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MONITORING AND EVALUATION OF TIMIŞ RIVER (BANAT, ROMANIA) WATER QUALITY BASED ON PHYSICOCHEMICAL AND MICROBIOLOGICAL ANALYSIS

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ABSTRACT

Flowing water, like rivers, represent an important drinking water source for Romania, their quality being influenced by the quantity of materials in suspension and in colloidal form, and their physicochemical and microbiological characteristics. The Timiş River is generally characterized by the presence of some impurities in natural state, their specific composition being dependant on the nature of the surrounding soils, the soils in the reception basin, waste water spills from different users, and the dissolving capacities of the gases in the atmosphere.

The Timiş River has in general a lower level of mineralization, the sum of mineral salts dissolved being below 280 mg/l and formed of bicarbonate, chloride, nitrate, phosphates, sodium sulphate, potassium, calcium and magnesium coming from the erosion of rocks, soils and precipitations. The concentration of hydrogen ions (pH) is situated around neutral, ranging from 7.3 to 8.8; among the dissolved gases is oxygen, with values ranging between 4.52 and 7.46 mg/l. The main characteristic of the water flow is represented by the variable charge (sometimes appreciable) of materials in suspension and colloidal materials (clay, sand, silica) but also by organic substances, the charge being directly proportional to the meteorological and climate conditions. This charge grows during rainfalls, reaching the maximum during large floods and the minimum during freezing periods (CCOMn max. 30.2 mg O_2). Heavy metals like mercury and arsenic are found in the Timiş waters, but in quantities that do not conclusively affect the water quality, their values being below the maximum allowable amounts.

Bacteriological contamination is also observed. Microorganisms, viruses and protozoa are derived from wastewater spills with human or animal waste, and microorganisms specific to the ecosystem. The total coliforms reach $5x10^3$/100 ml water, the fecal coliforms $2.2x10^2$/100 ml water, which results in several sectors of the river being classed as lower quality.

ZUSAMMENFASSUNG: Monitoring und Bewertung der Wasserqualität des Timiş-Flusses anhand von physikalisch-chemischen und mikrobiologischen Analysen.

Die Fließgewässer stellen eine wichtige Trinkwasserresource für Rumänien dar, wobei ihre Qualität von der Menge der Schwebstoffe und der kolloidalen Stoffe sowie deren physikalisch-chemische und mikrobiellen Charakteristika beeinflusst wird. Der Timiş-Fluss kennzeichnet sich allgemein im natürlichen Zustand durch das Vorhandensein von Verunreinigungen, die spezifische Zusammensetzung ist jedoch abhängig von der Art der Böden durch die das Wasser fließt, von den Böden im Einzugsgebiet, aber auch von den Abwässern die von verschiedenen Verbrauchern eingeleitet werden sowie der Lölichkeitskapazität.

Der Timiș-Fluss kennzeichnt sich allgemein durch eine niedrige Mineralisierung, wobei die Summe der gelösten Mineralsalze unter 280 mg/l liegt und aus Bicarbonaten, Chloriden, Nitraten, Phosphaten, Natirumsulfaten, Kalium, Kalzium und Magnesium besteht, die sich durch die Erosion der Gesteine, des Bodens und durch die Regenfälle gebildet haben. Die Konzentration der Wasserstoffionen (pH) liegt um den neutralen Wert, zwischen 7,3 und 8,8; von den gelösten Gasen ist der gelöste Sauerstoff mit Werten von 4,52 und 7,46 mg/l zu nennen. Das Hauptkennzeichen des Flusses ist die wechselnde Belastung (manchmal beachtliche) durch Schwebstoffe und kolloidale Stoffe (Ton, Sand, Silizium), aber auch durch organische Stoffe, die direkt proportional abhängig sind von den meteorlogischen und klimatischen Bedingungen. Diese steigen während Regenzeiten, erreichen ein Maximum während der großen Hochwässer und sinken auf ein Minimum während Frostzeiten (CCOMn max. 30,2 mgO_2). Schwermetalle wie Quecksilber und Arsen sind im Timiș-Fluss vorzufinden, jedoch in Mengen, die Wasserqualität kaum beeinflussen, da die Werte unterhalb der zugelassenen Höchstmengen liegen.

