MONITORING OF AQUATIC ECOSYSTEMS BASED ON BIOLOGICAL PARAMETERS

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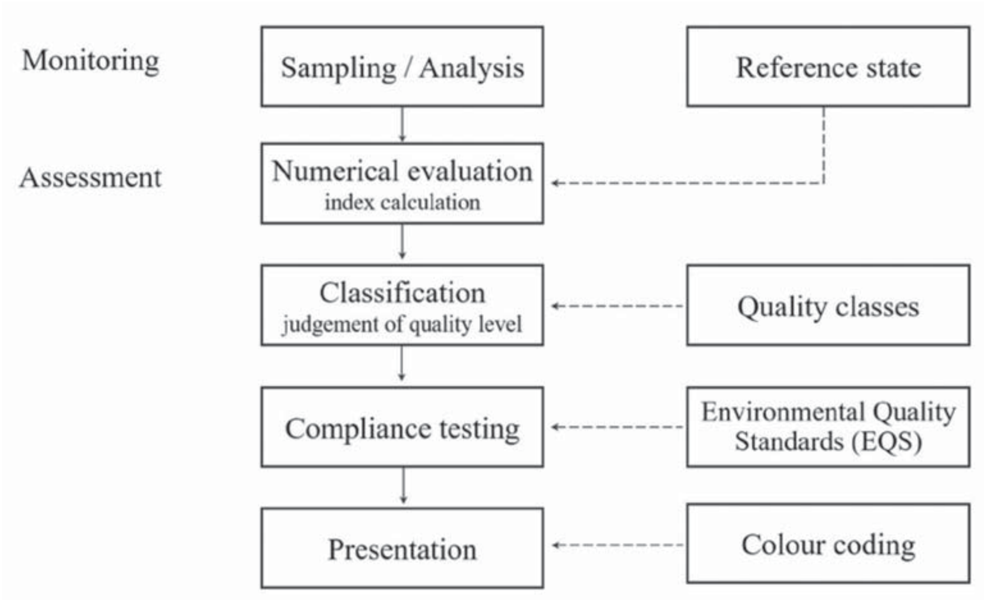
The composition of surface waters is dependent on natural factors (geological, meteorological, hydrological and biological) in the drainage basin and varies with seasonal differences in runoff volumes, weather conditions and water levels. Human intervention also has significant effects on water quality. Some of these effects are the result of hydrological alterations, such as the building of dams, flow regulation, draining of wetlands. Deterioration of water quality due to its use in human economic activities (discharge of domestic and industrial wastewaters, use of chemicals on agricultural land in the drainage basin) has such detrimental consequences as: harm to biological resources of water bodies, danger to human health, obstacle to water sports and recreation.

The main elements of *Aquatic Ecosystem Monitoring* are: on-site measurements, collection and analysis of samples, study and evaluation of the analytical results to assess spatial and/or temporal variations in water quality. The results of analyses performed on an instantly sample are only valid for the particular location and time at which that sample was taken. One of the monitoring purposes is *Water Quality Assessment*, which is the process of assessing the physical, chemical and biological state of water body in relation to natural quality, human impact and intended uses, particularly uses which may affect the functioning of the aquatic ecosystem itself.

In contrast to the chemical quality of water bodies, which can be measured by suitable analytical methods, the assessment of the biological state of aquatic ecosystem is a combination of quantitative and qualitative characteristics (parameters). Biological monitoring can generally be carried out at two different levels: the response of individual species to changes in their environment or, the response of biological communities to changes in their environment. The main elements of biological monitoring are the following [1]:



Environmental Quality Standards (EQS) are limit values of concentrations of the specific chemicals released by human activity, that have been established (Directive 2000/60/EC, Annex VIII; Directive 2008/105/EC, Annex I) to protect the environment and human health. Some standards are legally enforceable numerical limits in the EU, such as *Quality Standards for Priority Substances* under the Water Framework Directive. Others are not mandatory, but are contained in guidelines and codes of practice, as is the case for many soil and waste related limit values. According to the WFD, *ecological status* of rivers and natural lakes is classified by five classes, which correspond to the following categories: «High», «Good», «Moderate», «Poor» and «Bad», but all of these can only be used for biological parameters [2]. For general physico-chemical parameters, three categories are used: «High», «Good» and «Moderate». For heavily modified and artificial water bodies, three categories of *ecological potential* are used: «Maximum», «Good» and «Acceptable» (Fig. 1). For chemical status, only two categories are recommended: «Good» and «Failing to achieve good» [3].

