Measurements of chemical parametres in Lower Danube area

In according with 2000/60 Framework Directive of the European Union, Integrated Water Resources Management Plan is based on watersheds Management Plan throughout Romania. According to the European insurance [the Water Framework Directive no. 60.2000], for surface water quality knowledge, a number of physical-chemical and chemical parameters have to be analysed. In order to determine the water quality and taking into account that a great number of physical, chemical and biological parameters can be determined using laboratory analysis, a small number of these practices that are considered to be more important are used. The most used analyses are:

- Flow condition: flow rate (Q);
- Thermal and acidification conditions: temperature (^{0}C), pH, total and permanent alkalinity, HCO_3^- concentration;
- Turbidity;
- Conductivity;
- Oxygen condition: dissolved oxygen content (DO), chemical oxygen demand (CCO-Mn or/and CCO-Cr), biochemical oxygen demand (CBO_5);
- Nutrients condition: NH_4^+cation concentration, NO_3^-, NO_2^-, PO_4^{3-} anions concentration;
- Salinity: total suspended matter, electrical conductivity, filterable residue, SO_4^{2-} and Cl^- anions concentration;
- Content of metals: sodium , potassium , iron , manganese , chromium , mercury , arsenic , selenium , cadmium , lead, zinc , copper, nickel, cobalt, aluminium, barium;
- Other relevant chemical indicators (such as the content of toxic substances, hazardous substances and priority hazardous substances): phenol, CN^-, detergents, petroleum ether extract, petroleum products.

For the Lower Danube, it was considered useful to measure and determine the following chemical parameters: pH, OD, COD, BOD, NH_4, N-NO_2^-, N-NO_3^-, N-total, P-PO_4, SO_4^{2-}, Cl^-, Cr^{6+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+}, Zn^{2+}, As^{3+}. Some physico-chemical analysis were performed in-situ: pH and dissolved oxygen were measured using the portable multiparameter Hanna HI 9828 equipped with a multi-sensor electrode (pH / ORP, EC, DO, temperature).

The thermal and acidification condition is characterized in the following analysis of chemical and physical-chemical parameters: the concentration of HCO_3^- anions, the total and permanent alkalinity, the temperature (T^0C) and pH.

Oxygen condition is referring at the analyses of those parameters that are related to the presence of oxygen and its consumption due to oxidable substances that may be presented in water.

The most important water quality parameter, considering rivers and lakes water, is represented by the content of dissolved oxygen (DO), due to its vital importance for aquatic ecosystems and self - cleaning.

Chemical oxygen demand is defined as being the oxygen amount necessary for total oxidation of organic matter that may exist in a sample of water. It is the principal quality parameter in surface water analysis and for treatment system of waste water.

Biochemical oxygen demand (CBO_5) represents the amount of oxygen demand in biological processes that decreases the oxygen content in water.

Nutrient condition is characterized by the analyse of the following parameters: nitrates, nitrites, ammonia and phosphate.

Ammonia, nitrates and nitrites represent important stages of the presence of the nitrogen in biogeochemical cycle from nature and hence from water.

Such as nitrogen and sulphur, phosphorus is subjected to a nutritive cycle, being used by plants during the summer as a biogenic element but sometimes it may even lack from water. During mineralization processes, phosphorus is converted into phosphates. Phosphorus is an element that exists in water, especially as a phosphate ($PO4^{3-}$).

The mineralization degree of surface waters is offered by dissolved substances content primarily (**Rf**), suspended solids content (**MTS**), electrical conductivity, chloride anions concentration (**Cl^-**) and sulphate anions concentration (**SO_4^{2-}**).

The cations Ca^{2+}, Mg^{2+}, Na^+, K^+andanions HCO_3^-, Cl^-, SO_4^{2-}representthe major source of watersalinity.

The surfactants are exclusively anthropogenic subtances. Their presence into surface waters is the proof of thepollutionfromwastewaters of municipal effluents.

General methods for determination of physico-chemical parameters

1. *Temperature*

Temperature determination is done by reading the indicators of a thermometer that is graduated in tenths of a degree, after being placed directly into analyzed water.

2. *pH determination*

In order to determine the pH value of the water, colorimetric and electrometric methods are used.

