure at the characteristic parameters of this adsorbent, being recommended for practical purposes to remove hydrogen sulfide species from natural sulfurous groundwater.

11.3 Conclusions

It is considered that with increasing of oxygen content on the surface of carbon, both by the concentration functional groups and the chemisorbed oxygen, increases the adsorption capacity of hydrogen sulfide species and their oxidation to higher degrees of oxidation. Sulfur species with high oxidation degrees, S^{IV} and S^{VI}, prevail if the sulfide oxidation is carried out in the presence of oxidized activated carbon obtained from peach stones.

Active carbons impregnated with metals show a more pronounced catalytic activity in the oxidation of sulfur species. The state or form of the immobilized metal on the surface of the carbons essentially influences the reaction speed of the process, with a noted increase of the oxidation rate in the presence of catalysts in the order CAPO23Fe < CAPO23Cu < CAP23-NiO. In the presence of catalysts CAPO23Fe or CAPO23Cu oxidation products are thiosulfates, sulfites and sulfates and the colloidal sulfur is not formed during oxidation.

Comparative analysis of catalytic activity of obtained catalysts shows that the most effective catalyst is obtained from oxidized activated carbon from peach stones and impregnated with Cu^{2+}ions. In the presence of this catalyst oxidation products are thiosulfates, sulfites and sulfates, without the formation of colloidal sulfur. The catalyst shows pronounced catalytic activity at higher pH values of the solution, which is important from the practical point of view, ensuring efficient catalytic activity under to near natural groundwater alkaline pH. The catalyst can be used for a long time, keeping the pores unclogged and maintaining the porous structure at the characteristic parameters of this adsorbent, being recommended for practical purposes to remove hydrogen sulfide species from sulfurous groundwater.

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Chapter 12
Application of Bioactive Substances in the Biogas Technology

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Olga Covaliova and Valentin Bobeica

Abstract A new scientific-technological concept of the utilization of wine and distillery wastes is proposed. The results of complex research are given, related to the effect of biologically active substances (BAS) on biomethane and biohydrogen emission from the distillery wastes. It was shown that the test substances can provide a 3−4 times increase in fermentation efficiency, enhance the methane contents in biogas up to 90−95 % and activate the dehydrogenase thus stimulating the biochemical process. The kinetic indicators of processes and mechanism of BAS effect on anaerobic fermentation are discussed.

Keywords Biogas · Biochemical processes · Biologically active substances

12.1 Introduction

The biogas production is an important part of the general concept of sustainable development, based on the production of high-energy fuel agents from the renewable vegetable raw materials, in view of the partial substitution and savings of nonrenewable hydrocarbon fuels—oil, coal and natural gas.

The development of anaerobic fermentation technologies using the liquid and solid wastes from the agricultural products processing industries is one of

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perspective directions in the biogas production from vegetable raw materials and agricultural organic wastes. As energy materials, the winery, brewery, yeasting and diary wastes, different kinds of solid and liquid processing wastes of cereals, potatoes, sugar beets, fruits and vegetables, etc. can be used.

Biogas is a product of the organic substances anaerobic decomposition. The number of organic substrates that can be used for biogas production is huge, compared to the currently used ones. It was found that 86 % of biogas potential is contained in the agricultural raw materials and only 8 % in the industrial and municipal wastes [1, 2].

At present quite a number of biogas producing technologies has been elaborated and applied. They are based on the use of various biogas production conditions: temperature regime, humidity, microbial biomass concentrations, duration of microbiological processes, etc. [3]. However, the existing technologies and equipment have not yet provided the biogas production from the wastes with the highest possible yield. According to the technological parameter, only 30–60 % of organic admixtures are transforming into biogas, and methane contents in biogas in most cases is no more than 60–70 %.

An important new direction of this technology is the possibility to obtain biohydrogen in biochemical way [4]. In spite of the great number of publications and high availability of raw materials, these processes have not received the broad application yet. One of the causes is the lack of the appropriate research and new ideas [5].

Hydrogen is an accompanying element in many biochemical reactions. In the methanogenic technology it is emitted on the acetogenic stage of fermentation. Acetogenic bacteria, making a relatively small group, among them *Methanobacillus omelianskii*, decompose the alcohols and fatty acids, with the formation of acetic acid, hydrogen and carbon dioxide:

$$
\begin{aligned}
& C_2H_5OH + H_2O \leftrightarrow CH_3COO^- + H^- + 2H_2 \\
& CH_3CH_2COO^- + H_2O \leftrightarrow CH_3COO^- + HCO_3^- + H^- + 3H_2.
\end{aligned}
$$

In the methane formation processes, the methanobacteria use hydrogen for its transformation into methane: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$. The problem with biohydrogen generation is as follows: how to inhibit the methane formation and stabilize the biohydrogen emission? In addition, the practical aspect of this process which needs to be resolved, is the increase of the specific process rate per unit of the reactor volume, efficiency in case of the of substrate using and identification of the renewable raw material spectrum. However, the actual state of the problem of biohydrogen generation with microorganisms, still did not exceed the bounds of experimental-research works, despite the numerous publications in this field.

