



LEARNING TOXICOLOGY
THROUGH OPEN EDUCATIONAL
RESOURCES

ENVIRONMENTAL QUALITY WATERS MONITORING

Camelia DRAGHICI, Ileana MANCIULEA

Transilvania University of Braşov

c.draghici@unitbv.ro, i.manciulea@unitbv.ro



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1. INTRODUCTION

The presentation bellow is part of the Module 6, Topic 4, as additional information related to Unit 2.

This unit / course presents:

- specific sampling and sample pre-treatment requirements for water samples;
- standard analytical methods available for pollutants determination present in waters;
- EU regulations concerning the assessment of water quality.

At the end of the course, students will be able to:

- describe how can be determined the quality indicators / pollutants that are present in waters;
- use the available regulation containing the quality indicators of natural waters and the available analytical methods.

2. SAMPLING FOR WATER QUALITY MONITORING

Samples of Interest

The type of samples of interest for water quality monitoring are the natural waters, both groundwater (sometimes sediments too) and surface waters, including flowing waters (from springs to great rivers) as well as lakes, seas, oceans, even glaciers.

A special category are the transitional and coastal waters, given the multinational implications of the pollution along these waters.

Of less interest for this course are the wastewaters, which are liquid emissions, when released in the environment.

Representativeness of Water Samples

The need to ensure the representativeness of water samples is known. Surface and groundwaters may have variations in composition depending on seasons (dry or wet), on recent precipitation (pollutant dilution), and on water consumption.

The composition of surface water also depends on water stream flow, or on stratification phenomenon, that occurs in oceans, seas and deep lakes, or when two streams of water merge, especially when fresh waters are joining salty waters.

Amount of Water Sample

The amount of surface water and groundwater sample must be sufficient to ensure both the laboratory analysis and the requirements for quality assurance and quality control (QA/QC) tests. Usually, up to 20-40 L of water are up-taken.

Water Sampling Instruments

Of great importance for the water preservation are the sampling instruments, weighted / graduated bottles, thus, for different water samples are used different containers, flasks:

- colourless bottles chemically resistant (Pyrex glass) are used for organic compounds determination (Figure 1.a);
- polyethylene containers are used for inorganic compounds determination (Figure 1.b);
- special tubes are required for groundwater sampling (Figure 1.c), with peristaltic and submersible pumps pipes.

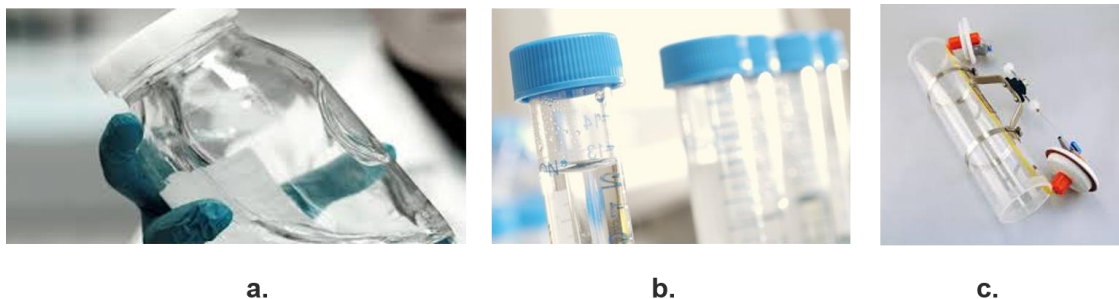


Figura 1. Containers used for water sampling: a. Pyrex glass; b. polyethylene flasks; c. sampling tubes.

Sample Preparation Techniques

The sample preparation techniques have already been presented in Module 6 Topic 3, Unit 2.1.

For this unit, two examples of water sample preparation were selected:

- samples designed for the determination of *heavy metals cations* dissolved in waters are pre-treated based on: precipitation, ion exchange or chelation and extraction;

- samples designed for the analysis of *semi-volatile and non-volatile organic compounds* are pre-treated based on: liquid-liquid or solid-phase extraction is used.

3. WATER POLLUTANTS DETERMINATION

Two important European Union Directives regulate the water quality monitoring:

- Directive 2000/60/EC establishing a framework for Community action in the field of water policy; it is known as EU Water Framework Directive, or even shorter as WFD;
- Directive 2009/90/CE establishing the technical specifications for chemical analysis and monitoring of water status.

Surveillance monitoring involves the following indicatives:

- parameters indicative of all biological quality elements;
- parameters indicative of all hydromorphological quality elements;
- *parameters indicative of all general physico-chemical quality elements*, these being of interest for this course.

3.1. WATERS QUALITY PARAMETERS

Several water quality indicators were selected to be presented. Table 1. presents groups of indicators to be monitored as well as the units in which the monitoring result is expressed.

