MONITORING TÂRNAVA MARE RIVER SIBIU COUNTY TERRITORY

Letiția, OPREAN[1] and Dana-Melania, POPA[2]
Lucian Blaga University of Sibiu, letitia.oprean@ulbsibiu.ro
Romanian National Gas Company ROMGAZ S. A. - Medias Subsidiary

ABSTRACT: This paper reports the results of monthly monitoring of water quality for River Tarnava Mare, considering the portion that crosses Sibiu County (taking as reference sections: Medias, Copsa Mica and Micasasa), during the years 2006 - 2007. Classification of surface water was based on values obtained from analyzing the following parameters: oxygen regime, nutrients, salinity and toxic chemical pollutants of natural origin. Summarizing these experimental results it was possible a final classification in Class II of water quality of River Tarnava Mare, accordingly to Norm 1146/2002.
Keywords: monitoring, river water, oxygen regime, quality indicators, quality categories

1. INTRODUCTION

Watercourses (rivers and tributaries) are generally characterized by a lower mineralization, the amount of dissolved mineral salts being below 400 mg/l. It is composed of bicarbonates, chlorides and sulphates of sodium, potassium, calcium and magnesium. Total hardness is generally below 15 degrees, consisting mostly of bicarbonate hardness.

The concentration of hydrogen ions (pH) is around neutral value, respectively, 6.8 - 7.8; among dissolved gases are present: dissolved oxygen, with saturation between 65 - 95 % and free carbon dioxide, generally below 10 mg/l.

The main feature of rivers is a variable load with suspended solids and organic materials, loading connected directly proportional to weather and climate. They increase during rains, reaching a peak during the floods of water and a minimum during periods of frost.

Discharge of insufficiently treated effluent has led to quality alteration in river flows and to the emergence of a wide range of contaminants: hardly degradable organic matter, nitrogen compounds, phosphorus compounds, sulphur compounds, microelements (copper, zinc, lead), pesticides, chlorinated organic insecticides, detergents etc. Also, in many cases, it is noted increased bacteriological pollution. A specific feature of water in rivers is self-purification capacity due to a series of natural biochemical processes, favoured by water - air contact.

To avoid contamination of rivers, as final receptors, water discharged into the sewage networks must be free of:

- suspended solids that can generate deposits, which may solidify and may obstruct the channel section, suspension harsh and abrasive, which can cause premature erosion of the channel;
- substances with high chemical or physical aggression;
- substances which, in combination with air, form explosive or toxic mixtures for pipes or for personnel;
- toxic or harmful substances;
- heavy metals, halogenated organic compounds or phosphorus compounds, chemicals used in wood, textile materials or leather processing;
- substances which, when mixed with water or air can emit unpleasant strong odours, and can pollute the air;
- pollutants that can change the colour of the natural receptor at the discharge of treated water and that can not be eliminated in the wastewater treatment plant;
- substances inhibiting the purification process (heavy metals, phenols, mineral oils, hydrocarbons, chlorides, etc.).

Exceeding the maximum admitted limits for polluters leads to increase of operating costs and to hinder the technological process of sewage treatment, with the risk of not respecting the legal rules for discharge treated water into the receiver.

Moreover, for some pollutants that often exceed the value from 002 NTPA for the indicator BOD5, pre-treatment solutions are very expensive and technically very difficult to apply. Consequently, after achieving the storage capacities in certain economic agents, it is advisable to prepare a program of discharge of such water in the city sewage network. This would allow the treatment plant to receive and to purge better high BOD5 loads.

2. MATERIALS AND METHODS

To monitor the level of wastewater treatment has been sampled water from the river Tarnava Mare. Evaluation of fitting in quality classes, in order to determine water quality, is made of chemical, biological and microbiological point of view.

The fitting of sections in 5 quality classes, relative to general indicators, was done in 4 main groups:

- oxygen regime;
- nutrients;
- salinity;
- toxic chemical pollutants of natural origin.