In biogas production technology from the organic wastes, the specifics of methanogenesis must be considered. The organic wastes transformation in biogas is the result of a complex sequence of biochemical conversions realized by microorganisms [6]. The schematic pathways of the organic substances

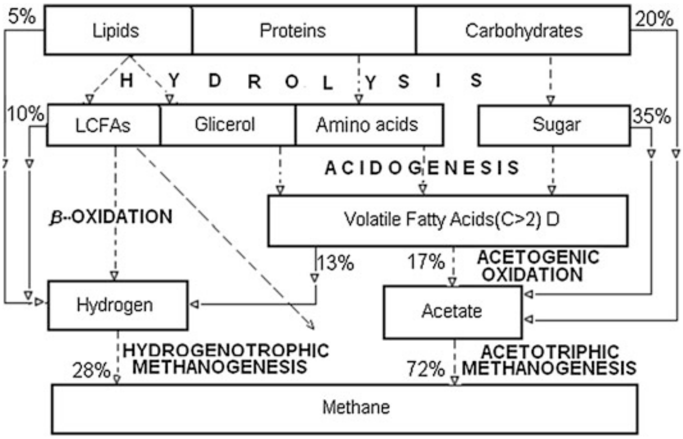


Fig. 12.1 The pathways of organic compounds metabolism during the anaerobic fermentation

metabolism during the anaerobic fermentation, according to the modern notions, are presented on Fig. 12.1.

The overall reaction for this process can be described as:

$$\text{Organic materials} + H_2O \rightarrow \text{biomass} + CH_4 + CO_2 + H_2 + NH_4^+.$$

The quality of biogas is determined primarily by the methane contents. Carbon dioxide dilutes the biogas and reduces its energy indicators. Moreover, according to the balance calculation, the amount of produced hydrogen is insufficient for the formation of CH_4. Therefore, the development of biotechnologies in order to increase the methane contents in biogas is actual. This can be achieved by the selective purification of biogas from the accompanying gases (CO_2, H_2S), optimization of its production technology by introducing the biologically active compounds that promoting the development of methanogenic bacteria.

Due to the adding of even small amounts of biostimulators in biochemical process, the bacteria growth rate and intensity of anaerobic fermentation is increased. This decreases essentially the process time, which in its turn can essentially reduce the capital and operating costs. The good results have been obtained with melaphen using as an additive—a synthetic plants growth stimulant, which is a melamine salt of bis-oxymethylphosphyne acid [7]. To study the processes of methanogenesis intensification, the direction was selected on preparation and testing of natural isoprene compounds with the increasing number of functional groups in the molecule.

Another perspective way to improve the biochemical technology with the scope to increase the yield of biomethane, is a separation of acetogenic and methanogenic zones in bioreactor to isolate emitted CO_2 from the other products of acetogenic stage and provide its subsequent mixing with hydrogen in the methanogenic zone.

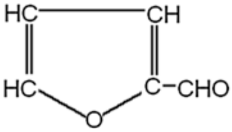
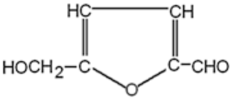
The scope of this research was to intensify the anaerobic fermentation of winery and distillery grains using the natural biologically active substances, to increase the biogas yield and methane contents in it, and to reduce the energy intensity of biochemical process.

12.2 Materials and Methods

General characteristics of post-distillery grains and sludge. The post-distillery grains contains the substances with the organic carbon (pentoses and organic acids), products of monosaccharides decomposition, as well as the liquid wasted from the spirits and furfural rectification. In dependence on the type of raw material processed, it may contain the components shown in the Table 12.1.

Bioreactors. The effect of bioactive substances on methanogenesis was studied using the especially developed set of four bioreactors (Fig. 12.2). The total volume of each bioreactor was 5000 cm^3, the useful volume—3500 cm^3. The equipment consists of a bench-scale bioreactor 1, placed in the thermostatically controlled reservoir, the devices to remove and control the volume of generated biogas, formed sludge and purified liquid. This equipment makes it possible to study the biogas purification from CO_2 and H_2S admixtures simultaneously.

Table 12.1 Composition of post-distillery grains and sludge

Indexes	Wood and molasses, weight %	Wood and grains wastes, weight %
Soluble substances (PB)	0.49–0.65	0.51–0.53
Furfural 	0.0005–0.002	0.0005–0.001
Oxymethyl-furfural 	0.059–0.080	0.064–0.066
Levulinic acid $HOOC\text{-}(CH_2)_2\ \text{–}CO\text{-}CH_3$	0.301–0.384	0.302–0.391
Lignofuranic substances	0.286–0.304	0.302–0.311
Organic acids	0.38–0.57	0.63–0.68
Absolutely dry substance	1.60–1.81	1.46–1.49
Monosaccharides	0.47 ± 0.12	0.405 ± 0.06
Arabinose	0.071 ± 0.014	0.063 ± 0.013
Xylose	0.40 ± 0.10	0.388 ± 0.08
COD, mg O_2/dm^3	21569–23137	22333–23040
pH initial	3.9–4.5	3.7–4.3