Electrometric method involves determining the pH value based on measuring the potential difference of an electrochemical cell, using a suitable pH meter (modern appliances are called multiparameter). The pH-meter is an electronic device that uses two electrodes: an indicator electrode and a reference electrode.

Multiparameters use combined (mixed) electrodes that can perform both functions. Immersing the pH electrode in the test sample, a galvanic cell is formed, in which electromotive force is dependent on the molar concentration of hydrogen ions $[H^+]$, that is, the pH of the solution.

This international standard specifies a method for determining the pH of rain water, drinking water, mineral water, bathing water, surface and underground water, municipal and industrial wastewater and liquid sludge in the range of pH 2 - 12, with a ionic strength of the solvent under I = 0.3 mol / kg (conductivity $\gamma_{25°C}$ < 2000 mS/m^3) and at a temperaturerangefrom 0^{0}C to 50^{0}C.

3. *Alkalinity*

The method involves determination by titration with a strong acid in water alkalinity due to the presence of biocarbonates, carbonates and hydroxides and, rarely, borates, silicates, phosphates, etc. hydrosulfide., in the presence of phenolphthalein or methyl orange indicators, respectively. Alkalinity determined by titration in the presence of phenolphthalein represents the permanent alkalinity (Ap). Alkalinity determined by titration in the presence of methyl orange is total alkalinity (TA). Both types of alkalinity are measured in meq/L.

4. Determination of turbidity

The principle of the method consists in determining the turbidity by Tyndall effect, the effect of a bright beam of light is a function of the content of suspended particles in a liquid. Quantitatively, the degree of opalescence is estimated by comparison with a liquid whose turbidity is known. Turbidity can be done and estimated by comparison with a standard emulsion in silica scale: 1 mg silica divided per one liter of distilled water represents the degree of turbidity (NTU).

5. Conductivity

The principle of the method consists in determining the electrical conductivity of water and relies on the property to conduct electrical current by measuring the electrical resistance of a aqueous solution column, of determined section and length. This method offers many informations on its ionized solutes content. Conductivity is measured in µS/cm at 20ºC or relates to this temperature. Conductivity value can be altered by about 2% when the sample temperature presents a difference of 1ºC compared to the reference temperature, this change takes place in the same direction as the temperature and to avoid this deviation, the sample water make up (20 ± 0.1)ºC by a thermostat. If the water sample was not thermostated at (20 ± 0.1)°C, the conductivity value determined at the temperature that was measured is multiplied by the appropriate factor. Conductivity determination is made using devices called conductometers.

6. Indicators of the oxygen condition

Oxygen is a soluble gas and is dissolved in water in the form of molecules, the presence of oxygen in the water conditioning the existence of a large majority of aquatic organisms. All types of water which are in contact with atmospheric air are containing dissolved oxygen.
The indicators class of the oxygen contains: dissolved oxygen (DO) oxygen saturation (Sat O2), biochemical oxygen demand (CBOn) andchemicaloxygendemand (COD).

a. Oxygen dissolved

The determination of the dissolved oxygen content can be done using various analytical techniques: volumetric, electrochemical and optical methods.

The standard method used is a modified Winkler method (iodometric method) that is based on the oxidation of manganese hydroxide to manganic acid.

b. Biochemical oxygen

Biochemical oxygen demand represents the amount of oxygen in mg / L, for oxidation of organic substances in water by means of bacteria over time (n = 2,5, or 10 days). The samples were incubated for a number of days (for example, BOD_5, BOD_{20}, BOD_{30}) and measure the amount of oxygen consumed during that period of time. The most common form is BOD_5.

The volumetric method involves determining the volume of oxygen consumed during 5 days of the micro-organisms from water by the difference between the amount of dissolved oxygen in the water sample determined immediately after harvesting and after 5 days incubation in the dark andthetemperatureismaintained at 20^0C.

c. Chemical Oxygen Demand

Chemical oxidation methods of oxidizable substances from wastewater are different by the nature of the oxidant and their reacting way. There are known two kinds of oxidative methods:

CCO-Mn that represents the chemical oxygen demand by oxidation with KMnO4 in acid or basic medium, depending on the concentration of the chloride from analyzed water. This index best correlates with BOD_5, noting that are oxidized in addition to about 30-35% of non-biodegradable organic substances.