Monitoring of sections was performed during 2006 - 2007, except that, in the table, indicators written in bold and red characters are those which led to a correct fitting in quality class. It should be noted that the heavy metals found in the analysis come from the nature.

Identification system was designed and identified to ensure that the sample can not be confused physically or in the records, starting with the collection and preservation and for the entire duration of its presence in laboratory for analysis.

Sampling bottles and work glassware were marked with numbers that, from the moment of sampling, corresponded to different samples. These identifying elements have been found in the records of all stages of work.

Samples were received on the notes accompanying sampling. At the reception was envisaged sample's integrity, that it is correctly identified and if the sample container is appropriate. Handling samples was avoiding the possibility of their impurification or chemical contamination. Storage of samples was done in the refrigerator, when the laboratory's program did not allow their immediate analysis.

Sampling and preservation of samples was done in laboratory.

Indicators of the oxygen regime

Oxygen is a soluble gas and is dissolved in water as molecules (O2), the presence of oxygen in water by providing the existence of the vast majority of aquatic organisms. All waters in contact with atmospheric air contain dissolved oxygen, while the groundwater contains very little oxygen. Solubility of oxygen in water depends on: atmospheric pressure, air temperature, temperature and salinity of water.

For this class of indicators are: dissolved oxygen (DO), chemical oxygen demand (COD), biochemical oxygen demand (BOD) and total organic carbon (TOC).

Salts dissolved

In natural waters there are, usually, cations and anions listed in Table 1, ions on which depend the most important qualities of water. In most cases, salts in natural waters consist of the following cations: Ca2+, Mg2+, Na+, K+ and anions: HCO-3, SO42-, Cl-. Other ions are usually in insignificant quantities, although sometimes influence essentially on water properties. Chlorides may be present in water in high concentrations due to their high solubility; thus, the solubility of the sodium or calcium chloride, at a temperature of 25 °C, is around 26 % and 46 %.

Table 1. Major ions in natural waters

CATIONS		ANIONS	
Name	**Formula**	**Name**	**Formula**
Hydrogen	H^{+}	Hydroxide	HO^{-}
Sodium	Na^{+}	Bicarbonate	HCO_3^{-}
Potassium	K^{+}	Chloride	Cl^{-}
Ammonium	NH_4^{+}	Hydrosulphite	HS^{-}
Calcium	Ca^{2+}	Nitrite	NO_2^{-}
Magnesium	Mg^{2+}	Nitrate	NO_3^{-}
Bivalent iron	Fe^{2+}	Fluoride	F^{-}
Trivalent iron	Fe^{3+}	Sulphate	SO_4^{2-}
Barium	Ba^{2+}	Silicate	SiO_3^{2-}
Aluminium	Al^{3+}	Orthophosphate	PO_4^{3-}

In essence, one can say that natural waters contain basic elements and specific features, of which 6 are the fundamental elements that are present in all natural waters, that is the molecule of H2CO3 and HCO3-, CO32-, H+, OH-, Ca2+ ions, and of the specific ions one can quote: SO_4^{2-}, Cl^-, Mg^{2+}, Na^+, K^+ ions etc. These elements may be present or not in natural waters in concentrations higher or lower, giving the water a certain character.

Monitoring methodology

All water quality standards are and will remain a subjective and imperfect instrument, from many causes. Truly scientific approaches are blocked by different mentalities and social skills, such as different perceptions of risk, first putting the man's interests all learned of the human nature etc. Also, the standards are still common, while water varies from river to river and samples for analysis are taken from time to time, revealing, therefore, only the situation in narrow time bands. Statistical methods may mask serious currently situation, interpretations varying according to analysis purpose; there are also economic and technical barriers that require compromise and focus solely on the "typical" situation etc. Thus, the very fundamental concept of "maximum admitted concentration" is a rather arbitrary concept in reality, a compromise, and in the interpretation must be known and taken into account the principles and methodology by which it established those values.