Es wurden auch bakteriologische Verunreinigungen festgestellt. Die dem Ökosystem eigenen Mikroorganismen, Viren, Protozoen stammen aus der Einleitung von Abwässern, die mit menschlichen oder tierischen Ausscheidungen verunreinigt sind. Die Gesamt Coliformen erreichen bis zu 5 x 103/100 ml Wasser, die fäkalen bis zu 2.2 x102/100 ml, was abschnittwese zur Einstufung des Flusswassers in eine niedrigere Qualitätsklasse führt.

REZUMAT: Monitoringul şi evaluarea calităţii apei râului Timiş pe baza analizei fizico-chimice şi microbiologice.

Apele curgătoare, precum râurile, reprezintă o sursă importantă de apă potabilă pentru România, calitatea acestora fiind influenţată de cantitatea de materii în suspensie şi coloidale, caracteristicile fizico-chimice şi microbiologice ale acestora. Râul Timiş este caracterizat în general, de prezenţa unor impurităţi existente în stare naturală, compoziţia specifică fiind însă dependentă de natura solurilor traversate de cursul de apă, a solurilor din bazinul de recepţie, dar și de apele uzate deversate de diferiţi utilizatori şi a capacităţii de dizolvare a gazelor din atmosferă.

Cursul râului Timiş prezintă, în general, o mineralizare mai scăzută, suma sărurilor minerale dizolvate fiind sub 280 mg/l şi formată din bicarbonaţi, cloruri, azotaţi, fosfaţi, sulfaţi de sodiu, potasiu, calciu şi magneziu, provenite din eroziunea rocilor, solului şi datorită precipitaţiilor. Concentraţia ionilor de hidrogen (pH-ul) se situează în jurul valorii neutre, fiind cuprinsă între 7,3 şi 8,8 oxigenul dizolvat prezintă valori între 4,52 şi 7,46 mg/l. Caracteristica principală a cursului de apă o prezintă încărcarea variabilă (uneori apreciabilă) cu materii în suspensie şi coloidale (argile, nisip, silice), dar şi substanţe organice, încărcare legată direct proporţional de condiţiile meteorologice şi climaterice. Acestea cresc în perioada ploilor, ajungând la un maxim în perioada viiturilor mari de apă şi la un minim în perioadele de îngheţ (CCOMn max. 30,2 mg O_2). Metale grele precum mercurul sau arsenul se regăsesc în apele râului Timiș, dar în cantități ce nu afectează în mod concludent calitatea acestor ape, valorile fiind sub limitele maxime admise.

De asemenea, se remarcă poluarea de natură bacteriologică. Microorganismele, virusurile, protozoarele provin din deversări ale apelor uzate contaminate cu dejecţii umane sau animale, microorganisme propri ecosistemului. Coliformii totali ajung până la 5 x 10^3/100 ml apă, cei fecali până la 2,2 x 10^2/100 ml apă, ceea ce pe anumite sectoare încadrează apele râului într-o clasă inferioară de calitate.

INTRODUCTION

One of humanity's biggest present problems is pollution. It is obvious that the natural environment is slowly deteriorating and ecosystems are no longer able to adapt to the pressure of anthropic factors, the self regulation of the ecosphere being no longer possible (Kirschner et al., 2009; Oprean et al., 2007; Balzer et al., 2010). Water pollution represents an alteration of its physical, chemical, biological, bacteriological and radioactive qualities above an established admissible limit that is directly or indirectly produced by human activity. Polluted waters become unsuitable for normal usage as potable water, in industry, recreation or agriculture (Oprean et al., 2009; Darie et al., 2007).

Biological pollution mainly represents a bacteriological contamination. It raises serious public hygiene problems, which disseminate fast. Polluted water accentuates the pathogen affections like: typhoid fever, dysentery, enteric viruses (Hirotani et al., 2010; Korajkic et al., 2010; Basemer et al., 2005).

The usage of water streams as dilution medium of the urban effluent may have severe consequences on the public hygiene. It has been demonstrated that water polluted by different organic matters allow numerous pathogen germ species to multiply in incommensurable proportions compared to a clean water medium (Oancea et al., 2007; Blanch et al., 2004).

