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Article

ARE THE SURFACE WATER SOURCES FROM TIMIŞ COUNTY SAFE FOR CHILDREN AND PREGNANT WOMEN HEALTH?

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ABSTRACT

Without claiming to achieve an integrated monitoring or intensive activities for the quality of surface water in the investigated area, this paper aims to assess the quality of water from Bega and Timiş rivers with regard to nitrites, nitrates and chlorides. This is part of a larger study on the quality of water sources in the region, with regard to the anionic and cationic pollutants. The study follows the impact of the drinking water on the human health, especially children and pregnant women. The considered parameters were below the admitted value, therefore no pollution problems were found.

Keywords: surface water, water quality, nitrites, nitrates, chlorides

1. INTRODUCTION

Any solid, liquid, gaseous or vapour that enters into the environment, changes the balance of its components and damage living organisms by bringing pollutants [1].

We define the background pollution as that not directly influencing the environment and show pollution impacts in areas directly affected by the pollution sources.

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The degradation of water quality may be caused by: low level of network equipment catalyst, manure removed from the breeding complexes and poultry, deposits of silt and garbage made on various surfaces, fertilizers and pesticides incorrectly administered on agricultural land.

Nitrates and nitrites are natural, soil components generated by organic matter mineralization of nitrogen of plant and animal origin. Nitrogen mineralization is primarily due to existing soil microorganisms. In countries with temperate climate, this process takes place with maximum intensity in summer [2].

Naturally, between nitrates and nitrites in the soil, water and plant exists a balance that can be broken by the intensive use of natural organic fertilizers (manure), especially nitrogenous synthetic compounds, in agriculture [2, 5]. Their degradation by-products can accumulate in plants growth to levels harmful to consumers.

Nitrates, as such, have a low toxicity (when used in small doses), and they were usually used as a diuretic.

Nitrate is absorbed very quickly by the small intestine and excreted by the kidneys, saliva and gastric juice [1, 2]. To generate problems, nitrate has to be ingested in large amounts (up to 10g per dose). Generally, symptoms of intoxication may be as follows: nausea, vomiting, cramps, diarrhoea, and sometimes blood [2].

The daily intake of nitrate allowed in humans has been established by FAO / WHO to 5 mg / kg body weight, which is 350 mg / day for a 70 kg person [1].

Nitrates have received much attention especially in connection with the so-called blue baby disease (methemoglobinemia). Concentrations between 10 and 20 mg/L produce illness and even death in children less than 6 months. In this case the blood ability to carry oxygen is impaired. This serious condition is caused by the conversion of nitrate to nitrite at increased pH of the infant's stomach and intestinal tract.

Numerous ground waters contain small amounts of nitrates, generally ranging between 0.1 and 4.3 mg/L. But there are plenty of situations where the values exceed 100 mg/L. Nitrate is present in both shallow and deep wells as a result of water infiltration through soils containing nitrate minerals. Improper use of agricultural fertilizers can be another source of nitrates occurring in excess in the water for consumption. Nitrates are also one of the decomposition compounds of animal or human waste. Therefore, the nitrate in water supplies indicates a possible pollution.

During decomposition, slurry undergoes chemical transformation. Where normally groundwater does not contain natural nitrates, their expanding concentrations, is also an indicator of pollution.

Nitrites are more toxic than nitrates. They are found in small quantities in food as a natural compound. But their concentrations can increase to dangerous levels by reducing the action of microorganisms on nitrates.

Lethal doses of nitrite are in the range of several grams per adult and 0.2 to 0.5 g for children whose blood pigments are more sensitive to oxidation, because they are the higher proportion of foetal type [1]. Therefore, nitrite, daily intake was set at 0.2 mg / kg body weight, respectively 14 mg / day for a 70 kg person.

The oxidant effect is manifested on all cytochromes and redox systems of the body. The effect manifests in terms of oxidant deficiency of vitamin E and vitamin A [2].

A major risk that is borne by nitrates and nitrites presence in food and water is the possibility of forming nitrosamines, substances with mutagenic malignant potential [4].