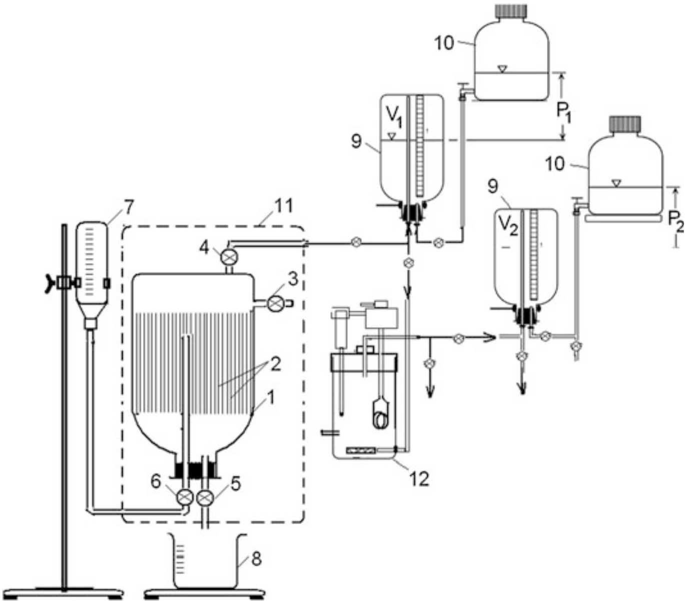


Fig. 12.2 The scheme of the bench-scale reactor for biochemical generation of biogas and its purification from admixtures: *1*—bioreactor; *2*—package for microflora immobilization; *3–6*—valves; *7*—reservoir for the nutrition solution; *8*—glass; *9*—calibrated reservoir; *10*—water reservoir; *11*—thermostat; *12*—biogas purification device

Biogas produced in the bioreactor 1 was accumulated in calibrated reservoir 9, displacing water into the reservoir 10. The parameters of accumulated biogas were controlled—volume (V_1) and pressure (P_1), the latter being measured by the water levels difference. After the amount of biogas necessary for the experiment was accumulated, the valve 4 was closed. With the increasing of levels difference in reservoirs 9 and 10, the pressure was created in the reservoir 9, necessary for the gas passing through the purification device 12. The liquid introduced from the water storage reservoir 10, displaced the gas from the calibrated reservoir and directed it to purification device with necessary pressure and flow rate. The purified gas was collected in the similar reservoir, consisting of calibrated reservoir 9 and water reservoir 10. At the outlet of gas purification device, the volume (V_2), pressure (P_2) and gas temperature were controlled again.

The equipment makes it possible to control the operation of different biogas purification devices, logging them into the scheme one-by-one.

To ensure the additional surface for microflora immobilization, the grapevine rods have been introduced in bioreactor, with the total package surface of 8000 cm^2. The experiment was conducted under anaerobic conditions, the temperature was maintained as of 33.0 ± 0.1 °C.

The cultivation and adaptation of anaerobic microorganisms was performed, following the well-known procedure with sludge inoculation, taken from the

Chisinau municipal wastewater treatment plant. The biomass growth of methanogenic microorganisms was carried out in bioreactors within one month under the controlled process parameters, with permanent introducing of the nutrition mixture containing sugar and milk (3:1). The microflora cultivation was performed with the periodic cyclic introduction of substrate. The indicators of acidophilic process transition to methanogenic in bioreactors, the achievement of pH = 7.4−7.6 and stable amount of the emitted gas were served. On the first stage, the intensive CO_2 emission occurred, and the liquid in the bulk of bioreactor was acidified due to the acidophilic fermentation. To accelerate the transition process, the nutrition mixture was alkalified with NaOH to pH = 13.0 during 15 days. During the next 20 days, the regime of the nutrition mixture introduction was remained the same, and pH in bioreactors was maintained within the range 7.4−7.6. At the same time, the emitted gas volume and composition was measured. Once these indicators were stable for all bioreactors during 5−7 days, this meant that the microflora growing process was finalized.

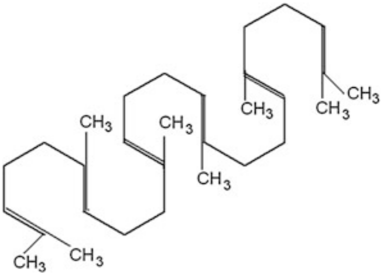
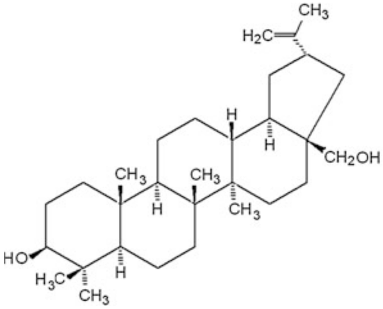
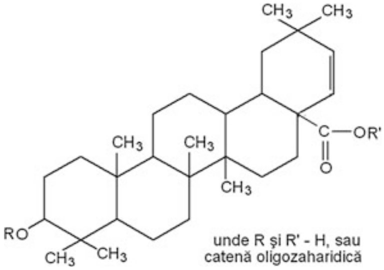
At next stage, the nutrition mixture was gradually substituted (step-by-step, by 25 %) with the distillery grains from "Bardar" winery. After each substitution, the nutrition mixture was kept till the stable indicators of gas yield were reached. One of the bioreactors served as a control. Following the first set of experiments, all the bioreactors were fed with the same nutrition mixture, and once the stable indicators of pH, gas volume and composition were reached, they were ready for the next set of experiments.