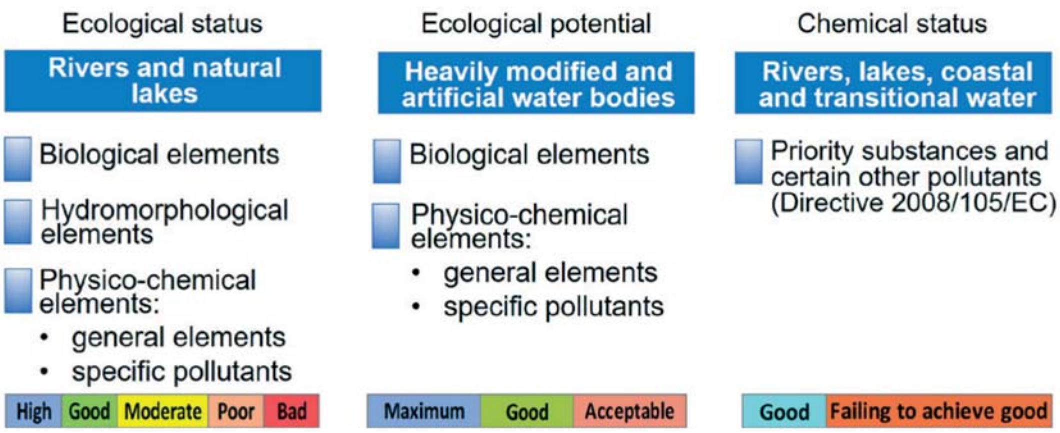


Fig. 1. Methodological approach to assessing the ecological or chemical status and ecological potential of surface water bodies within the framework of the EU water policy

Good chemical status means that no concentrations of priority substances exceed the relevant EQS established for surface waters in the Directive 2008/105/EC. These standards aim to protect the most sensitive species in aquatic ecosystems from direct toxicity of ubiquitous persistent, bioaccumulative and toxic substances (uPBT) identified in the Priority Substances Directive 2013/39/EU. The uPBTs are: mercury, brominated diphenyl ethers (BDE), tributyltin (TBT) and polycyclic aromatic hydrocarbons (PAHs). In the amended Water Framework Directive (Directive 2013/39/EU), the importance of bioaccumulation for assessing the chemical status of water bodies has already been recognized through the establishment of new environmental quality standards – EQS(biota). When assessing the chemical status of a water body, EQS(biota) is more relevant than EQS(water), since the concentrations of bioaccumulated and non-metabolizable substances accumulated in aquatic organisms differ from their concentration in the habitat. Implementing the ecotoxicological monitoring for compliance with these new EQS(biota) is one of the challenges for the EU member states in the near future (Table 1).

Table 1. EQS for priority substances and other substances relating to chemical status [3]

Substance	CAS number	PhS*	AA-EQS in µg/L	MAC-EQS in µg/L	Biota EQS in µg/kg wet weight
			watercourses and lakes		surface waters
Heavy metals					
Lead (Pb) and its compounds	7439-92-1		1,2	14	
Cadmium (Cd) and cadmium compounds	7440-43-9	X	≤ 0,08 (cl..1) 0,08 (cl. 2) 0,09 (cl. 3) 0,15 (cl. 4) 0,25 (cl. 5)	≤ 0,45 (cl..1) 0,45 (cl. 2) 0,60 (cl. 3) 0,90 (cl. 4) 1,50 (cl. 5)	
Nickel (Ni) and its compounds	7440-02-0		4	34	
Mercury (Hg) and its compounds	7439-97-6	X		0,07	20
Industrial pollutants					
Anthracene	120-12-7	X	0,1	0,1	
Benzene	71-43-2	X	10	50	
Brominated diphenylether (BDEs)	32534-81-9	X		0,14	0,0085
Di(2-ethylhexyl) phthalate (DEHP)	117-81-7	X	1,3	N.a.	
C_{10-13} chloroalkanes	85535-84-8		0,4	1,4	
1,2-Dichloroethane	107-06-2		10	N.a.	
Dichloromethane	75-09-2		20	N.a.	
Hexabromocyclododecane (HBCDD)	3194-55-6	X	0,0016	0,5	167
Fluoranthene	206-44-0		0,0063	0,12	30
Hexachlorobenzene (HCB)	118-74-1	X		0,05	10
Hexachlorobutadiene	87-68-3	X		0,6	55
Naphthalene	91-20-3		2	130	
Nonylphenols (4-Nonylphenol)	84852-15-3	X	0,3	2,0	
Pentachlorobenzene	608-93-5	X	0,007	N.a.	
Pentachlorophenol	87-86-5		0,4	1,0	
Benzo(α)pyrene	50-32-8	X	$1{,}7 \times 10^{-4}$	0,27	5