COD-Cr represents the chemical oxygen demand by chemical oxidation using $K_2Cr_2O_7$ in an acid medium. This indicator determines the oxidizable organic matter from wastewater, including biodegradable.

These methods described above are not suitable to determine the volatile organic substances.

7. *Indicators of mineralization degree*

Mineral content of natural waters is closely linked to meteorological and climatic factors. Thus, during rainfall or snow melting periods, the rivers decrease their mineralization due to the dilution process with mineral waters exhibiting a poor mineral content.

a. *Filterable residue*

Filterable residue represents all substances dissolved in water, stable after evaporation at 105^0C or 180^0C, the majority of which are inorganic in nature. Residual value fixed in various natural water varies depending on the characteristics of rocks in contact with water.

The content of organic and inorganic substances dissolved in the water is determined gravimetrically by evaporation and weighting. The principle of this method is the evaporation of a volume of non-filtered water in the water bath and the residue is dried at 105^0C andweighed.

b. *Total suspended material*

Coarse particles are insoluble in water and they can be separated by filtration, centrifugation or sedimentation. Suspended matter in a water sample can be surface sediment and floating unsettleable.

Determination of total suspended matter (MTS) is made using a gravimetric method involving filtering or centrifuging of a well-known sample volume through a filter paper (recommended for different types of water with a high content of suspended solids) or a crucible coated Goch asbestos (recommended for different types of water containing low suspended solids). Determination of total particulate matter by centrifugation material is further used for samples with large amounts of colloidal material.

After filtration, the filter paper is dried at 105^0C to constant weight in an oven, cooled in a desiccator and reweighed. The difference between the final and initial mass of the filter paper sample related to the used sample volume represents the amount of all materialssuspended in the test sample.

c. The electrical conductivity

Conductometric methods of analysis are based on measuring conductometric properties of ions present in a liquid sample (measuring electrical resistance or the size of the mutual conductance of electrolyte solutions). The electrical conductivity of liquid samples is determined using conductometric bridges.

Determination of electrical conductivity of the surface water samples is made directly using an conductometer whose electrode is pre-calibrated according to the manufacturer specifications.

d. Chlorides

Chlorides present in a liquid sample are volumetric determined by argentometry method. Depending on the amount of chlorides contained by the analyzed sample, titration with AgNO3 is used (Mohr method or Volhard's method). Considering the surface water case, Mohr's method is a direct method for halide anions dosage (Cl^-, Br^-, I^-).

e. Sulphates

Sulphates in water can be determined by gravimetric, complexometric (for high concentrations of sulphates), volume (for current analysis of sulphates) and turbidimetric (for low concentrations of sulphates).

In the case of surface water, where the sulphate anion concentrations are generally small, such determination is made by using a turbidimetric method which is based on the precipitation of $BaSO_4$ and maintaining the resulting precipitate in suspension. The obtained turbidity is determined using a standard scale of a nephelometer or spectrophotometer (at $\lambda = 420$ nm).

Removing interference is possible through dilution withwater or byflocculation, using $AlCl_3$.

8. ***Nutrient condition***

Ammonia, nitrites and nitrates are important stages of nitrogen presence in his biogeochemical cycle in nature and hence in water. Nitrogen is a key element for sustaining life, occuring at different stages of plant and animal life. The forms in which nitrogen compounds are occurring in water are the molecular nitrogen (N_2), nitrogen connected in various organic combinations (organic nitrogen), ammonia (NH_3), nitrites (NO^{2-}) and nitrate (NO^{3-}).

a. Ammonium

Determination of ammonium cations is carried out using a spectrophotometric method which is based on their reaction with salicylate ions and hypochlorite, in the presence of nitrozopentacianoferat (III) sodium salt (sodiumnitroprusside).

b. Nitrates

The principle of the method for spectrophotometric determination of nitrate anions consists in absorbance measuring of yellow compound formed by reaction thereof with sulfosalicylic acid (formed by the addition to the sample of sodium salicylate and sulfuric acid), followed by treatment with alkaline solution.

c. Nitrites

Spectrophotometric determination of nitrite is accomplished at 520 nm. The principle of the method consists in converting nitrite to the diazonium salt, using sulphanilic acid and considering a strong acidic medium (pH = 2-2.5) in the presence of α-naphthyl-amine.

d. Phosphates

Determination of the phosphates is achieved by reacting them in an acid medium with ammonium molybdate and potassium antimony tartrate.