This is trying to be partly offset by choosing multiple categories of values determined in the analysis of water. As mentioned, for various reasons, for some indicators can be obtained data that, if interpreted separately, can lead to wrong appreciation. Some unrealistic conclusions can mitigate or eliminate by linking and comparing indicators for different categories: organoleptic, physical, chemical, biological, bacteriological, etc.

The interpretation of data must consider the various factors involved in the planning, collection, preservation, transport and processing samples of water taken for analysis. All sampling and analysis are made, theoretically, after rigorous standardized methods, which in theory should ensure consistency and comparability. However, there are parameters for which standardized methods of analysis are not available or for which there are problems of equipment (too old or incorrect or defective or uncalibrated etc.) or reactive (lack or improper etc.); human error is also involved, problems of contamination of water samples etc. In addition, there is always the risk that the samples collected are not representative, even if everything looks good methodological at sampling - for example, to have just occurred upstream, a massive discharge, point sources of pollutant. Conversely, by a systematic pollution, but discontinuous, if the sample is taken just in the "window" between discharges into the river, the result is wrong. These circumstances are trying to be avoided by repeated sampling, by ignoring the results obtained when the sample was taken at the flood regime etc. Suspensions, for example, vary greatly in rivers, which should lead to a more frequent review. In addition, there is great heterogeneity in the river section, which should lead to not use a sampling point, but a sampling front, with samples collected both on shore and in the middle, both bottom and surface of river etc. It would also be essential sampling for suspensions to flash flooding, when the transport reaches a maximum, instead of ignoring those samples, as is often practiced.

90% of sediment is transported during 10% of the year. Therefore, by "regular" analysis one may reach a strong underestimation of the actual transport of suspension and, therefore, of pollutants, for which the UN specialized agencies (WHO and UNEP) recommend higher frequency than the usual monthly analysis.

A major problem stems from the methodology of statistical processing and interpretation of data. Analyses are done for water samples regularly taken. For, in the current design, valid in Romania and in many countries, the main purpose is to monitor water, as potential of use for various human utilizations and as level of pollution produced by various human utilizations (for the calculation of the total amount of pollutants transported by water, or penalizing or amending polluters, etc.). The results announced are the statistical mean that, if we do not know how to calculate, may disappoint us deeply on water quality, even if, in itself, each sample was correctly sampled and analyzed, and results of each analysis are very stringent. Thus, a first typical case is that usually, in case of rivers, are retrieved and processed statistically not the actual, real concentrations/amounts, but the weighted flow. These concentrations show that the increase or decrease the level of a given pollutant is real, indicating higher or lower discharge, and is apparently due to different dilution by oscillating flow of water. The result is very useful for monitoring pollution sources, but not for aquatic life.

A problem also represents the overall quality assessment, based on the quality shown by various indicators. Of course it is not practical to have only the conclusions on each indicator or group of indicators separately, but must exist, in many cases, the overall conclusions. There appear, however, the same problems, though some indicators show quality

I and others quality II or III or "degraded". The final conclusion, inevitably, will mask the details and can give wrong deep impressions. Because the main purpose of the present system of surface water management area is to provide raw water for various human utilizations and, here, calculation methodologies used consider the overall quality and consider it good, if most indicators fall within the desired range, even if some (often many and crucial) show reduced or degraded water quality. This generalization helps to monitor the overall progress of quality, the decrease in percentage of parameters that fit the lower categories, leading to an increase in percentage of water falling in the higher categories, showing the disappearance of certain pollution.

However, this is how those methods for assessing the overall quality of surface waters work, giving to the whole the value resulting from the majority, even if some parameters indicate a much worse situation. There is anything wrong, is just a different purpose than assessing biologically the quality of possible in situ effects on aquatic life or the direct consumption by living organisms. Living world is an indicator more accurately than physical-chemical analysis, because is not usually influenced by short-term changes; in exchange they register the systematic ones, even if it relates to one component of the water. Therefore, the overall statistical assessments based on chemical and physical characteristics, frequently show water of quality I, but biological analysis indicates only the quality II or III.

