STUDY CONCERNING THE MATHEMATICAL SIMULATION AND THE INTERPRETATION OF QUALITY INDICATORS OF SUCEAVA RIVER

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Abstract: Mathematical simulations have been started to be used frequently in the simulation and interpretation of environmental phenomena. New approaches in this sense propose a new vision on monitoring (by monitoring meaning taking, analyzing and interpreting the data concerning the environment) the quality of the environment. This paper aims at presenting a study on the quality of surface waters, more precisely about the quality of the water in Suceava River. The analysis will monitor the quality of the waters by using the monitoring system shaping the data obtained with the help of the mathematic apparatus and by using physical and chemical coordinates as quality indicators.

1. The Principles of Mathematical Simulation

We live in a world governed by models. Our consciousness and our own ego are simplified forms of our entire being, that is to say they are models. The life of each one of us is a permanent confrontation between the model of our ego and the model of the surrounding world.

All sciences were born and evolved significantly after models have been elaborated, (Cleine K., 2007). In the mathematical simulation of a process, some general rules have to be followed, such as:

- ⇒ The analysis of similar models taken as a whole. This can lead to an adaptation and improvement of the existing models.
- ⇒ Collecting the necessary information and selecting the information related to those parameters useful to the fixation and the proper understanding of the issue.
- ⇒ Projecting, as a first step, of a simplified model that can be improved later on by adding some details; thus, a flexible model can be obtained.
- ⇒ The analysis of external cases and establishing a hierarchy of the results, sorting the information function of the degree of the impact with the expectation, the evaluation of the results and developing a preview situation are needed.

There can be rarely the case of a perfect situation, especially in case of mathematical simulation of some environmental phenomena, and the projects undergoing mathematical functionality are rarely met. Simulation in environment pollution is considered to be the art of discovery, as well as the art of compromise satisfaction.

When the simulation aims at determining a «positive function» describing the evolution of data in an experiment in order to develop a system or an ecological complex, the mathematic apparatus used is the data switching along with the results given by the numeric analysis; but at the same time, the random processes, physical phenomena and the chaos theory cannot be excluded.

Getting back to the issue of the present study, which is measuring the quality level of the surface water in Suceava River, the mathematical process will be structured on the method specific to the mathematical interpolation and especially the interpolation of splene cubic function.

2. The Mathematical Projection of the Study

Usually, in case of a process analyzed function of the statistic data, the analysis of these data is made in Excel or other specialized software able to present averages, deviations, limit data presentation and anomalies registrations; however, in very few cases this analysis takes into account the inertial evolution of the increase and decrease phenomenon of the parameters in precise time intervals.

We suppose that the process of evolution of the data collected in time is a manageable one, with a continuous C_1 class function. We rely on the information that the evolution of the analyzed parameters cannot have an evolution consisting of sudden increase or decrease.

By interpolation we mean determining the value of an unknown function within a given interval, by using known values at the start and ends of the interval. The fact that the qualitative data collected regard measurements made every two months using the interpolation will allow covering of all the twelve months of a year with interpolative data.

The existence of a function allowing realizing such a model is based on the Weierstrass theorem. This sets the theoretical base of the existence of this function, but does not offer practice criteria of determining the proper function.

For the present study we propose the splene cubic function and the analysis and the interpretation of the data in this sense will either confirm or infirm the model itself.

The request of setting an at least 6 degree polynomial function (corresponding to the 6 months when samples were collected) over the existing data is invalidated.

In order to realize the graphic analysis we have used the MATLAB, (Muraru C. V., 2006), working device, which offers complete and unitary solutions to interpolation problems, by means of splene function interpolation.

In the examples we have analyzed we have used the possibility of numeric data analysis by means of splene cubic functions.

Let it be

$$\Delta: a=x_0<x_1<\ldots<x_{i-1}<x_i<\ldots<x_n=b,$$

a random division of the [*a*,*b*] interval. The ***splene cubic function*** is a function of the type

$$s:[a,b]\rightarrow \mathbb{R}$$

having the following properties:

(i) The restriction of *s* for every subinterval $[x_{i-1}, x_i]$ is a polynom of a third degree at most;

(ii) s, s', s'' are continuous on [*a*,*b*]

The MATLAB package has a splene function, which allows the interpolation of a function *f* , in the points x_1, x_2, ….x_n, for any natural number n, finite, by a splene cubic function, if the y_1, y_2, …y_n, are known in the loops x_i,. The call sequence is the following: y_i=spline(x,y,x_i) (**fig. 1**).