The indicators are grouped according to their common characteristics in:

- indicators that provide information on *oxygenation conditions*: dissolved oxygen, chemical oxygen demand (COD), and biochemical oxygen demand (BOD);
- indicators that provide information on the presence of *nutrients*, which may contribute to the phenomenon of eutrophication; nutrients are classes of substances that contain nitrogen atoms (ammonium, nitrates, nitrates, organic nitrogen compounds) or phosphorus atoms;
- *salinity* indicators: given by the general content of anions and cations;
- in the *pollutants of natural origin* category are included mainly the heavy metal cations;
- other relevant *indicators of organic origin* are phenols, anionic surfactants, absorbed organic halides (AOX).

Table 1. Water quality indicators.

Group of indicators	Water quality indicators	Unit
oxygenation conditions	dissolved oxygen, chemical oxygen demand (COD), biochemical oxygen demand (BOD)	mg O ₂ /L
nutrients conditions (contribute to eutrophication)	ammonia (NH ₄ ⁺), nitrates (NO ₂ ⁻), nitrites (NO ₃ ⁻), total nitrogen (N)	mg N/L
	orthophosphates (PO ₄ ³⁻), total phosphorus (P)	mg P/L
	chlorophyll A	µg/L
salinity (general ions)	dried filtrate residue at 105 ⁰ C, chlorides (Cl ⁻), sulphates (SO ₄ ²⁻), Ca ²⁺ , Mg ²⁺ , Na ⁺	mg/L
pollutants of natural origin	total Cr (Cr ³⁺ , Cr ⁶⁺), Cu ²⁺ , Zn ²⁺ , As ³⁺ , Ba ²⁺ , Se ⁴⁺ , Co ³⁺ , Pb ²⁺ , Cd ²⁺ , total Fe (Fe ²⁺ , Fe ³⁺), Hg ²⁺ , total Mn (Mn ²⁺ , Mn ⁷⁺), Ni ²⁺	µg/L
other relevant indicators	phenols, anionic surfactants, absorbed organic halides (AOX)	µg/L

Besides the chemical quality indicators established by the European Union regulations, there are other categories of interest for the water quality monitoring studies carried out in the framework of research projects, for research based monitoring. These pollutants are from different categories:

- soluble and insoluble compounds (suspensions);
- inorganic and organic compounds;
- with low molecular or high molecular weight.

For example, organic anions (acetate, formate) and persistent organic pollutants such as pesticides, polycyclic aromatic hydrocarbons (PAHs) or polychlorinated biphenyls (PCBs) are also studied.

3.2. ANALYTICAL METHODS FOR WATERS QUALITY PARAMETERS DETERMINATION

For all the water quality indicators, standards of analytical methods are available as European Norms (EN) or standards from ISO series, which are emitted by the International Standards Organization (ISO).

Table 2. gives a selection of the EN and ISO standards and the related analytical methods on which the standards are based for the determination of water quality indicators (selection).

Table 2. Water analysis – standard methods (selection).

Water quality indicator	Standard*	Analytical method
dissolved oxygen (DO)	EN 25813:2000/C91:2009	titrimetric
chemical oxygen demand (COD)	EN ISO 8467:2001	
biochemical oxygen demand (BOD)	EN 1899-1:2003	
total nitrogen	EN 25663:2000	
ammonia	EN ISO 11732:2005	
Cd, Ni, Cr, Pb, Cu, Co, Zn cations	EN ISO 15586:2004	atomic absorption spectrometry (AAS)
Ca, Mg cations	EN ISO 7980:2002	
Hg cations	EN ISO 12846:2012	
nitrate	EN ISO 13395:2002	molecular absorption spectrometry (UV-Vis)
nitrite	EN 26777/C91:2006	
total cyanide	EN ISO 14403-1:2012	
total phosphorus	EN 6878:2005	
anionic surfactants	EN 903:2003	
Br ⁻ , Cl ⁻ , F ⁻ , nitrate, nitrite, phosphate, sulphate	EN ISO 10304-1:2009	liquid chromatography (LC / IC)
Li ⁺ , Na ⁺ , NH ₄ ⁺ , K ⁺ , Mn ²⁺ , Ca ²⁺ , Mg ²⁺ , Sr ²⁺ , Ba ²⁺	EN ISO 14911:2003	
adsorbed organic halides (AOX)	EN ISO 9562:2005	gas chromatography (GC)

For example, titrimetric methods are used to determine the oxygen, total nitrogen or ammonium ion indicators. Cations of heavy metals are determined by atomic absorption spectrometry. Some of the inorganic anions and anionic surfactants are determined by UV-VIS molecular absorption spectrometry. Generic ions, (anions and cations) can be determined by liquid chromatography and ion chromatography, while gas chromatography is applied to determine adsorbed organic halides.