9. ***The content of metal ions,*** *such as* Cr^{6+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+}, Zn^{2+}, As^{3+} *is determined by photocolorimetric or spectrophotometric methods.*

10. Surfactants

Synthetic detergent anion-active in aqueous acidic solution reacts with methylene blue and a blue colored hydrophobic complex is formed. The coloured complex is extracted with chloroform and the color intensity is measured; its intensity is proportional to the surfactant concentration [EN 903.2003].

Photometric determination is made at a redfilterphotometer (560 nm).

Sampling methods for determining the chemical parameters

Generally taking water samples is an important step preceding chemical analysis because samples must be representative . For collection of water samples for chemical analyses we used plastic containers (polyethylene) , glass or borosilicate glass, if determining the organic compounds are prohibited to use neoprene gaskets recipients. For this research, water samples were collected in 1 L plastic bottles with airtight stopper. Sampling from the three studied rivers: Danube, Siret and Prut river was made upstream of any influence of any effluent and downstream about 15m from the shore. The samples did not require conservation as they have been deposited in a cooler for immediate analysis in Credential laboratory of the Centre Regional for Research and Monitoring of Environmental Quality, "Dunarea de Jos" University of Galati. The temperature maintenance during transport was 2 - 50 ° C.

Water quality index – Useful tool for assessing Danube water quality- practical example

Water quality assessment is done also through water quality index (WQI). WQI numerically summarizes the information from multiple water quality parameters into a single value. Once the overall WQI score is known, it can be compared against the following scale (table 1) to determine how appropriate to use the water is on a given day [1].

The Water Quality Index uses a scale from 0 to 100 to rate the quality of the water. It was found that the WQI was very useful for the classification of the waters monitored. In table 1 are presented the values for WQI and the correspondence with water quality.

Table 1: *Water quality index (WQI) scale* (Chowdhury et al., 2012):

WQI Water Rating Scale	
> 100	Unsuitable for drinking
76-100	Very poor water quality
51-75	Poor water quality
26-50	Good water quality
0-25	Excellent water quality

For the determination of the water quality index of the different watersheds studied, the following empirical equation was used:

$$WQI = \sum W_n q_n / \sum W_n \quad (1)$$

where WQI is a number between 0 and 100 to indicate the water quality index; q_n is water quality score of parameter, n the number of parameter used to calculated WQI and, W_n the weighting factor of parameter n, a number between 0 and 1. q_n is calculated as following:

$$q_n = 100[V_n - V_{io}]/[S_n - V_{io}] \quad (2)$$

wereV_n represents estimated value of the n^{th} parameter at a given sampling station; V_{io} represent ideal value on n^{th} parameter in pure water (this is 0 for all parameters, except pH for which is 7 and dissolved oxygen for which is 14,6 $mg \cdot L^{-1}$); S_n represent standard permissible value of the n^{th} parameter.

Unit weight is calculated with following expression:

$$W_n = k/S_n \quad (3)$$

where k is a constant value.

The WQI was calculated using Romanian standard on surface water quality classification to establish the ecological status of water bodies and World Health Organization standards when there a no values in Romanian standards.

To determine the WQI, the following ten water quality parameters are measured: pH, electrical conductivity, total hardness, total dissolved solids, nitrates, dissolved oxygen, biological oxygen demand, Ca^{2+} and Mg^{2+}. **The values obtained by experimental methods are presented in table 2.**

For the Lower Danube, it is considered useful to include in calculation of WQI Index, as measurable parameters, concentrations of heavy metals which came in surface waters both by the nature of economic activities in the area (industrial harbor which supplies the largest iron and steel company in Eastern Europe, other economic activities with an exhaust system common wastewater and municipal water discharged into the Danube and Siret without prior treatment by 2013) and the potential contribution of the two major tributaries of the Danube, Siret and Prut rivers (Iticescu et al., 2013).