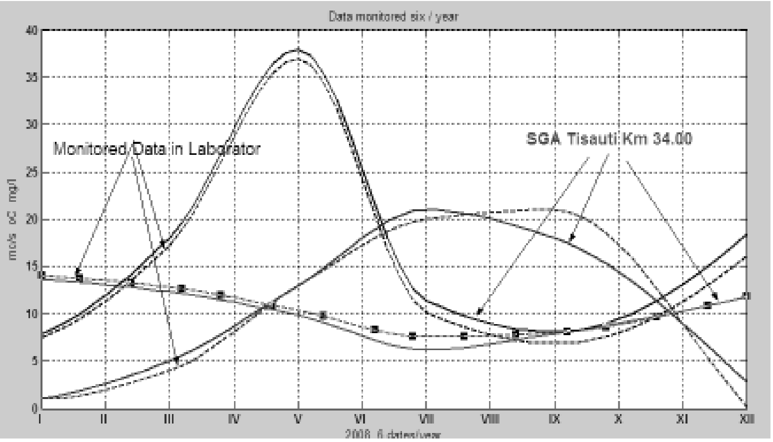

Fig. 1 *– Working space in MATLAB for data interpolation*

3. Presentation of the Suceava River characteristics and their monitoring

3.1 The areas of study

The Suceava River rises from the North extremity of Obcina Feredeului, more precisely from the North side of the Aluniş mountain at 1.200m height and it is formed of two tributaries, *Izvor* and *Aluniş*, which join at Izvoarele Sucevei. It flows into Siret River at Roşcani-Liteni, at 232 meters height (**fig. 2**).

Fig. 2 *- Hydrographic basin of Suceava River (the Romanian side)*

The Suceava River falls into the branch of Eastern Romanian rivers, being a right side tributary of the Siret River. It is the third most important after Bistriţa and Moldova Rivers and at the same time it is the only important river gathering its waters from the territory of a single county, except for the Ukrainian side.(Răduianu I.,2009)+++

3.2 Monitoring system

The annual water discharges usually vary greatly, according to the pluviometric characteristics of a year. Generally, the largest water discharges are registered on most of the rivers in April and June. The large water discharges during these two months are explained by the high pluvial contribution of the tributary rivers, to which add the water resulting from the melting of the snow. The lowest water discharges are registered during the autumn and winter months.

Along Suceava River the amount of water discharges increase from upstream to downstream: the maximum value **53.2 m^3/s** at Mihoveni (12.06.2008) and the maximum value **37 m^3/s** at Tişăuţi (15.05.2008). The monthly temperatures of Suceava River waters at the hydrometric stations Mihoveni and Tişăuţi oscillates between a minimum value registered in January and a maximum value registered in July 2008. On Tişăuţi section, the water temperature varies between 1ºC and 20ºC (2008) and between 2ºC and 21ºC (2009), and on the Mioveni section the water temperature varies between 01ºC and 19ºC (2008) and 0ºC and 21ºC (2009). The average values of these temperatures rise along with the decrease of the altitude that is from West to East.

We have analyzed the quality of the water on two monitoring sections of Suceava River, which are Mihoveni and Tişăuţi.

The dissolved oxygen is one of the main water quality indicators very important for the aquatic life. It is essential both for plants and animals. When the level of the oxygen present in the water reaches about 3 parts per million (ppm), the fish and many other aquatic organisms cannot survive. *A large amount of dissolved oxygen in the water will determine a rapid oxidation of the toxic substance, thus leading to the detoxification of the liquid and thus extend the period of survival of the organism*, (Carabet A., 2001).

We have noticed that during a year interval the average concentration of the dissolved oxygen in the Suceava River water decreases from February to July (when the monthly maximum value is registered) , but then increases until December/January (depending on the control section). During the winter we have registered the greatest amounts of dissolved of dissolved oxygen in the water, due to the fact that low temperatures diminish the oxidation processes and favor the dissolution of the oxygen in the air. During autumn, as the temperature of the water decreases, the amount of dissolved oxygen in the water increase as well.