Another problem is the choice of parameters. One can not study, virtually, all the features. If those physicals can, the chemicals ones could be, possible, for inorganic and some simple organic compounds. But there is an enormous diversity of organic compounds that will not ever be isolated, identified and weight and are only incidentally found in water, in testing with advanced analytical equipment. Therefore, by all water quality analysis is determined, in fact, some parameters considered most relevant and which are considered to give indirect information and about the level or presence likelihood of other compounds, including some very toxic or infectious ones that we like to detect and dose first, but we can not practice routine.

3. RESULTS AND DISCUSSIONS

Water quality is checked monthly, in the sections listed below and based on the results obtained in control sections, is made watercourse classification of quality categories (accordingly to Normative 1.146/2002).

Thus, the river Tarnava Mare, left tributary of the Mures, in length of 246 km, are identified the following reference sections for the portion that runs through Sibiu county:

- Medias;
- Copsa Mica;
- Micasasa.

In Table 2 are included exceeding quality indicators that determined the quality class for each group of parameters represented graphically in Figure 1 (only for classes 3 - 5), indicators that led to the final classification in the category of quality (from 1 to 5) being written on red and bold characters. Generally, there were recorded exceedances metals loading: Cr, Cu, Zn, Pb, Ni, Cd and, sometimes, Co and Mn.

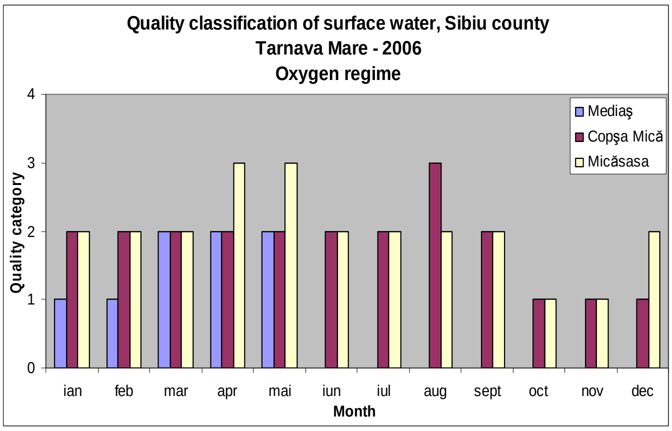
In case of water pollution with heavy metals, it does not usually reach to acute poisoning but heavy metals are able to concentrate in living organisms, showing a chronic toxicity. Are relatively well known toxic levels for humans, but is impossible to assess it for the immense diversity of aquatic organisms. Human contamination is very dependent on dietary habits, age, health status etc. It also matters very much the form, the absorption and toxicity level. Thus, toxicity of Cr^{3+} is different from Cr^{6+}, or metallic mercury to the organic bound mercury.

From the parameters given in Table 1, one can see the gradual loading of river with pollutants from upstream to downstream, as it passes through heavily polluted areas such as Copsa Mica, whose impact on river water quality is marked by increasing exceeded indicators. In this respect, one can see that the most serious repercussions are felt by the section of Micasasa.

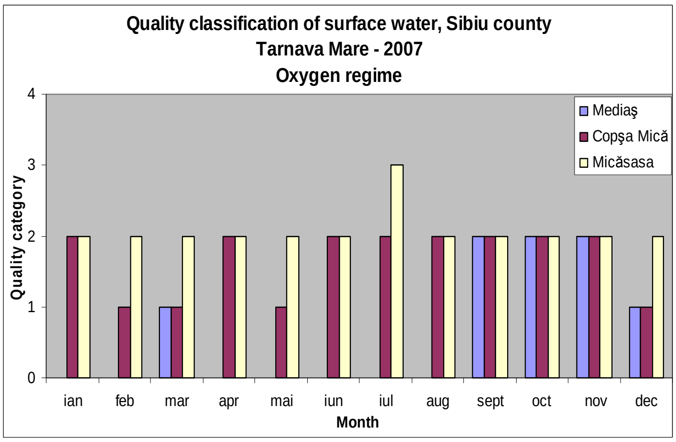
Table 2. Monitoring river Tarnava Mare, Sibiu county