Tetrachloroethylene	127-18-4		10	N.a.	
Carbon tetrachloride	56-23-5		12	N.a.	
Trichlorobenzenes	12002-48-1		0,4	N.a.	
Trichlorethylene	79-01-6		10	N.a.	
Trichloromethane	67-66-3		2,5	N.a.	
Pesticides					
Alachlor	15972-60-8		0,3	0,7	
Atrazine	1912-24-9		0,6	2,0	
Chlofenvinphos	470-90-6		0,1	0,3	
Chlorpyrifos (chlorpyrifos-ethyl)	2921-88-2		0,03	0,1	
DDT total	N.a.		0,025	N.a.	
Para-para DDT	50-29-3		0,01	N.a.	
Diuron	330-54-1		0,2	1,8	
Cyclodiene pesticides:					
total of aldrin	309-00-2		$\Sigma = 0,01$	N.a.	
dieldrin	60-57-1				
endrin	72-20-8				
isodrin	465-73-6				
Endosulfan	115-29-7	X	0,005	0,01	
Hexachloro-cyclohexane (HCHs)	608-73-1	X	0,02	0,04	
Isoproturon	34123-59-6		0,3	1,0	
Simazine	122-34-9		1	4	
Tributyltin compounds (TBT)	36643-28-4	X	0,0002	0,0015	
Terbutryn	886-50-0		0,065	0,34	
Trifluralin	1582-09-8		0,03	N.a.	
Dicofol	115-32-2	X	$1,3 \times 10_{-3}$	N.a.	33
Perfluorooctane sulfonic acid and its derivatives (PFOS)	1763-23-1	X	$6,5 \times 10^{-4}$	36	9,1
Quinoxyfen	124495-18-7	X	0,15	2,7	
Heptachlor	76-44-8	X	2×10^{-7}	3×10^{-4}	$6,7 \times 10^{-3}$

*PhS: Priority hazardous substance; AA-EQS: annual average EQS; MAC-EQS: maximum allowable concentration; N.a.: not applicable

General approaches to the analysis of chemicals in biota today are based on modern analytical methods such as mass spectrometry or liquid/gas chromatography. The most common standard method to quantify the total content of trace metals and metalloids in organisms is microwave acid digestion followed by inductively coupled plasma mass spectrometry (ICP-MS). For some analytes, like mercury, direct quantitative methods are available (e.g. cold vapor atomic absorption spectrometry method, CV-AAS). Coupling ICP-MS to an electrothermal vaporization unit (ETV) is an alternative approach for multielement analyses. In the ETV, the sample is vaporized within seconds by heating in a graphite furnace up to approximately 2,000°C. Advantage of the direct method, combined with high sensitivity of the ICP-MS, is direct transfer of a dry aerosol to the plasma (no oxygen-based interferences from water).

The list of chemical compounds that are often called as *emerging substances* is constantly growing. Insufficient information about their impact or inadequate performance of the analytical method for quantifying its level of occurrence in the environment do not allow an emerging substance to be correctly evaluated and may lead to its being overlooked if conventional prioritization methodologies are applied. In order to evaluate the risk of a chemical compound or to determine its priority in the context of other pollutants, ecotoxicity threshold values (*Predicted No-Effect Concentrations* = PNECs) can be used. For systematic collection of ecotoxicity studies and harmonised derivation of environmental quality standards, the NORMAN Network of reference laboratories, research centres and related organisations was established in 2009 for monitoring of emerging environmental substances (www.normannetwork. net). The expert group of the NORMAN Network organises the development and maintenance of various databases for the collection and evaluation of information on emerging substances in the environment. The PNECs derived by this expert group are based on the raw ecotoxicity data. Ecotoxicity threshold values of the PNECs were used in the chemical screening of the Dniester river's water, sediment and biota, that was realized in the framework of the Moldovan-Ukrainian project «*Enabling transboundary cooperation and integrated water resources management in the Dniester River Basin*». Screening covered the most common substances in the environment such as pesticides, pharmaceuticals, personal care products, flame retardants, food additives, illicit drugs, industrial chemicals, etc. The result is displayed in the pie chart (Fig. 2), where the highest percentage belongs to pesticides and pharmaceuticals (in both cases some of them exceeded their PNEC values).

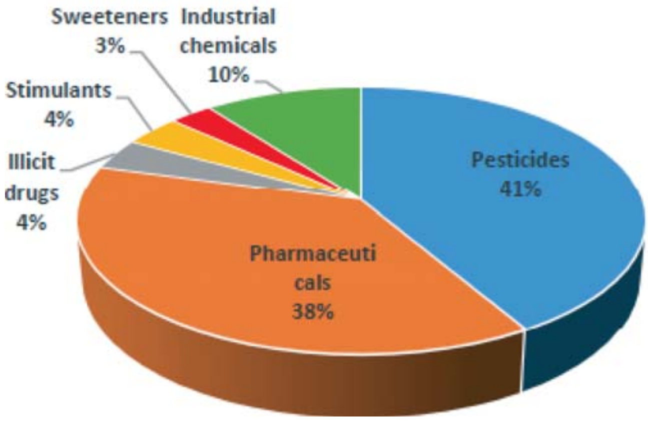


Fig. 2. Percentage of pollutants in the Dniester River Basin [4]