Water flows (rivers and their tributaries) are generally characterized by a low mineralization, the total amount of dissolved minerals being below 400 mg/l. This mineralization is usually formed by dicarbonates, chloride and sodium, potassium, calcium and magnesium sulphates. The overall hardness is usually less than 15 degrees, in most cases this hardness being represented by dicarbonate hardness. The concentration of oxygen ions (the pH) has usually a neuter value, pH=6.8-7.8. Of the dissolved gases there are usually present the dissolved oxygen, having 65-95% saturation, and the free carbon dioxide, usually less than 10 mg/l.

The main characteristic of the water streams is the variable load of matter and organic substances in the suspension; this load is directly related to the climatic and meteorological conditions. These usually go up during the raining period, reaching their maximum during the floods, and their lowest value during the frost period.

The waste of some effluents, which are insufficiently purified, led to the alteration of some water streams and to the appearance of a wide range of impurities, such as slowly degradable organic substances, nitrogen, phosphorous, sulphur compounds, microelements (such as copper, zinc and plumbum), pesticides, organic chlorinated insecticides, detergents etc. In many cases there can be also find plenty bacteriological impurities. A characteristic particularity of river water is the capacity to clean itself, due to a series of natural biochemical processes favored by the water-air contact [4].

Monitoring the water streams is a permanent process which is usually applied to control sections characteristic for each natural stream. The present monitoring system for surface waters can perform 4 determinations a year for those sections having a periodic control rhythm and 12 determinations a year for those sections having a monthly control rhythm. The indicators given in the reference normative for surface water quality classifications have been divided into several main groups (oxygen rate – RO, nutrients – N, mineralization degree – GM, metals – M, micro-pollutants - TS), as follows:

- The «oxygen rate» group, comprising: dissolved oxygen, CBO_5, CCO-Mn, CCO-Cr;
- The «nutrients» group, comprising: ammonium, nitrite, nitrate, total azote, orthophosphate, total phosphorus, chlorophyll;
- The «general ions, salinity group», comprising: dry filterable residue, sodium, calcium, magnesium, total iron, total manganese, chlorides and sulphate;
- The «metal» group, comprising: zinc, copper, total chrome, arsenic. Metals such as plumbum, mercury, cadmium and nickel have been placed into the priority substances category;

The «organic and inorganic micro-pollutants», comprising: detergents, phenols, AOX, mineral oil hydrocarbons. Other substances, such as PAH-s, PCB-s, lindane, DDT, atrazine, trichloromethane, trichloretane, tetrachloretane and others have been listed under the priority substances group.

3.3 Data Analysis

The measurements made every two months have been overlapped on the data obtained from the SGA Suceava[1], which have been monthly taken, with some small exceptions. The data have been interpolated using the splene cubic

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[1] SGA stands for ***Sistemul de Gorspodărire a Apelor Suceava*** (***Water Management System Suceava***), part of the **«Romanian Waters» National Administration,** having the following main attributions:

1. unitary and long lasting water resources management both for the surface and for the underground waters, and their protection against exhaustion and degradation like rational and balanced sharing of these resources.
2. administration, operation and maintenance of the National System of Water Management infrastructure, found within it's own administration;
3. administration, operation and maintenance of minor water river beds, lakes and ponds, in their natural or fitted condition, of the sea wall and beach , wetlands and other areas protected under heritage;
4. administration, operation and maintenance of the National Hydrological and hydro-geological infrastructure system;
5. administration, operation and maintenance of the National System of Water Resources Quality Supervision;
6. Realizing the informatics and telecommunications system within the Water Management System units, developing software products in the field of water management, hydrology and hydro-geology;
7. ensuring the functions of being a single operator for the natural water resources found on the surface or which have just been upgraded , regardless of any title holder of the arrangement, and for the underground water resources, regardless of their nature and related facilities, with their natural potential, with the exception of the living aquatic resources that are found under law provisions, except the ones expressly provided in the specified rules;
8. allocating the right to use the resources of the surface waters and groundwater in all its forms, for use with their natural potential, with the exception of living aquatic resources, based on subscriptions and in accordance to the provisions of the Water Law No. 107/1996, and with subsequent amendments;
9. defense against floods through the work of the Water Management units found in it's administration and manage the stocks of materials and specific means of defense against floods;
10. maintenance and operation works of water management of the public domain of the state, as a defense against floods, found in administration;
11. the approval and authorization from the viewpoint of the water management works and activities that take place on waters or related to waters;
12. staff training and improvement within the field of water management in their own training units and / or in collaboration with other specialized institutions;
13. yearbooks development, synthesis, studies, projects, instructions, books and publications in the field of water;
14. developing the directory schemes for planning and managing river basins;