Canal systems, municipal and industrial insufficiently treated wastewater, human or animal directly spilled dejections into surface waters can produce bacteria, virus and parasite contaminations which lead to water transmissible diseases also called hydric diseases (Korajkic et al., 2010).

MATERIAL AND METHODS

Water samples have been collected from 11 key points, (T1-T11), the following parameters being kept track of in the physicochemical analysis of the water in the Timiş River: pH, electric conductivity, filterable dry residuum at 105°C, CCOMn, CCOCr, CBO5, ammonia azoth, nitrates, nitrites, orthophosphate, sulfurs, sulfates, matter in suspension, heavy metals.

- The pH determined according to SR ISO 10523/1997 acid or basic disrupts the biological treatment and auto treatment processes;

- The chemical and biochemical oxidability, respectively CCOCr (SR ISO 6060/1996) and CBO_5 (SR ISO 5815/1991), are global indicators of the organic substances; the CBO_5/CCOCr proportion, if it is below 0.4, indicates the presence of non-biodegradable substances in the water;

- Nitrogen, in a ammonia form, represents the main indicator that highlights the organic azoth pollution degree of wastewater, being determined according to (SR ISO 7150-1/2001), nitrate according to SR ISO 7890-3/2000 and nitrite according to SR ISO 6777/1996;

- Sulphides (SR 7510/1997) can influence the biologic purification processes when their quantities exceed certain limits; they can appear in the effluents coming, in general, from textile producing companies, tanneries, etc.;

- Heavy metals (As, Cd, Hg) are toxic for the microorganisms participating to the biological purification of water.-The above mentioned metals have been determined by using the SR EN ISO 15586/2004 "Water quality - Determination of trace elements using atomic absorption spectrometry with graphite furnace" method. Graphite Furnace Atomic Absorption Spectrophotometer a ZEENIT 650 - Analytik Jena Germany equipped with a graphite atomizer, a Zeeman-effect background correction, and an integrated auto sampler were used.

Graphite furnace atomization is a technique of improving the sensitivity and limit-of-detection for atomic absorption measurements. A small amount of sample or standard solution is placed inside a hollow graphite tube. This is resistively-heated in a temperature program to remove sample, burn off impurities, atomize the analyte to form a plume of free metal vapors, and finally clean the tube. Graphite tubes with coating and platforms made of pyrolytic graphite were used throughout the work. Argon of 99.998% purity was used as the purge gas. All reagents were of analytical–reagent grade, unless stated otherwise. For both techniques, ultrapure concentrated HNO_3 solution (Merck) was used. Standard solutions were prepared daily from the stocks, in PFA tubes, with deionized water (0.055 µS cm^{-1}conductivity). High purity ICP Multi Element Standard Solution XXI CertiPUR obtained from Merck (Darmstadt, Germany) was used for calibration during all quantitative analysis. For quantitative determinations, a calibration curve was obtained for each element. All plastic labware used for the sampling and sample treatment were new or cleaned by soaking 24 h first in 10 % HNO_3 then in ultra-pure water.

In view of a better correlation of the obtained results, the physicochemical indicators have been grouped depending on their chemical role as such: SOT – implies total oxidable substances (homogenous sample) or dissolved (decanted sample for 30 min.), expressed in CCO-Cr or CCO-Mn and CBO_5.

- S – salts – chloride have been included here, fix residuum, sulfates; represent the sum of azoth containing compounds which confer water quality groups classification qualities. The bacteriological evaluation of water and especially of coliforms bacteria can be done both by using the multiple tubes method as well as the filtering membrane method. This method presents the advantage of quick filtering of the water samples (100 m L) and of the dilutes (10^{-1}, 10^{-2}), with a porosity membrane 0.45µm. The dilutions 10^{-1} are realized as follows: a 10 mL water sample is pipette in 90 mL of normal saline solution and the mix is homogenized. After homogenization, 10 mL of dilution 10^{-1} is harvested and introduced in another 90 ml of normal saline solution to obtain a dilution of 10^{-2}.