The effect of biologically active substances was estimated following the rate of gas emission and methane contents in it. As ***stimulating microadditives***, belonging to the class of bioactive substances (BAS), the compounds of isoprenoid nature were used (Table 12.2). It was supposed that these substances should stimulate the microbal activity, accelerate the biochemical processes, increase the biogas yield and exert the selective effect during the biomethane and biohydrogen emission. The BAS have been chosen proceeding from their biological activity, simplicity of synthesis and availability of raw materials. The selective generation of the molecular hydrogen was performed under pH = 5.2−7.5 and mesophyllic conditions, temperature of 33 ± 2 °C, with biomass agitation and permanent removal of hydrogen from the bioreactor.

The tests were carried out with the scope to reveal the BAS' possible activating (inhibiting) effect on the microorganisms. In the experiments the nutrition medium was used, and BAS were added in concentrations of $10^{-2}\ldots10^{-5}$ %. The subjects of tests were aerobic bacteria from the distillery grains, obtained in the control text in the bench-scale bioreactors. The tests were performed under the anaerobic mesophyllic conditions.

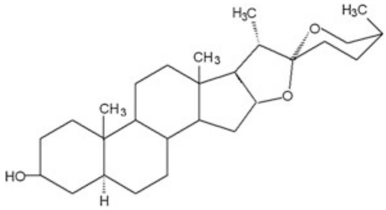
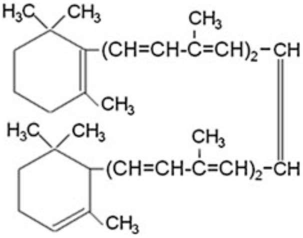
Chemical indices. At the preliminary stage, pH, humidity, total solids, total carbon contents in the initial distillery grains were measured by standard techniques. COD and BOD_5 values were registered following the standard method, gas volume—by volumetric method, qualitative gas composition—by chromatographic method. The peak on the chromatograms related to the 16th second, is characterized with the hydrogen (H_2) emission, the peak related to 27th

Table 12.2 Bioactive substances tested for stimulating of biogas processes

#	Name and structural formula	General characteristics
1.	*Squalene* (2,6,10,15,19,23-hexamethyltetracosa-2,6,10,14,18,22-hexaen) 	Hydrocarbon of natural origin, belonging to triterpene series, is contained in amaranth seeds, in olive, cotton, flax oil. Squalene contents in the amaranth seeds makes 8–10 % [8] Squalene was obtained from the non-saponifiable fraction of amaranth under the exposure to hydrochloric acid and extraction with low-polarity organic solvents—chloroform or acetone
2.	*Betulinol* ($C_{30}H_{50}O_2$) 	It is contained in the birch-tree juice and tar, giving the white colour to the birch-tree trunks. It can be readily extracted from the birch bark, containing the triterpene compounds, the most important from them being betulinol. Betulinol exerts a wide spectrum of biological effects on microorganisms. Due to the antioxidant, antimutagenic and antihypoxant activities, it stabilizes the cellular membranes of microorganisms, increases their resistance to the damage under the oxygen deficiency and simultaneously prevents the peroxide oxidation of lipids
3.	*Gypsogenine or gypsogenine glycosides* 	It is white and yellowish powder-like substance, consisting of the mixture of triterpene glycosides, found in the roots of *Gypsophila* plant species. It exerts numerous physiological properties and is used in medicine

(continued)

Table 12.2 (continued)

#	Name and structural formula	General characteristics
4.	*Neothigogenine saponin—steroid of C_{27}-spirostane series*  	Neothiogogenine saponins are contained in many plant species of *Jucca* genus, having the natural habitat in subtropical and tropical zones. They are also contained in the plants species cultivated throughout the globe, such as tomato, and can be produced by extraction with water-alcohol mixture
5.	*β-carotene*  	It is contained in the tissue of many plants as yellow or red pigment and belongs to the group of unsaturated compounds of hydrocarbon-terpene series with the large number of double conjugated bonds. It can be obtained by extraction from dried carrots, lucerne, buckwheat and many other vegetable materials

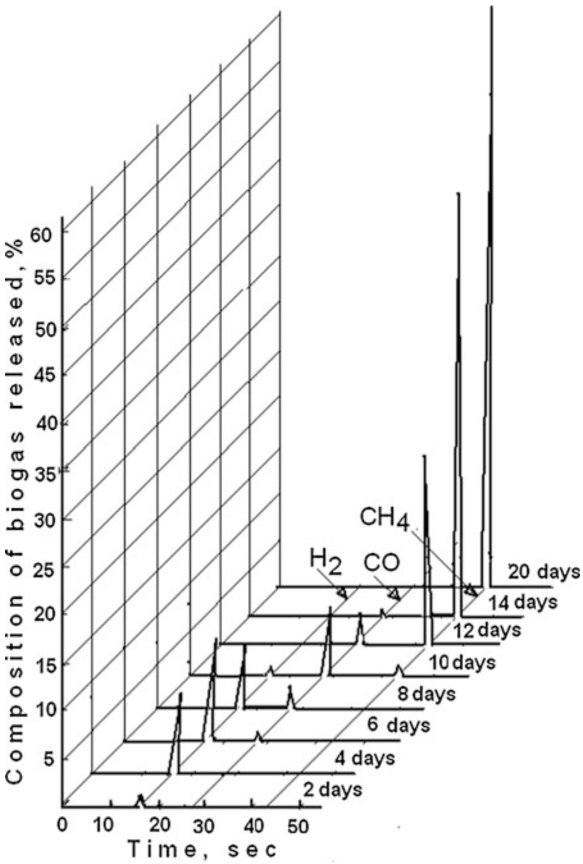
second—reflects the carbon monoxide (CO) emission, whereas the peak on the 43rd second shows the emission of methane (CH_4) (Fig. 12.3). CO_2 contents in biogas was estimated as a difference between the total amount of emitted gas and the summary contents in other gases.