Methemoglobinemia has been long considered the main condition caused by exposure to nitrates and nitrites from drinking water, especially in infants under 4 months. A big portion of the children's hemoglobin is in the form of fetal hemoglobin which is much easier oxidized to methemoglobin than that of the adults. Therefore, children, especially premature children, are particularly sensitive. Infants were identified as the most sensitive subpopulation because their gastrointestinal pH is more acid, favoring the growth of bacteria that convert nitrate to nitrite (nitrate-reducing bacteria), which in turn binds to hemoglobin to form methemoglobin Instead, the stomach of adults is typically too acidic to allow significant bacterial growth and the resulting conversion of nitrate to nitrite. On the other hand, the amount and activity of the enzyme which reduces methemoglobin is deficient in infants up to 6 months.

At birth, NADH-dependent methemoglobin reductase (also called cytochrome-b5 reductase), the main enzyme responsible for reducing methemoglobin back to normal hemoglobin, presents only half of the activity that adults have and does not reach the level of an adult at least till 4 months of age. Pregnant women and their fetuses are another high-risk group. Pregnancy, with its oxygen demand and increased levels of oxidative stress can overwhelm the body's ability to reconvert methemoglobin back to hemoglobin, leading to increasing levels of methemoglobin [9, 10].

However, recent studies have shown that the effects on thyroid function cannot be neglected. In this respect, effects have been observed in school age children but no study has considered infants, although it would be expected that they are the most vulnerable. Infants remain the most sensitive population because the half-life and storage time of their thyroid hormones are much shorter. In addition, exposure to nitrate during pregnancy can affect the production of thyroid hormones, which could have an impact on fetal development. Therefore, pregnant women at or near the 30 week of pregnancy and their fetuses may be more susceptible to the toxicity of nitrites and nitrates [9, 10].

Also, current research suggests an association between cancer and exposure to nitrates and nitrites from drinking water due to the formation of nitrosamines in the human body.

In water, chlorine reacts to form hypochlorous acid and hypochlorites. All three species exist in equilibrium with each other, the relative amounts varying with the pH. In dilute solutions and at pH levels above 4.0, very little molecular chlorine exists in solution. The concentrations of hypochlorous acid and the hypochlorite ion are approximately equal at pH 7.5 and 25 °C. Chlorine can react with ammonia or amines in water to form chloramines [7, 8].

Chlorine is present in most disinfected drinking-waters at concentrations of 0.2-1.0 mg/L [6]. Calcium hypochlorite has an oral LD50 in the rat of 850 mg/kg of body weight [5].

This paper aims to present some important aspects of quality of surface water resources in the area of Bega and Timiş rivers by monitoring parameters indicating their degree of pollution such as: nitrates, nitrites and chlorides. As part of a larger study on the quality of water sources in the region, the present research tries to identify some anionic and cationic pollutants, which may have an impact on human health. Especially children and pregnant women are sensitive population groups that are prone to be affected when using an improper drinking water. The results of the present study may be of great importance in interpreting the correlation between water quality and various health issues.

The main methods of identifying the nitrite and nitrate anions in water are presented in Table 1.

Table 1: The main methods of identifying NO_2^- and NO_3^- anions from water

ANIONS **REAGENTS**	NO_2^-	NO_3^-
H_2SO_4 concentrated	$NO + NO_2$ - brown gas	$NO + NO_2$ - brown gas
$AgNO_3$	-	-
$FeSO_4$	$Fe^{2+} \rightarrow Fe^{3+}$ - yellow brown solution	$Fe^{2+} \rightarrow Fe^{3+}$ - yellow brown solution
Zn(metal) in presence of NaOH	Blackened paper impregnated with $Hg_2(NO_3)_2$	Blackened paper impregnated with $Hg_2(NO_3)_2$
Diphenyl-amine	Blue coloration	Blue coloration
Antipyrine - solution 5%	Carmine red coloration, nitro-antipyrine	Green coloration, nitroso-antipyrine
Naphthylamine + acid sulphanilic	-	Azocolorant red

2. MATERIALS AND METHODS

Sampling and Conservation

Samples must be representative and must not introduce changes in the composition and water quality due to poor sampling techniques or improper storage conditions of the samples.

Sampling site should be chosen to ensure a representative characterization of the water source.

The volume of the collected samples depends on the number and type of analyses performed, aiming at collecting water samples to ensure at least three determinations of the same type for each analysed parameter.

Sampling frequency, in general, and frequency variations exceed maximum parameters to follow or overlap with it.