Water course	Section	Exceeding indicators												
		Year	Month											
			Jan	Feb	Mar	Apr	Mai	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Tarnava Mare	Medias	2006	NH_4^+ Mn Cu Zn	NH_4^+ Mn Cu Zn	Cu Pb	Pb	Zn Cu	-	-	-	-	-	-	-
	Copsa Mica		NH_4^+ Cr Cu Zn Pb	NH_4^+ Cr Cu Zn Pb	Cu Zn Pb	-	Pb	Zn Cu	Pb	CCO_{Cr} Pb	Pb	NO_3^- Pb	-	Pb
	Micasasa		Zn NH_4^+ Cr Co Cu Pb	Zn NH_4^+ Cr Co Cu Pb	Zn Cu Pb	CCO_{Cr} CCO_{Mn} Zn Cu Cd Pb	CCO_{Cr} CCO_{Mn} Zn Cu Cd Pb	Pb	Pb	Pb	Pb Cd	Pb Cd	-	Cd Pb
	Medias	2007	-	-	Ni Pb						-	-	-	-
	Copsa Mica		Pb Cd Ni	-	Ni Pb	Ni Pb	Cr Ni Pb	NO_2^- Cu Pb	NH_4^+ NO_2^- Cu Pb Ni	NH_4^+ NO_2^- Cu Pb Ni	NO_2^-	-	Co Cu Pb	-
	Micasasa		Cd Pb	Cd Pb	Ni Cd Pb	Pb	Cd Cu Pb Cu Cd Ni Pb	NO_2^- Cu Pb	CCO_{Mn} CCO_{Cr} Cu Pb Ni	Cu Pb Ni Cd Fe Pb	P_{total} NO_2^- Ba Cd Cu Pb Cu Pb	-	Cu Pb	-

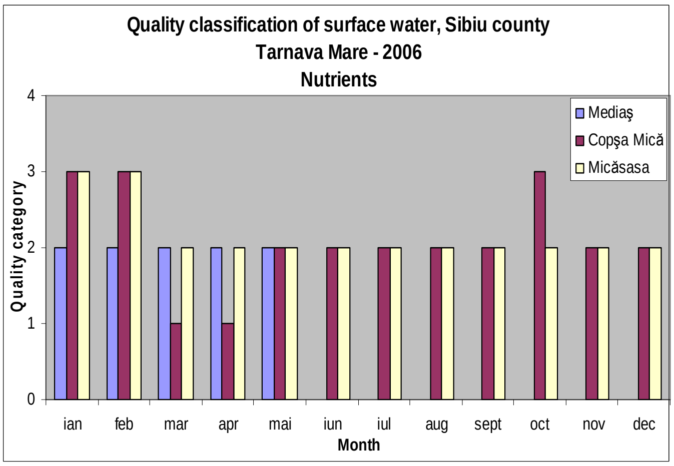
The experimental results obtained from tests carried out monthly on water samples collected from the river Tarnava Mare during 2006 - 2007, are shown in Figure 1 (a), (b), (c), (d), (e), (f), (g), (h) and (i).



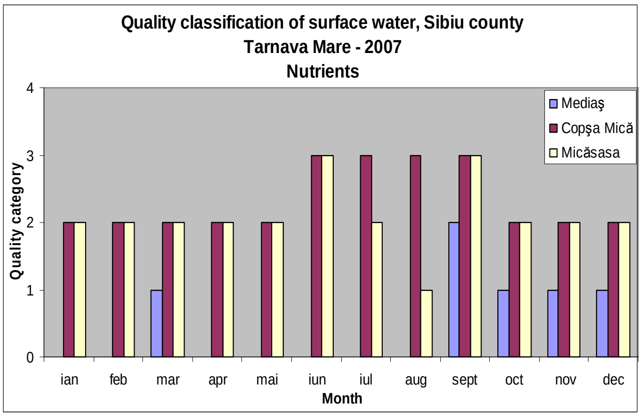
(a) – oxygen regime, 2006;