functions, with the same 0.2 time unit digitization. Thus, the evolution of the described parameters (water flow, water temperature and the level of dissolved oxygen) was analyzed. By analyzing the two fig.s bellow (**fig. 3** and **fig. 4**) we notice some conformities as well as some disturbances described as follows:

- In the time interval comprised in the 4th, 5th and 6th month there has been registered a significant water flow variation, hidden in the case of the monitoring done every two months. Thus, the water flows are over 60. This implies the presence of a corresponding amount of N-NO_3 (**fig. 4**) during the 4th and 5th month, which implies, in its turn, a decrease in the amount of dissolved oxygen (DO).

Thus, during those time intervals when the water flow registers significant variations or when the temperature varies greatly, the frequency of data monitoring, registration and interpretation has to increase. Otherwise, over limit increased water flows would be overlooked (check **fig. 5**, 5th month of 2008).

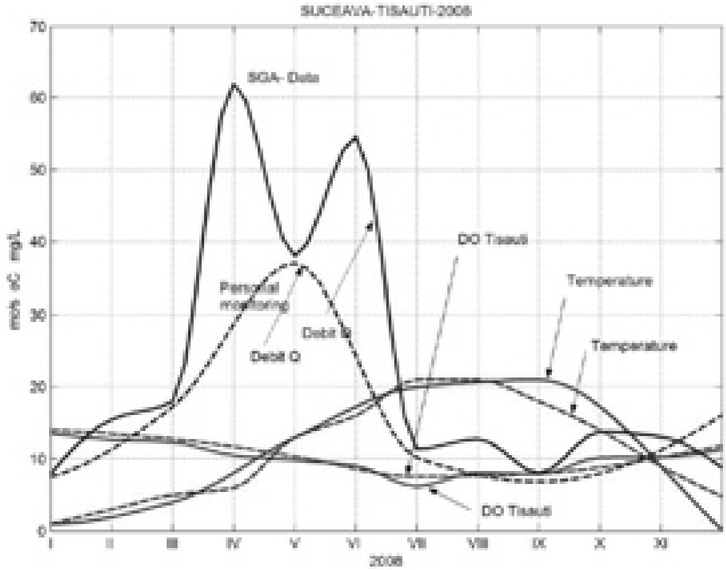

Fig. 3 *– Monthly registered data by the SGA Suceava, overlapped with the data gathered in 6 months’ time and then interpolated*

15. fulfilling the commitments made by the Romanian state through international agreements and conventions in the field of water;
16. implementation the EU directives in the field of water.

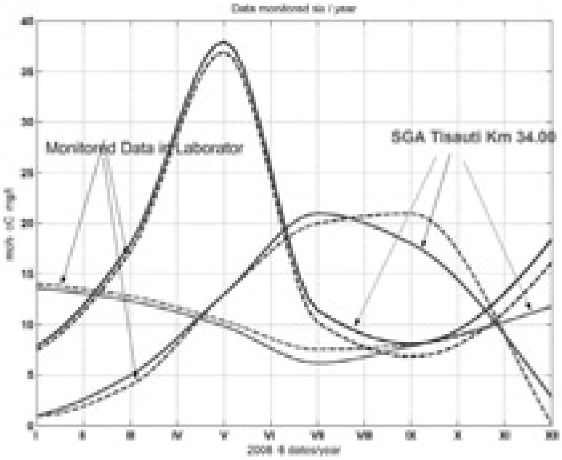

Fig. 4 *– The data gathered from the Tişăuţi section in 6 of the 12 monitored months, overlapped, interpolated over the data the authors have collected on their own. Some values can be observed, such as the minimum and maximum limits*

3.4 Determining the amount of dissolved oxygen

The electrochemical method using a floater - the experiment has been performed according to the SR EN 25814 ISO 5814/Nov. 1999 – Water Quality.