For surface waters, the analysis is performed 2-4 times a year, the most critical periods of pollution being the minimum flows in winter (lowest temperatures) and in summer (highest temperatures) and spring peak flows and / or fall (as rain or melting snow).

The water samples were collected in sealed polyethylene containers for physical-chemical analysis. Recipients were previously washed with hydrochloric acid and detergent, then rinsed with tap water, distilled water and then with the sample to remove any organic or other impurities that may distort the composition of the sample.

To minimize sample changes during sampling, their transport was performed in the shortest possible time, and until their analysis was done they were stored in dark and temperature of approx. 4° C.

There were two water samples taken from each set, given in Table 2.

Table 2: Place of sampling

Samples	Place	GPS coordinates
S1	Lugojel village – Timiş River	45.666858, 21.973176
S2	Coştei village – Timiş River	45.734432, 21.856143
S3	Jabar village – Timiş River	45.731905, 21.818478
S4	Babsa village – Timiş-Bega Channel	45.773397, 21.770354
S5	Bazoş village – Timiş River	45.725161, 21.497938
S6	Şag village – Timiş River	45.63886, 21.187129
S7	Remetea Mare – Bega River Bridge	45.777711, 21.376048
S8	South Recaş – Bega-Timiş Channel	45.77545, 21.513878
S9	Ghiroda village – Bega River	45.762725, 21.304406
S10	Utvin village – Bega River	45.706469, 21.089912

In general, the following analyses have to be made in a short time interval after sampling, within 24 hours.

Measurements

All the reaction agents used in this study were of analytical quality.

The solutions, of different concentrations, were obtained by dissolving the adequate quantity of salt (KNO_3, KNO_2, NaCl), weighed by analytic balance with an accuracy of ± 0.0001 mg, in bidistilled water, in a volumetric flask.

The operations were carried out at room temperature (25 ± 1ºC), without adjusting the pH of the working solutions.

The concentration of the nitrate and chloride (NO_3^-, Cl^-) in the samples was potentiometrically determined using a nitrite-sensitive and chloride-sensitive electrode, ELIT 8227 – NICO 2000 and ELIT 8444 – NICO 2000 respectively. Also, a double junction reference electrode ELIT 003N – NICO 2000 was used.

Potentiometer anion-selective sensors based on liquid membrane / polymer is a method increasingly used to control water quality, due to capacity fast and accurate determination of these parameters.

The measurement process was performed with the help of a customizable Virtual Instrumentation [11, 12]. This solution was preferred mainly because of the possibility to adapt the application to the different calculus requirements involved with the experimental part. Automation of sensor calibration and the flexibility with which one can exploit the calculus power of the PC are two important advantages which the authors considered.

The hardware component consisted of the NI USB 9215A data acquisition device, produced by National Instruments. This device is capable of performing ADC on 16 bits, it provides 4 analog input channels and accepts a max. of ±10 V_{pp} for the input signal. Signal conditioning was implemented using the MCP 601 Single Supply Amplifier. This was necessary since noise reduction/removal is an important issue in data acquisition systems. Visual inspection of acquired data (with and without amplification) showed that fluctuations due to noise presence can be limited if the useful signal is amplified by a factor of 10.

The hardware device was controlled by a dedicated software application programmed in National Instruments' LabVIEW development environment. For running the software components, the authors used a notebook computer with Dual Core – 1.8 GHz CPU, 2 GB DDR3 and Internet Connection. Interaction between the software component and the NI USB 9215A is performed by the NI-DAQmx driver. The measurement procedure was divided into three main parts: acquisition, analysis, and presentation of data. The features include data logging, statistical calculations and graphical presentation of recorded data. Each measurement lasts 130 s and the established sampling period is 1 s. So automated calculations are performed over records of 130 samples and the following parameters are presented: sensor output voltage, sensor output average voltage (over the last 10 samples), calculated concentration, adsorption capacity and process return.

Concentration of nitrite (NO_2^-) in water samples was determined by spectrophotometer. Measurements were performed using a spectrophotometer type T90, measuring range 190-900 nm.

Wavelength at which measurements were made was $\lambda = 650$ nm.

3. RESULTS AND DISCUSSIONS

The results presented in 2013 by the Romanian National Administration of Water [13] suggest that the quality objective of good environmental status was not reached by 4 water bodies, representing 13.33% of the total natural water bodies - rivers from Bega-Timis-Caras basins, and 86.45 km respectively, representing 7.82% km river - natural bodies for which the ecological status was determined.