Scientifically based field expedition planning and collection of representative samples are critical in ensuring the reliability of monitoring results for any ecosystem. Non-representative results can be obtained if: 1) the samples were taken in the wrong place, 2) sampling was carried out at the wrong time, 3) the type of samples (sampling technique) does not correspond to the monitoring purpose. Therefore, the sampling of each type of biological quality elements (bacterioplankton, periphyton, phytoplankton, zooplankton, phyto- and zoobenthos, macrophytes and fish) has its own characteristics, methods and requirements. Each of these groups of aquatic organisms has its own biomarkers and bioindicators, the specific reaction of which to changes in the habitat allows us to assess the degree of anthropogenic load.

The consequence of anthropogenic pressures on the environment (unlimited use of natural resources, emissions and discharges of pollutants) is the deterioration of the habitat (including climate change) both for human itself and for other living organisms, the biodiversity of which is rapidly decreasing. Natural self-purification of surface water bodies is a multifactorial process (Fig. 3), in which all factors are interrelated and interdependent [5]. The most vulnerable component is the biological one, therefore, a decrease in biodiversity, destruction of biotopes and change in hydromorphological characteristics lead to disruption of the self-purification mechanisms of water bodies and watercourses.

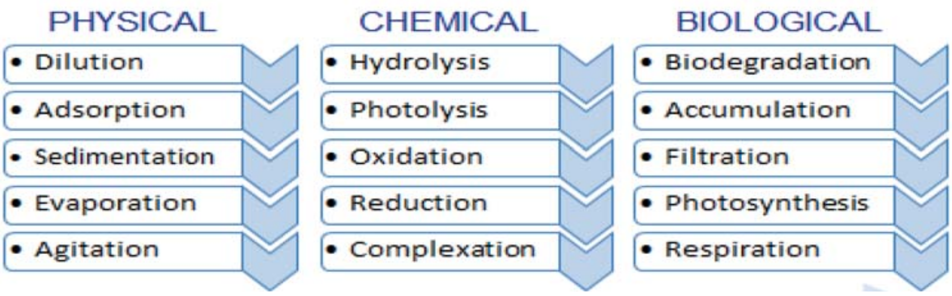


Fig. 3. The main factors that ensure self-purification of the river ecosystem

All aquatic organisms participate in the biological self-purification of water bodies. However, the main role belongs to aquatic microorganisms, as well as omnivorous and bacterivorous protists, the quantitative and qualitative composition of which depends on the hydrological season, the structure of hydrobionts communities, the amount and composition of biogenic elements, organic compounds and toxic substances in water. It should be noted that neither bacterioplankton nor zooplankton are included in the group of biological elements of the WFD classification system of water bodies. However, some countries (Ukraine, Belarus, Russia, as well as the Republic of Moldova), at the level of their national regulations, take into account the quantitative and qualitative parameters of these groups of hydrobionts to assess the quality of surface waters (Table 2).

Table 2. Bacterioplankton parameters regulated for surface waters quality in the Republic of Moldova [6]

Hydrobiological parameters	Units	Water Quality Class				
		I	II	III	IV	V
Total number of bacteria	million cells/ml	1,0	2,0	5,0	7,5	>7,5
Number of saprophytes, 22°C	thousand cells/ml	0,5	2,5	5,0	7,5	10

Conclusion

Methods for assessing biological quality elements in inland surface waters are sensitive to several types of significant impacts. However, there are no methods for assessing biological quality elements that are sensitive to chemical pollution, hydrological changes, acidification or salinization, even if these effects are significant. Thus, an assessment of the ecological status is an assessment of the functioning of the aquatic ecosystem as a whole. The processing and analysis of community-level research data is suitable for assessing the water quality, since biomarkers and bioindicators can be useful for investigating the causes of habitat disturbances.

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Bibliography

1. Water Quality Assessments – A Guide to Use of Biota, Sediments and Water in Environmental Monitoring – Second Edition. Edited by Deborah Chapman. London, 1996.
2. Guidance Documents no. 10 Rivers and Lakes – Typology, Reference Conditions and Classification Systems. Luxembourg: Office for Official Publications of the European Communities, 2003.
3. Directive 2013/39/EU amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. Official Journal of the European Union, L 226, 24.8.2013.
4. Research on identification of chemical status of surface water bodies of the Dniester river basin. Final report. Environmental Institute, Slovakia, 2019.
5. Ostroumov S.A. Biomachinery for maintaining water quality and natural water self-purification in marine and estuarine systems: elements of a qualitative theory. International Journal of Oceans and Oceanography Vol.1, No.1 (2006).
6. Regulation on quality requirements for surface waters. GD RM no. 890. Chisinau: Official Monitor of the Republic of Moldova no. 262 – 267, November 22, 2013.