The determination of the probable number of coliform bacteria (total coliforms)(CT)

Three Petri plates are prepared with dehydrated VRBA medium. The culture medium is being hydrated according to the producer's indications. Two dilutions will be harvested (10^{-1}, 10^{-2}) and afterwards filtrated with membranes of 0.45µm porosity. The membranes will be taken with sterile pincers and introduced into the Petri plates with rehydrated VRBA medium. The 3 Petri plates will be incubated at 37°C for 24 h. The counting will be carried out bearing in mind the dilution.

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The determination of the probable number of thermo tolerant bacteria (fecal coliforms)(CF)

Petri plates are prepared with dehydrated MFC medium. The culture medium is being hydrated according to the producer's indications. Two dilutions will be harvested (10^{-1}, 10^{-2}) and afterwards filtrated with membranes of 0.45µm porosity. The membranes will be taken with sterile pincers and introduced into the Petri plates with rehydrated MFC medium. The three Petri plates will be incubated at 44°C for 24 h. The counting will be carried out bearing in mind the dilution.

RESULTS AND DISCUSSIONS

The pH varies during the run from 7.31 neutral, to basic reaching the harvest point 10 with a value of 8.81 (Fig. 1). A basification of the water can be concluded, under the influence of the exterior effluents, coming from industry or human settlements. The legislation permits a maximum pH value of 8.5. For the collection points 10 and 11 a correction intervention will be undertaken along with an investigation of the causes of this growth in pH.

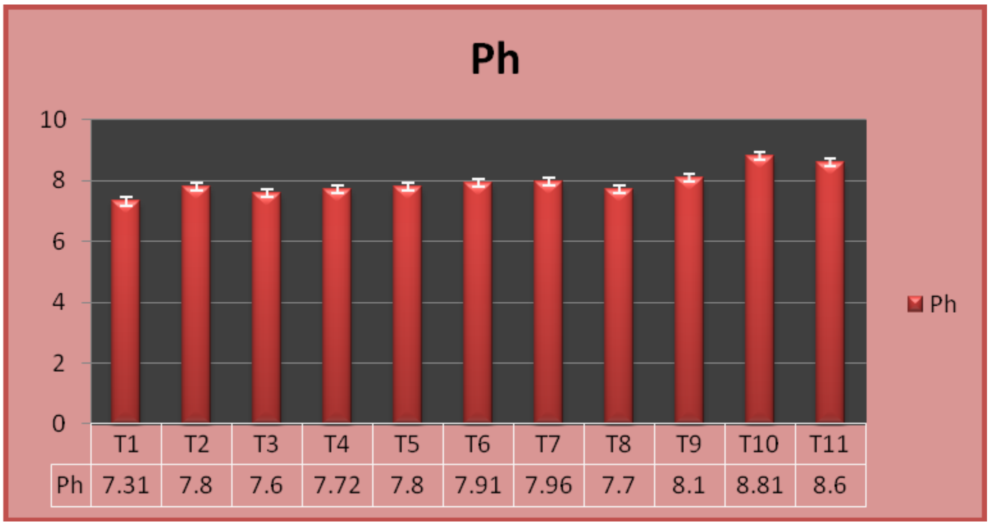

Figure 1: pH evolution in the 11 collection points along the Timiş River.

Following the oxygen regime, it can be concluded that it presents a series of particularities depending on the collection point. The most pronounced organic charge is identified in collection point T4, according to figure 2, and the lowest in T1, where the determination value ranges from 30.72 mg/L to 50.08 mg/L.