The WQI was calculated using Romanian standard on surface water quality classification to establish the ecological status of water bodies and World Health Organization standards when there are no values in Romanian standards. In table 4 we present these values.

Table 2: Variation of physicochemical parameters in two different months:

Nr. crt	Parameters		March	April
1	pH		8,14	8,02
2	Electrical conductivity	$\mu S \cdot cm^{-1}$	527	516
3	Total hardness	$mg \cdot L^{-1}$	220	240
4	Total dissolved solids	$mg \cdot L^{-1}$	276	258
5	Chlorides	$mg \cdot L^{-1}$	28,276	29,674
6	Nitrates	$mg \cdot L^{-1}$	5,38	5,54
7	Dissolved oxygen	$mg \cdot L^{-1}$	8,15	10,65
8	Biological oxygen demand	$mg \cdot L^{-1}$	3,24	3,36

9	Ca^{2+}	$mg \cdot L^{-1}$	56	60
10	Mg^{2+}	$mg \cdot L^{-1}$	17	18

Table 3: Standards values of physical-chemical parameters measured and unit weight (W_n):

Nr. crt.	Parameters	Standards	Unit weight
1	pH	6,5-8,5	0.152155
2	electrical conductivity	1000	0.001156
3	total hardness	250	0.004626
4	total dissolved solids	500	0.002313
5	chlorides	50	0.023128
6	nitrate	3	0.385459
7	dissolved oxygen	7	0.165197
8	biological oxygen demand	5	0.231276
9	Ca^{2+}	100	0.011564
10	Mg^{2+}	50	0.023128
		$\sum W_n =$	1.00

Used the values obtained for unit weights and the measured values WQI were calculated and the obtained values are presented in tables 4 and 5.

Table 4: WQI value in March

Nr. crt	Parameters	Standards	Measured values	Wn	q_n	$W_n q_n$
1	pH	6,5-8,5	8,14	0,100	76,00	7,6
2	electrical conductivity	1000	527	0,0075	52,70	0,395

3	total hardness	250	116	0,003	46,4	0,139
4	total dissolved solids	500	276	0,0015	55,20	0,082
5	chlorides	50	28,276	0,015	56,55	0,848
6	nitrate	3	3,38	0,240	112,66	27,04
7	dissolved oxygen	7	8,15	0,100	84,86	8,486
8	biological oxygen demand	5	3,24	0,150	64,80	9,72
9	Ca^{2+}	100	56	0,0075	56	0,042
10	Mg^{2+}	50	17	0,015	34	0,51
					$WQI = \sum W_n q_n / W_n =$	74,24

Table 5: WQI value in April:

Nr. crt	Parameters	Standards	Measured values	Wn	q_n	$W_n q_n$
1	pH	6,5-8,5	8,02	0,1	68	6,8
2	electrical conductivity	1000	516	0,0075	51,60	0,038
3	total hardness	250	125	0,0025	50,00	0,00125
4	total dissolved solids	500	258	0,001	51,6	0,051
5	chlorides	50	29,674	0,015	59,33	0,889
6	nitrate	3	3,54	0,24	118,00	28,32
7	dissolved oxygen	7	10,65	0,100	51,97	5,197
8	biological oxygen demand	5	3,36	0,15	67,20	10,08
9	Ca^{2+}	100	60	0,0075	60	0,45
10	Mg^{2+}	50	18	0,015	36	0,54
	$WQI = \sum W_n q_n / W_n =$					74,178

The conclusions of this research were:

It could be observed that the Danube water quality is situated in the “poor” category in the spring period mainly because the tributaries (on the Romanian territory they are poor and “very poor” quality) bring important quantities of pollutants especially resulted from agricultural nutrients as nitrates. Nitrates have an important contribution to the water quality and the basic water treatment is not efficient. Common sources of nitrates from Danube river include fertilisers and manure, animal feedlots, municipal wastewater and sludge or septic systems.

As a short and midterm strategies in the area the single water treatment has to be associated with a drastic reduction of production of nitrates through the municipal wastewater treatment and limitation of intensive use of fertilisers. On the other hand it is important to increase the quantity of underground water coming from Northern part of the county in order to increase drinking water quality and to minimise the treatment costs.

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