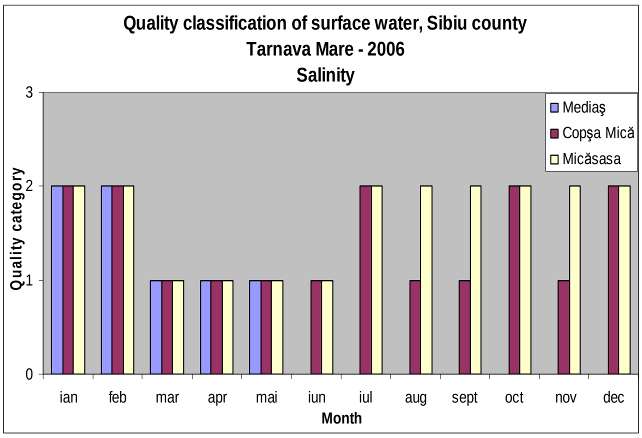
(b) – oxygen regime, 2007;



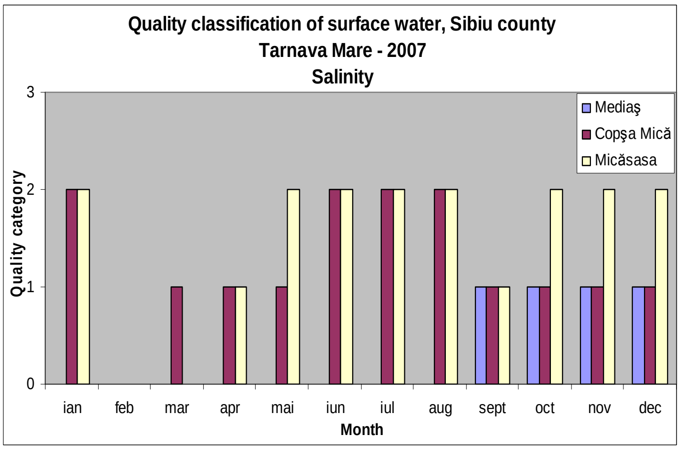
(c) – nutrients, 2006;



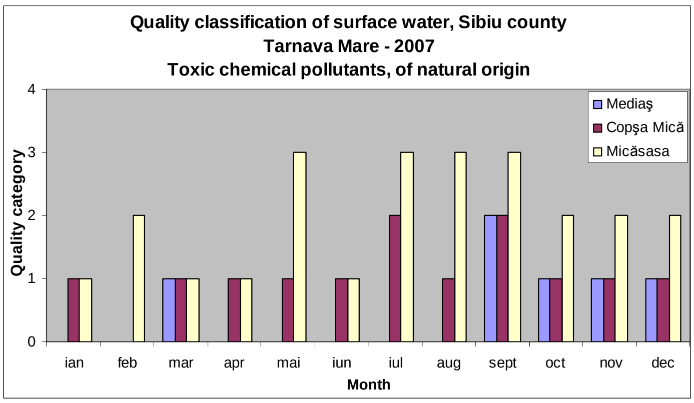
(d) – nutrients, 2007;



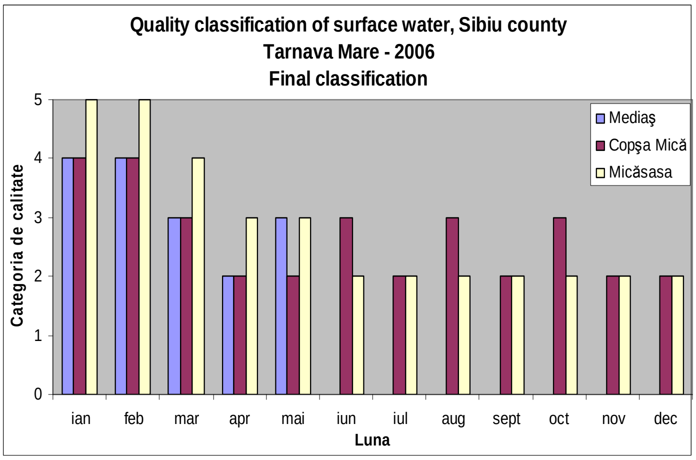
(e) – salinity, 2006;