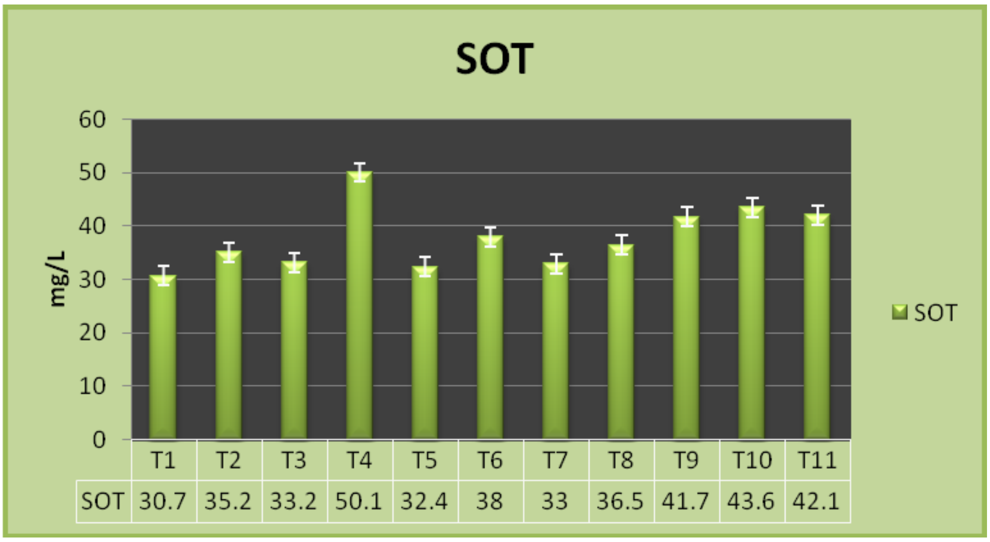

Figure 2. The evolution of total and dissolved oxidizable substances in the 11 collection points, along the Timiş River.

The quantity of organic substances that can be degraded by the bacteria (biodegradable) that is present in the waters of the Timiş River, represented by CBO5, reaches maximum values of 1.43 mg/L, values which are within the maximum obligatory frame for the first quality class. The total quantity of organic substances present in the river water, which can be chemically oxidized (by the potassium dichromate and/or potassium permanganate) reach values of 13.6 respectively 30.2 mg/L, which places segment 4 of the river in quality class III.

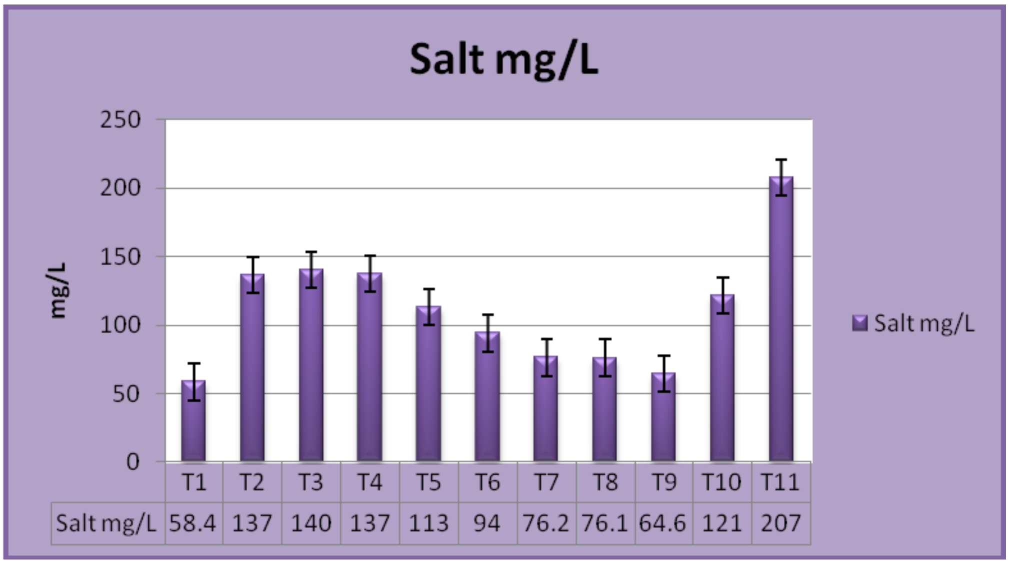

Figure 3: Salt evolution (chloride, fixe residuum fix, sulphates) in the Timiş River, along the 11 collection points.

The salt quantity measured in the 11 collection points during the monitoring period indicates that water reaches T1 with a charge of 58.441 mg/L salts, then grows to 140.19 mg/L at T3 and drops from T3 to T9 up to 64.64 mg/L, while in T10 and T11 it grows again up to 207.44 mg/L. According to figure 3 and to the salt indicator, the water subjected to the monitoring process fall into the first quality group, their accumulation not exceeding 210 mg/L, the actual standards allowing double this value.