Microbiological and enzymatic indices. The microbial biomass (MB) in sewage sludge was determined with rehydratation method. The number of microorganisms (including the aerobic heterotrophic ones) was determined by seeding on solid nutrition mediums [9]. The methane bacteria in the initial distillery grains were determined using the Hungate's technique. CO_2^-producing capacity of sewage sludge was estimated by titration. The dehydrogenase activity was determined by the colorimetric technique [10].

12.3 Results and Discussion

The distillery grains used in our experiments was a liquid yellowish suspension with the humidity 91.3–91.6 %, with insignificant contents of dry substance—8.4–8.8 % and acid pH (pH = 5.4). The total carbon contents makes 4.25 % of the wet and 49.5 % of dry mass of the waste. The distillery grains is characterized with the high COD and BOD_5 values—28250 and 17800 mgO_2/l, accordingly. The initial grains contains the aerobic heterotrophic microorganisms in the amount of 7.39 CFU—CFU (colony-forming units) $\cdot 10^6$/ml. Following the neutralization and

Fig. 12.3 Kinetics of gas emission during the anaerobic fermentation of the distillery grains



alkalinization, the grains were used as a medium for cultivation of methane-forming bacteria.

Another initial material was sewage sludge, used as a source of methanogenic microorganisms. According to the microbiological studies, the sewage sludge is a material with slightly alkaline reaction (pH = 7.5), and high contents in organic matter (an average of 21.3 %). As a result, sludge has a high number of bacteria, CO_2—producing capacity and dehydrogenase activity. This determines the high number of bacteria, CO_2—producing capacity of the sludge and its dehydrogenase activity (Table 12.3).

It was found that that sewage sludge is a biologically active material, in which bacteria are predominant among the microbial community. The number of fungi is insignificant. Microbial carbon contents in the dry waste is 2.5 mg C g^{-1}. One tone of waste contains about 5.0 kg of dry microbial biomass. The sewage sludge contains methane bacteria in the amount of 350 × 10^3 CFU g^{-1}.

Kinetics of the distillery grains' anaerobic fermentation. The studies of the grains anaerobic fermentation testifies on the complicated enough combination of

Table 12.3 Microbiological and biochemical characteristics of sewage sludge

MB (mg C/g)	Heterotrophic bacteria (CFU·10^6/g)	Nocardia (CFU·10^6/g)	Actinomycetes (CFU·10^6/g)	Methane bacteria (CFU·10^3/g)	Fungi (CFU·10^3/g)	CO_2 (mg/100 g/24 h)	Dehydrogenase activity (mg TPF/10 g/24 h)
2.5	1286.8	249.3	22.8	350	5.4	1.91	11.8

various biochemical reduction–oxidation processes. According to the gas-chromatographic studies of quantitative composition of the emitted biogas (Fig. 12.3), the initial biochemical process after inoculation, in the absence of BAS, is characterized with the initial hydrogen evolution, which contents in the emitted gas is gradually increasing, reaching the maximum of 7−10 % in 4−6 days.

Then, the biohydrogen contents starts to decrease, and carbon monoxide (CO) appears in the biogas composition. Its contents also reaches the maximum (about 7 %) in 9−11 days from the process beginning. Only on the third stage of the process (in 10−12 days), with the decrease in H_2 and CO contents, the methane appears in biogas composition. Then, the methane contents in biogas is gradually growing and in 16−20 days is stabilized on the level of 58−62 %. BOD values in bioreactors are thus decreasing from 23200 to 2800 mg O_2/l.

These processes occur under the anaerobic conditions on the first (acetogenic) stage, and are associated with the formation of intermediate fermentation products—pyruvate, formate, acetaldehyde and pyridine nucleotides (NAD(PH)H_2). As a result, the microorganisms consortium is capable to reduce the protons during the fermentation, getting rid of the excessive reducer. Consequently, hydrogen and CO_2 emission proceeds, following the schemes [11]:

$$\begin{aligned}&\text{Piruvite} \rightarrow \text{Acetyl} - \text{CoF} + CO_2 + H_2\\&\text{Formiate} \rightarrow CO_2H_2\\&\text{Acetaldehyde} \rightarrow \text{Acetate} + H_2\\&\text{NAD(PH)}H_2 \rightarrow \text{NAD(PH)} + H_2\end{aligned}$$

Hydrogen emission is thus catalysed with two enzymes: hydrogenase and specific CO-hydrogenase, acting in common. Therefore, in the absence of the final electrons' acceptor (oxygen, nitrates and nitrites, etc.), emission of carbon monoxide (CO) begins. To ensure the occurrence of these anaerobic fermentation reactions, the bacteria consortium uses organic substances. According to [6], this bacteria consortium involves 25 % of known bacteria species, among them *Escherichia coli*, and also pathogenic for humans bacteria such as *Salmonella.* Along with the hydrogen release, a part of the energy evolved during the organic matter fermentation, is consumed for the formation of other secondary products, such as acetic acid, which causes the pH shift to the acidic area.