The principle of this method:

In the water undergoing this analysis a floater (consisting of a close cell of a selective membrane, containing the electrolyte and two metal electrodes) has been immersed. Due to the potential difference between the electrodes, caused by the galvanic action or by an external source of electricity, the oxygen passes through the membrane and it is revived at the cathode, while the metal ions in the solution migrate towards the anode. The electricity thus obtained is in direct ratio with the speed the oxygen passes through the membrane and the electrolyte layer, and consequently in direct ratio with the partial pressure of the oxygen from the analyzing sample. The interpolated data using spline functions indicate minimum and maximum values for the dissolved oxygen ranging from 8.46 to 13.67 mg/l (**fig. 5**).

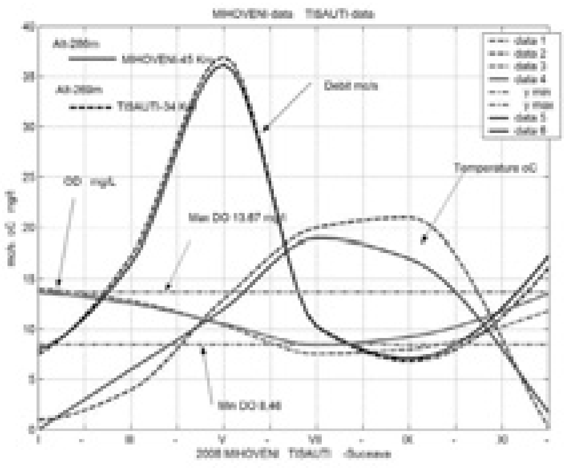

Fig. 5 *– Monitored and analyzed data in the two locations, Mihoveni and Tisăuti, at a distance of 11 km, minimum and maximum data for the dissolved oxygen*

3.5 Correlations of the physic-basic indicators

Determining the biochemical oxygen consumption after 5 days (CBO5)

The biochemical oxygen consumption after 5 days (CBO5), expresses as mg/l of oxygen, is calculated using the following relation:

$CBO5=ODo-OD_5$, where:

- ODo is the concentration of the dissolved oxygen in the sample under determination in the initial moment;
- OD_5 is the concentration of dissolved oxygen in the sample under determination after 5 days' time.

Determining the chemical oxygen consumption CCOCr referring to the determination of the amount of bichrome the organic and inorganic bichrome oxidizable substances present in the water environment have used

The samples taken are to be analyzed no later than 5 days after their collection. If the sample needs conservation before the analysis, 10 ml of sulphuric acid for every liter of sample will be added, and then the sample will be kept at 0º-5ºC. This method is applied to those samples having their CCOCr between 30 – 700 mg/l. The chloride content cannot exceed 1000mg/l. If their value exceeds 700mg/l, the water sample will be diluted. In order to get a real result, the CCOCr value will preferably be between 300-600 mg/l.

The chemical oxygen consumption, CCOCr, expressed in mg/l, is calculated using the following formulae:

$$\mathrm{CCOCr} = \frac{8000c(V_1 - V_2)}{V_0}$$

Where:

- ✓ c is the substance concentration of the ferrous sulphate (II) solution and ammonium, mol/l;
- ✓ V_0 is the volume of the sample undergoing the analysis before its dilution (if this has been done), ml;
- ✓ V_1 is the volume of the ferrous sulphate (II) solution and ammonium used for the titration of the witness sample, ml;
- ✓ V_2 is the volume of the ferrous sulphate (II) solution and ammonium used for the titration of the sample to be analyzed, ml;
- ✓ 8000 is the molar mass of ½ O_2 in mg/l.

Determining the chemical oxygen consumption CCOMn referring to the determination of the amount of potassium permanganate used by the organic and inorganic potassium permanganate oxidizable substances present in the water environment.

If from the moment the water sample was collected and until the actual determination pass more than 2 hours, the water sample must be conserved by adding 2 ml of sulphuric acid for every 100ml of water sample. The analysis must be performed on an unfiltered water sample. When necessity asks for it, filtered water can be used as sample, but this should be mentioned in the analysis documents.