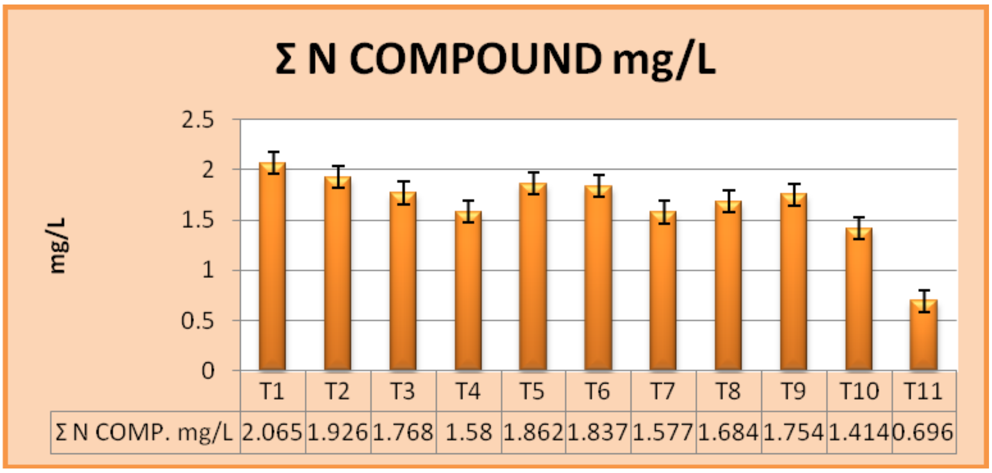

Figure 4: The evolution of the azoth compounds, along the 11 collection points.

Regarding the azoth based compounds, figure 4 shows a uniform evolution, meaning that maximum values are found in T1, T2 and minimum values in T11. The uneven evolution of these compounds is firstly due to the chemical structure of the rock along the river as well as to the human and animal dejections, industrial residuum and agrochemical waste contamination. The oscillation of these values leads to the 1-2 quality category framing for the Timiş River. The NO_3 is actually the compound which determines this framing because it frequently exceeds the values of 1, admitted by the normative.

Heavy metals, As, Cd and Hg, have been identified in reasonable quantities, their amount not exceeding the maximum admitted values in the Timiş River. The tracked metals have only been found in three3 collection points, according to figure 5.

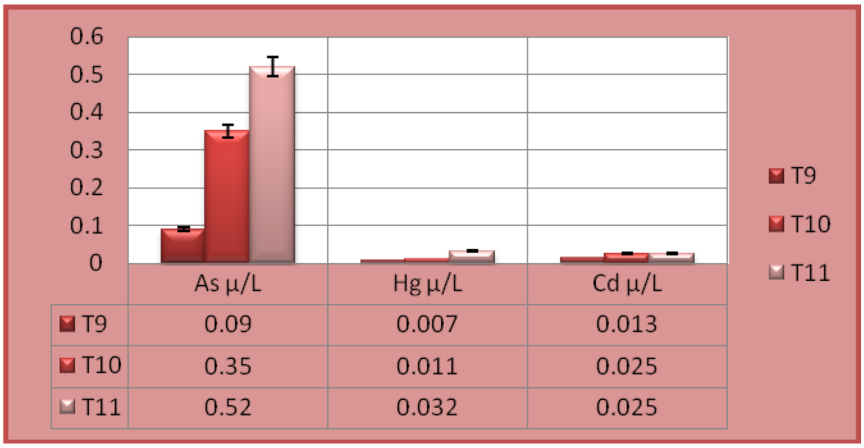

Figure 5: The evolution of Arsenic, Lead and Cadmium in the Timiş River.

The determination of the probable coliform bacteria number (total coliforms)

By observing figure 6, it can be concluded that total coliforms has been identified in Timiş River in quantum of $7 x 10^3$ coliform /100cm³, in collection point T2, and the lowest is T11, where this value does not exceed 79 units. The most crowded areas are T2 and T6, followed by T3, T5, T4 where they are situated around 2.2-2.8x10^3units. From this point of view, the waters are classified in quality class II.