One of the main biochemical reactions, connected with the hydrogen release, is based on the one-stage conversion of carbon monoxide (CO) into carbon dioxide: $CO + H_2O \rightarrow CO_2 + H_2$. With the evolution of biochemical process, the amount of CO released in the composition of biogas is reducing, up to its complete absence, due to its interaction with water molecules.

Then, with the development of methanogenic bacteria and their vital activity, the methanogenic transformation of CO_2 and water molecules and other intermediates occurs, with the release of methane, which yield becomes prevailing.

In methane formation processes, a limited number of substrates is used by bacteria, the most important of them being acetate (up to 75 %), and also carbon dioxide, formate, methanol, methylamines, carbon monoxide. The processes thus running can be presented as follows [12]:

$$\begin{aligned}
&CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O\\
&4\,HCOO^- + 4\,H^+ \rightarrow CH_4 + 2\,H_2O + 3\,CO_2\\
&4\,CO + 2\,H_2O \rightarrow CH_4 + 3\,CO_2\\
&CH_3COO^- + H^+ \rightarrow CH_4CO_2\\
&4\,CH_3OH \rightarrow 3\,CH_4 + CO_2 + 2\,H_2O\\
&4\,CH_3NH_3^+ + 2\,H_2O \rightarrow 3\,CH_4 + CO_2 + 4\,NH_4^+\\
&2\,(CH_3)_2NH_2^+ + 2H_2O \rightarrow 3\,CH_4 + CO_2 + 2\,NH_4^+\\
&4\,(CH_3)_3NH_3^+ + 6\,H_2O \rightarrow 9\,CH_4 + 3\,CO_2 + 4\,NH_4^+
\end{aligned}$$

The other carbon compounds do not support the growth of methanogenic bacteria. These bacteria transform into the methane up to 90–95 % of used carbon, the other part is consumed for the biomass growth. The microorganisms are specialized with regard to the types of the substances converted: bacteria *Methanobacterium halophilous* and *Methanobacterium uliginosum* are involved in the conversion of H_2, CO_2 and formate, whereas in the conversion of methanol, acetate and methylamines, bacteria *Ms.barkeri and Ms.vacuolata* are participating. All the methanogenic bacteria have cellular walls, formed with the protein subunits. They are very different from the other microorganisms by composition of electron transporters and co-enzymes, as well as by the metabolism specifics.

Effect of BAS on methanogenesis. Betulinol and squalene favor the intensification of anaerobic fermentation of the organic distillery grains, and, as a consequence, promote the increase in total biogas yield, and in some cases—increase in methane contents in biogas (Fig. 12.4). Use of betulinol (reactant—betulin) makes it possible to reach 3–4 times increase in the gas release rate, as well as that of the methanogenesis efficiency. At the same time, the extract of amaranth (reactant—squalene) did not manifest any pronounced influence on the biochemical process rate, however, which is important, it caused the increase in the share of methane in the biogas composition from 65–70 % to 90–95 %. Therefore, it was of special interest to study the effect of the BAS mixture on the methanogenic process.

According to the experimental data (Fig. 12.4), introducing of the mixture of additives provides 2.5–3-times increase of the biogas release rate. Methane contents in biogas thus increases from 58–60 % in case of control, and up to 90–92 % for the variants in which the mixture betulinol + squalene was used. BAS make it possible to obtain practically the same biogas volume, as in case of

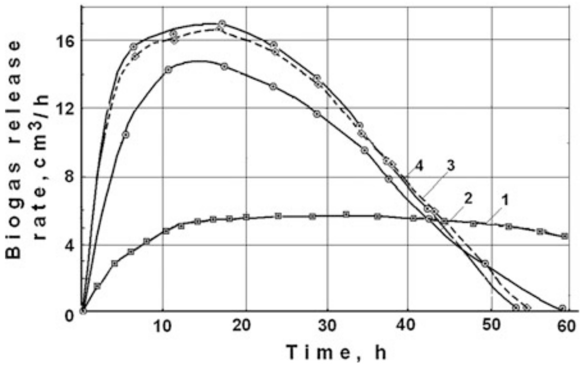


Fig. 12.4 The rate of the methane-containing biogas evolving in dependence on the BAS concentration (betulinol + squalene 1:1): *1*—control; *2*—2.5 mg/l; *3*—5.0 mg/l; *4*—10.0 mg/l

control, but 3.7 times faster. The 4-times increase in the rate of biogas release is thus reached. An increase in BAS concentration above 5.0 mg/l of grains is not accompanied with the increase in the gas producing rate and methanogenesis intensity, therefore is not reasonable.

It is to be noted, that use of the mixture betulinol + squalene is not only reducing the *lag*-phase and activating the rapid growth of microbial community in bioreactors, but also essentially shortens the stationery phase of its development. This promotes the acceleration of biochemical methanogenic processes, increase in the biogas yield and makes it possible to utilize the waste more quickly.

From the practical point of view, this makes for the possibility to reduce the capital and operational costs for the construction of bioreactors and waste water treatment plants as a whole.