The method applies to all samples having their CCOMn level between 4 to 25 mg/l O_2/l. The values obtained after applying this method are known as potassium permanganate oxidizability or chemical oxygen consumption determined by using potassium permanganate (CCOMn).

The chemical oxygen consumption (CCOMn), expressed in mg/l or mg O_2/l is calculated using the following formulae:

$$\text{CCO-Mn} = [(V_1+V_2)f-V_3]c\ 1000/V_4 \qquad [\mathrm{mgKMnO_4/l}]$$

where:

- ✓ c – the amount of potassium permanganate measured in mg, corresponding to 1 ml of potassium permanganate 0.01n(0.316mg) or (3.16mg) for 0.1n;
- ✓ V_1 is the volume of the potassium permanganate solution 0.01n or 0.1n initially added, in ml;
- ✓ V_2 is the volume of the potassium permanganate solution 0.01n or 0.1n used for the titration of the water sample to be analyzed, in ml;
- ✓ V_3 is the volume of the oxalic acid solution 0.01n or 0.1n added to the solution, in ml;
- ✓ V_4 is the volume of the working water sample, in ml;
- ✓ f is the factor of the potassium permanganate solution 0.01n or 0.1n;
- ✓ (CCO-Mn) expressed in mgO_2/l:

$$\mathrm{CCOMn}=\mathrm{KMnO_4}\ 0{,}253[\mathrm{mgO_2\ /l}]$$

where:

$KMnO_4$ is the calculated amount of potassium permanganate in mg/l;
0.253 is the amount of oxygen in mg corresponding to 1mg of $KMnO_4$. (Popa R, Pecingină I., 2008)

Other important indicators which have been determined by experiment and further used in the study of the quality of the water in Suceava River are ammonium, nitrates, nitrites.

Nitrates pollution has increased over the past decades, due to the extensive use of azoth fertilizers in agriculture.

Ammonia can get into the water either from the soil or by mineralizing the organic substances in auto-purification process of the water.

If we analyze the experimental data, we can conclude that:

- The water of Suceava River on the Mioveni section, in 2008, can be classified as 1st class water considering the value of the ammonia concentration, which does not exceed the maximum ammonia concentration limit for the 1st class water type (0.4 mg N/l).
- The water of Suceava River on the Mioveni section, in January 2008 , the value 0.085 mg N/l exceeds the maximum limit for a 3rd class water quality (which is 0.06 mg N/l); during spring and summer, on the Mihoveni section the river is not polluted with nitrites, but starting with August and for the rest of the autumn, the concentration value of ammonia exceeds the maximum limit for the 1st class water, and thus the water falls into the 2nd class quality.

The concentration of nitrates on the Mihoveni section of Suceava River in 2008 does not exceed the maximum limit of 1st class water quality.

On the other hand, is we analyze the experimental data, we can conclude that:

- In 2008, on the Tişăuţi section of Suceava River, the water can be classified as 2nd class, since the concentration value of ammonia exceeds the maximum limit for 1st class waters (which is 0.4 mg N/l), in January 2008 this value corresponding to the 3dr class water quality.
- In 2008, on the Tişăuţi section of Suceava River the indicators reflecting the concentration value of the nitrites exceeds the maximum limit established for the 2nd class water quality (which is 0.03 mg N/l), and thus Suceava River falls into the 2nd and 3rd class water quality category.
- On the Tişăuţi section of Suceava River, the concentration of nitrates slightly exceeds the maximum admitted value for 1st class water quality, thus falling into the 2nd class water quality type.

In conclusion, Suceava River is more polluted downstream, on the Tişăuţi section, than on the Mihoveni section.