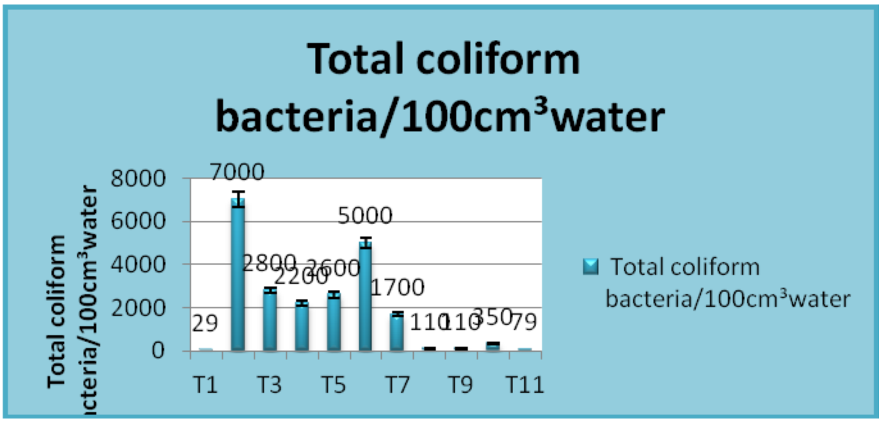

Figure 6: The evolution of the total number of coliform bacteria that has developed at 37ºC, along the 11 harvest points on the Timiş River.

As shown in figure 7, the fecal coliforms, the contamination factors made of human and animal dejections, are present in large numbers in harvest points T2 and T4, where their values exceed 200 de units / 100cm^3 water. The recommendation for these points is the stopping of the fecal pollution by means of uncontrolled spills in the Timiş River. The fecal coliforms number is reduced throughout the following harvest points, explained by the regulation and control over the spills but also possible dilutions from tributary rivers. The values of the fecal coliforms detected throughout points T1, T6, T7, T8, T9, T10 and T11 are situated under 100, the legal limit established for I quality class waters since 1996.

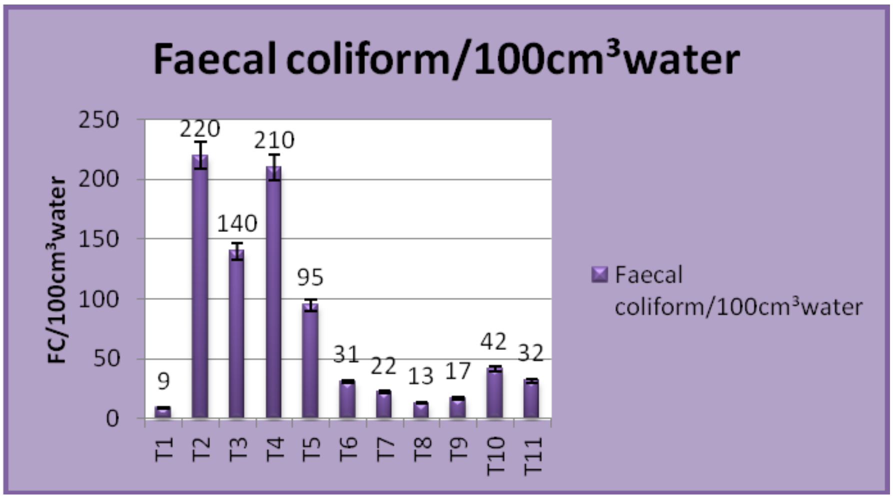

Figure 7: The evolution of the total fecal coliforms number that has developed at 44ºC along the 11 harvest points on the Timiş River.

CONCLUSIONS

The water sample swab in the 11 harvest points led to obtaining precise results but revealed neuralgic zones in the Timiş River.

From a physicochemical point of view, the waters can be classified in I-II quality class, not being affected by the heavy metal contaminations.

A more efficient monitoring over the organic substances spills which lead to oxygen level and active fauna drops is recommended.

From a microbiologic point of view, the waters are classified as being I-II quality class, but a more rigorous control from the qualified factors over these zones is recommended in view of stopping the touristic pollution in the area, especially in holiday houses and improperly decorated areas.

To conclude with, the appreciation of water quality and implicitly the usage possibilities in different purposes is a complex activity. The simple existence of some precise results based on a great variety of organoleptic, physical, chemical, biological and bacteriological analysis proves to be insufficient for a correct interpretation, for establishing the causes, predicting the evolution tendencies and establishing the other necessary elements for a proper management.

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