Effect of BAS on microorganisms and dehydrogenase activity. As it is known, the biomass and extracts of the various plant species, specifically lavender, goldenrod, milfoil, morning-glory, amaranth render the stimulating effect on the methane-forming microorganisms.

It is assumed that BAS promote the intensification of the anaerobic fermentation of the organic substrate due to their antioxidant, antimutagenic and antihypoxant biochemical activities. BAS stabilize the cellular membranes of microorganisms, decrease the peroxide oxidation of lipids and prevent the damage of cellular membranes. Equally important is the fact that the protein of amaranth leaves, with respect to its amino acid composition, is similar to the ideal protein and has a high nutritional value. The perspectives of the nutrition media preparation on the basis of amaranth for the microorganisms cultivation are discussed in the scientific literature.

It was shown that squalene and betulinol 2.2–2.4 times stimulate the heterotrophic aerobic bacteria growth and reproduction (Fig. 12.5). This can activate the aerobic stage of wastes treatment and improve their preparation for methanogenesis. These results suggest indirectly the existence of the mechanism of biologically active impact of these substances on microorganisms.

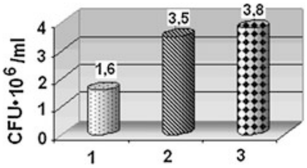


Fig. 12.5 Stimulation of heterotrophic bacteria growth in the bench-scale bioreactors: *1*—control; *2*—squalene 0.0005 %; *3*—betulinol 0.0005 %

The mechanism of energy processes of methanogenesis has not been decoded yet; however, the general principal regulations were established. Obtaining of the energy, at least during the oxidation of H_2, conjugated with the reducing of CO_2, is associated with the functioning of electron-transfer system, including dehydrogenases, electrons and reductase carriers. Hydrogenase and formiatdehydrogenase have been identified as dehydrogenases (Fig. 12.6).

In this way, microbiological testing of various BAS types has demonstrated the stimulating effect of amaranth and betulinol in concentration of 0.033 %, with regard to dehydrogenases' activity (Fig. 12.6). Amaranth activated dehydrogenases by 25 %, and betulinol—1.8 times. Their application was estimated as being perspective. However, hypsozide, like other selected additives (spirostan, *β*-cresol), has inhibited this process. So, amaranth and betulinol have been recognized as being the perspective additives.

The study of the biogas composition, formed in the process in which the bioactive additives (hypsozide and spirostan) were used, has shown that the biologic transformation of the organic matter is shifted to the area of hydrogen release in the gas phase. During the research period (24 days) neither CO, nor methane have been detected in the composition of the evolving gas.

Specifics of the BAS effect on biohydrogen release. Considering the character of BAS effect on dehydrogenase activity, the studies of the processes in the presence of the additives inhibiting the methanogenic processes of biochemical emission of hydrogen, were carried out. These are of practical importance for the development of biohydrogen power engineering.

As follows from the experimental data obtained (Fig. 12.7), the contents in hydrogen was increasing within the first 10 days and reached 67.8 и 40.2 % in the presence of the additives of hypsozide and spirostan, accordingly. It should be noted, however, that hydrogen release does not result in COD decrease. During 24 days COD value has changed from 23200 to 19500 mg O_2/l. The estimate of

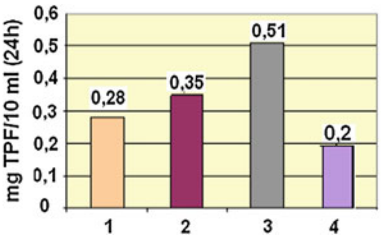


Fig. 12.6 Effect of BAS on dehydrogenase activity in the distillery grains: *1*—control; *2*—squalene 3.3 × 10^{-2} weight %; *3*—betulinol 3.3 × 10^{-2} weight %; *4*—hypsozide 3.3 × 10^{-2} weight %

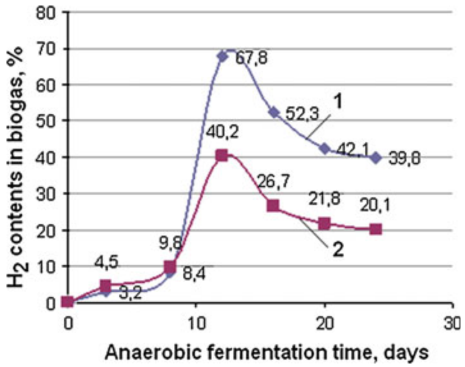


Fig. 12.7 Change in hydrogen contents in biogas in the presence of BAS, 5×10^{-3} mass %. *1*—hypsozide; *2*—spirostane

the released hydrogen balance and the organic compounds in biomass has clearly indicated, that hydrogen detachment occurs not only as a result of biochemical destruction and mineralization of organics, but due to the involvement of hydrogen atoms from water molecules in this process.

Explanation of the mechanism of bioactive additives action, having the isoprenoid molecular structure, is probably associated with the selective inhibition of methanogenic bacteria activity, which suppressed the dehydrogenase activity. Therefore, hydrogen, which in the absence of BAS is used by the methanogen for methane release, is re-oriented to the release in the molecular form.