Similar to the air samples analysis, besides the standard analytical methods, used according to the regulations for certain water quality parameters, other non-standard analytical methods for any pollutant of interest are also available and accepted in the laboratory practice. Both categories of analytical methods are subject to method validation and laboratory accreditation, according to the ISO/IEC 17025:2005, with the recent revision, ISO/IEC 17025:2017.

In this respect, Directive 2009/90/EC provides that: Member States shall ensure that all methods of analysis, including laboratory, field and on-line methods, used for the purposes of chemical monitoring programmes carried out under Directive 2000/60/EC are validated and documented in accordance with EN ISO/IEC-17025 standard or other equivalent standards accepted at international level.

To exemplify, Table 3. gives examples of analytical methods and techniques available for the determination of heavy metals from environmental samples (Draghici 2011).

Table 3. Heavy metals determination from environmental samples.

Methods and techniques	Symbol	Single- / multielement analysis	Applications
Optical techniques			
atomic absorption spectrometry	AAS	single- / multielement	-widely used method -standard method
inductively coupled plasma – atomic emission spectrometry	ICP - AES	simultaneous multielement	-widely used method -environmental trace analysis

inductively coupled plasma – mass spectrometry	ICP - MS		-widely used method -also used for isotope determination
neutron activation analysis	NAA		-most elements -some with limitation (Pb)
atomic fluorescence spectrometry	AFS		-mercury, arsenic, and selenium
molecular absorption spectrometry			-speciation analysis (Cr, As, Se, Sn, Hg, and Pb)
Separation techniques			
gas chromatography	GC	simultaneous multielement	-volatile or thermally stable compounds of Hg, Sn, Pb
liquid chromatography	LC		-speciation analysis (Cr, As, Se, Sn, Hg, and Pb)
ion chromatography	IC		-metallic cations
capillary electrophoresis	CE		-metallic cations -oxoanions of As, Se -organic metallic compounds
Electrochemical techniques			
electrochemical techiques		consecutive analysis of metallic ions	-speciation analysis (Cr, As, Se, Sn, Hg, and Pb)
Biochemical techniques			
immuno chemical technique		single-element	-any pollutant for which a suitable antibody can be generated

All these methods and techniques are used to determine metallic and metalloid compounds, present in different environmental matrixes. Some of the methods are especially applicable as single-element techniques (AAS, AFS, spectrometry,

immuno chemical methods), or as simultaneous multielement techniques (AAS, ICP–AES, ICP–MS, NAA, GC, LC, IC, CE). This characteristic may be considered an advantage or disadvantage, depending on the sample content and the analytical aim. Some of the methods and techniques are suitable to determine the cationic or oxoanionic forms of the heavy metal, and others for the organometallic forms. Speciation analysis of a particular element (metal) is also possible. Speciation analysis is important due to the fact that the concentration of toxic species is relevant in setting the environmental and ecological standards.

Other examples of analytical methods available for pollutants determination from different environmental matrixes are given in Table 4., containing separation techniques applied for pesticides analysis. In order to show the interest for method validation not only for routine laboratories, but also for research laboratories, the table also presents a selection of validation criteria that have been used in research publication (Draghici, 2013).

Table 4. Pesticides determination from environmental samples.

	Pesticides	Matrix	Analytical separation technique	Validation criteria							
				Selectivity	Repeatability	Interim precision	Recovery	Linearity	LOD	LOQ	Robustness
1	hexazinone, tebuthiuron, diuron	soil	HPLC-UV		√	√	√	√	√	√	
2	heterocyclic insecticides	waters (tap, lake)	HPLC-DAD		√		√	√	√		
3	fungicides; carbamates; organophosphorus	sludge	LC-MS	√	√		√	√	√	√	
4	pesticides	surface and ground-water	GC-MS		√	√	√	√	√	√	
5	procymidone	soil	GC-MS		√		√	√	√	√	
6	organophosphates	water	GC-MS		√		√	√	√	√	√
7	dimethomorph	soil	GC-ECD		√		√	√	√	√	
8	fenpropidin	soil	LC-MS/MS:				√	√	√		

Abbreviations: GC-ECD – gas chromatography-electron capture detector; GC-MS – gas chromatography-mass spectrometry; HPLC-UV – high performance liquid chromatography-UV detection; HPLC-DAD – high performance liquid chromatography-diode array detection; LC-MS – liquid chromatography-mass spectrometry; LC-MS/MS liquid chromatography-tandem mass spectrometry-mass spectrometry.

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<https://toxoeer.com>

Project coordinator: Ana I. Morales
Headquarters office in Salamanca.
Dept. Building, Campus Miguel de Unamuno, 37007.
Contact Phone: +34 663 056 665