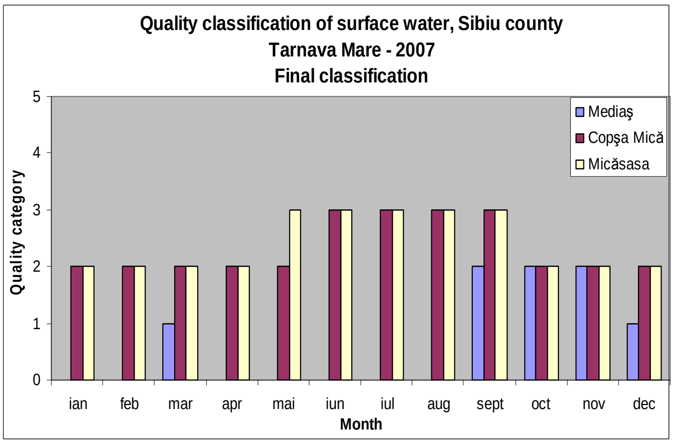
(f) – salinity, 2007;



(g) – toxic chemical pollutants of natural origin, 2007;



(h) – final classification, 2006;



(i) – final classification, 2007

As can be seen from the trend of represented parameters, water quality of river Tarnava Mare for the monitoring period (2006 - 2007) is kept relatively constant, approximately around the second quality class.

In Figure 1 (g) can be seen a large enough loading of toxic chemical pollutants of natural origin, in Micasasa section, which lies from its downstream positioning by Copsa Mica, an area recognized as one of the most heavily polluted in the country.

4. CONCLUSIONS

Under the overall assessment, in the years 2006 - 2007, most of the monitored sections meet, on average, the corresponding limits of quality class II, considered target-value.

Correct interpretation of organoleptic, physical, chemical, bacteriological and biological data, obtained by water analysis, requires a good knowledge of the river basin, the geological nature of the soil, human activities, the potential sources of pollution and hydro-meteorological conditions, otherwise with the risk misinterpretation.

Reducing pollutants at entering the sewage plants are, in the community, an awareness of the need for environmental protection, reflected by the choice of clean technologies, with a tendency to improve the technological processes of production and the withholding and destruction of polluting substances.

It will materialize in this manner, the following goals:

- classification of purified water, at leaving the sewage plants, within the values of parameters provided for the eviction in the receiver, in accordance with legal norms and conventions to which Romania participate;
- reducing operating and maintenance costs in sewage plants and thus reducing resource consumption, particularly electricity;
- increase the treatment efficiency, with high-impact in the community decision, on completion of environmental protection desideratum;
- avoiding major shocks due to toxic pollutants, on the river Tarnava Mare, and also on the whole chain, to the Black Sea;
- ensuring normal operation in the step of biological treatment, which is most sensitive to disturbing factors.

Connect as many households to the sewerage system, respectively the reduction of water use and discharges from industry, represents also a method to reduce the impact of sewage.

In conclusion, the assessment of water quality and hence the possibility of using it for various purposes, is a task of great complexity. The mere existence of accurate results of a wide diversity of organoleptic, physical, chemical, biological and bacteriological analysis proves insufficient for a correct interpretation, determining causality, prediction of evolutionary trends and other elements necessary to establish an appropriate management.

It is required interdisciplinary collaboration between geographers/hydrologists, geologists, meteorologists, biologists, physicists, doctors, chemists, computer scientists etc.

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