The inhibiting capacity of the proposed isoprenoid compounds as stabilizers of biohydrogen process can be explained by the strongly unsaturated bonds in molecules. For their molecular structure the presence of double bonds is typical (up to two-three double bonds in the molecules of monoterpenoids, up to seven-eight—in the tetraterpenoids (carotenoids). Another specific feature is the variety of cyclic structures: from one cycle up to 5–6 cycles in the molecular structure in different combinations: coupled, condensed, ternary-, pentamerous- and hexamerous cycles, and oxygen-containing heterocycles.

Another specifics of the isoprenoids molecular structure is a combination of various functional groups and structure groupings (such as a spirochetal grouping in steroid sapogenines) within one and the same molecule. Due to the such variety of chemical structural elements, the proposed BAS belonging to the isoprenoid substances of vegetable origin, play the role of oxygen and electrons carriers in the biochemical processes. They also act as membrane-acting agents, favoring to the change in the microorganisms' membrane permeability and electric potential. In its turn, the change in the cellular membranes permeability causes the violation of homeostasis of microorganisms' cells. As a result, some organelles and enzymes lose their functions and suspend the hydrogenases functioning and inhibit the methanogeneses during the methanogenic fermentation. Therefore, the methane formation is re-oriented to the conversion of CO and H_2O for the release of the molecular biohydrogen. That is why 20 % of biomass only is used in the conventional biohydrogen technology.

As water is the main source of the produced biohydrogen, up to 80 % of biomass is not used in this process. So, from the practical viewpoint, the two-stage biochemical fermentation process is more advantageous: on the first stage the stable process of biohydrogen must be realized in a separate bioreactor, whereas on the second stage, in order to use the biomass' energy more completely, the operation of next bioreactor should be switched to the methanogenic biochemical process of biomethane generation, following the conventional technology.

In this way, the BAS (specifically, vegetable substances of isoprenoid nature), introduced in the biomass, make it possible to reduce selectively the dehydrogenase activity, to inhibit the activity of methanogenic microorganisms and prevent the possibility of fermentation transformation into the methanogenesis, suppressing its development. Under these conditions, fermentation process will be selectively switched to the reactions, connected with the biochemical interaction of the initially formed CO with water molecules, following the scheme: $CO + H_2O \rightarrow H_2 + CO_2$, as well as the other reactions, which determine the predominant release of biohydrogen. Due to the methanogenesis inhibition, methane release stops practically completely. Water is a main source of the produced hydrogen, and in the lesser degree—organic substrate.

In the overall biochemical process under these conditions, hydrogen, which is not used by methanogenes, is molized and emitted in the free molecular form (H_2) in large amounts. Moreover, under these conditions a part of the microorganisms' consortium, responsible for the biochemical release of hydrogen, start working more intensively, thus promoting the overall efficiency increase of these processes.

As a result, the efficiency of biochemical generation of the molecular biohydrogen is increased, along with the enhancing of its yield in biogas' composition. Its biochemical production can be made cheaper, provided the organic substrates of agricultural wastes are used, including the winery and distillery grains. Stabilization of hydrogen release in this case can be reached by the maintaining of the proposed BAS concentration on specified level.

One of the specifics of biohydrogen technology is that the released molecular hydrogen obstructs the work of microorganisms in bioreactor. This means that during the reactors design, the measures are to be taken to ensure the intensive mass-exchange and mass-transfer and permanent removal of biohydrogen from the reactor.

The produced biohydrogen (50−70 %-contents in biogas) and CO_2 can be used without the special treatment as the efficient energy agent for generating of heat and electric energy in the industrial co-generation plants. These products can also be used as a gas fuel in vehicles, and as a raw material in chemical industry. Biohydrogen obtained could be used as well for the other scopes, including in the fuel elements for power-supply of the apartment blocks [13–15].

However, since the development of the industrial biohydrogen technology is currently still on the initial stage, in order to ensure its broader application, it is necessary to consider the development of the related technologies of its using, including its purification from the admixture gases, systems of storage, transportation, etc.

12.4 Conclusions

1. The problem of winery and distillery liquid wastes utilization can be resolved due to the elaboration of ecologically friendly technologies of anaerobic fermentation. The increase in the biogas formation efficiency with higher contents in biomethane, from vegetable raw materials and agricultural processing wastes, can be achieved by using of biologically active substances of natural origin.
2. The proposed technology of grains anaerobic fermentation is based on neutralization of acid wastes up to $pH = 7.0-7.2$ and using of biologically active substances as additives stimulating the methanogenesis.
3. It was found that use of betulinol and amaranth extract in the ratio 1:1 and in concentrations $5.0 \times 10^4 \ldots 1.0 \times 10^{-3}$ weight % is an efficient way to accelerate the methanogenic processes. These substances increase the dehydrogenase activity, reduce the lag-phase, activate the exponential growth of microbial community and essentially shorten the stationery phase of its development. Application of betulinol and amaranth extract mixture increase of the biogas yield in 2.5–3 times, increase the methane contents in it from 58–60 % to 90–92 %. This makes it possible to utilize the winery wastes more efficient and rapid and prevent its discharges into the environment and penetration into the natural water bodies.
4. Betulinol, amaranth extract and hypsozide are capable to stimulate the growth of heterotrophic bacteria. This can be used on aerobic stage of liquid distillery and winery wastes utilization and improve their preparation to the anaerobic digestion. The mechanism of the biologic effect of additives on methanogenesis and on microorganisms is discussed.

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