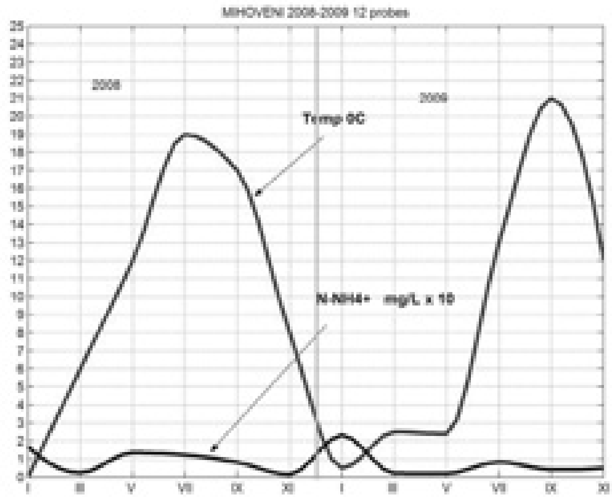

***Fig. 6** – The temperature in ºC and N-NH_4^+ (mg/Lx10)*

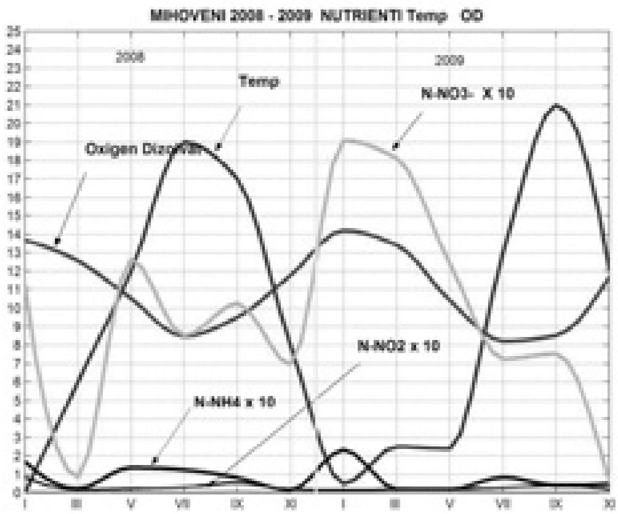

Fig.7 *– The nutrients regimen, dissolved oxygen and temperature*

We can easily observe the conformity between the temperature and the dissolved oxygen, and the most obvious of all is the conformity between the dissolved oxygen and N-NO_3, when the amount of dissolved oxygen increases and the concentration of the nutrient decreases.

CONCLUSIONS

The quality characteristics and the pollution parameters have to be evaluated on a regular basis and frequency, considering the ecological and hydrological aspects of the water stream in discussion, as well as the typical pollution emissions in this particular hydrographic basin.

The term monitoring encloses, most of the time, all the aspects related to quality data collecting. Thus,
Monitoring = collecting information from pre-established points and at pre-established time intervals;
Monitoring = presenting the data in order to emphasize the required conditions and determine the possible tendencies;
Monitoring = evaluation.

All water quality standards are and will be a biased and imperfect instrument for various reasons, such as:

- The true scientific approaches are blocked by all kinds of mentalities and social habits, such as the different perception of risk, placing the interests of the community first;
- The water standards are still uniform, regardless of the fact that the water is different from one water stream to another and that the water samples are taken at a certain moment and thus the situation they envisage are only temporary and from temporary limited segments. In the present study, these evolutions have been rendered by using continuous and differentiable functions, without sudden variations. We can call these functions we have used «almost limited functions».
- The «short» temporal situations can «cover» momentarily serious situations; the interpretations and analysis come across different kinds of technical and economical limitations and thus compromises are necessary, as well as an emphasis only on typical situations.
- In reality, the expression «maximum concentration admitted» is only arbitrary and more of compromise than anything else; thus, in the process of data interpretation must be the principles and the methodology which have led to the admission of those data must also be considered;
- There is a stringent need of analysis and implementation of periodic monitoring methodologies assisted by specialized information software able to increase the quality data frequency, as well as creating a data base comprising wider time intervals and able to make predictions regarding risk phenomena by using statistic-mathematical methodologies;
- Data monitoring and analysis must be adapted to the specific level, especially for such water streams as internal rivers, where sudden concentration variations can appear and have a different evolution from those of large water streams. Last but not least, the aeration level characteristic for water streams with a large flow and

high flowing speed must be taken into account; this asks for a waterfall monitoring system, identifying the areas with a large auto-purification capacity, as well as using the floodable projected areas for controlling the auto-purification process.

The following directions of utmost interest become paramount: analyzing and settling periodic control methodologies assisted by specialized information software able to increase the quality data frequency, as well as creating a data base comprising wider time intervals and able to make predictions regarding risk phenomena by using statistic-mathematical methodologies.

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