Considering the biological elements (phytobenthos, phytoplankton, benthic macroinvertebrates and ichtyofauna) the 30 water bodies monitored and evaluated on a length of 1105.60 kilometers were considered of very good condition (16 water bodies) good (13 water bodies) and moderate condition (1 water body) the decisive elements being the benthic macroinvertebrates and ichtyofauna.

Thirty water bodies were generally monitored and evaluated taking into account also the physico-chemical properties. The results are as following: 21 bodies (70.00%) were classified in good condition and 9 bodies (30.00%) were classified in moderate condition, the decisive elements being the oxygenation conditions and the nutrients.

Potentiometric results obtained for the water samples listed in Table 1 are found in Table 5 for nitrates and Table 6 for chlorides, respectively.

It should be noted that because the Mohr method ($AgNO_3$ and $K_2Cr_2O_7$) is a standard one, chlorides were determined also by volumetric method but the values are so small, that fall within the method error.

The spectrophotometric results of nitrite for the water samples listed in Table 1 are given in Table 7.

Table 5: Nitrate content of surface water samples

Sample	NO_3^- - spectrophotometric		NO_3^- - potentiometric		Differences between the two methods (%)
	mg/L (ppm)	moles/L	mg/L (ppm)	moles/L	
S1	4.10	$0.66 \cdot 10^{-4}$	4.17	$0,67 \cdot 10^{-4}$	1.68
S2	3.80	$0.613 \cdot 10^{-4}$	3.98	$0,64 \cdot 10^{-4}$	4.52
S3	6.60	$1.06 \cdot 10^{-4}$	6.29	$1.01 \cdot 10^{-4}$	4.70
S4	8.10	$1.31 \cdot 10^{-4}$	8.48	$1.37 \cdot 10^{-4}$	4.48
S5	6.60	$1.06 \cdot 10^{-4}$	6.94	$1.12 \cdot 10^{-4}$	4.90
S6	12.90	$2.08 \cdot 10^{-4}$	12.93	$2.08 \cdot 10^{-4}$	0.23
S7	18.00	$2.90 \cdot 10^{-4}$	18.24	$2.94 \cdot 10^{-4}$	1.32
S8	12.40	$2.00 \cdot 10^{-4}$	12.70	$2.05 \cdot 10^{-4}$	2.36
S9	5.40	$0.87 \cdot 10^{-4}$	5.73	$0.92 \cdot 10^{-4}$	5.76
S10	11.50	$1.85 \cdot 10^{-4}$	11.58	$1.87 \cdot 10^{-4}$	0.70
			LD = 0.3	LD = $0.05 \cdot 10^{-4}$	
Values range (Law 458/ 08.07. 2002)	**50**	**$8.06 \cdot 10^{-4}$**	**50**	**$8.06 \cdot 10^{-4}$**	

Table 6: Chloride content of surface water samples

Sample	Cl^- - potentiometric		Observations
	mg/L (ppm)	moles/L	
S1	4.8920	$1.3800 \cdot 10^{-4}$	Chlorides were determined by volumetric and Mohr ($AgNO_3$ and $K_2Cr_2O_7$) methods, but the values are so small, that fall into the method error.
S2	5.4660	$1.5418 \cdot 10^{-4}$	
S3	5.8203	$1.6417 \cdot 10^{-4}$	
S4	5.7163	$1.6124 \cdot 10^{-4}$	
S5	6.8262	$1.9254 \cdot 10^{-4}$	
S6	9.1605	$2.5838 \cdot 10^{-4}$	
S7	6.9842	$1.9700 \cdot 10^{-4}$	
S8	6.4816	$1.8282 \cdot 10^{-4}$	
S9	8.4008	$2.3696 \cdot 10^{-4}$	
S10	27.318	$7.7054 \cdot 10^{-4}$	
	LD = 1.000	LD = $0.3 \cdot 10^{-4}$	
Values range (Law 458/ 08.07. 2002)	**50**	**$8.06 \cdot 10^{-4}$**	

Table 7: Nitrite content of surface water samples

Sample	**NO_2^- - spectrophotometrically**		**Observations**
	mg/L (ppm)	**moles/L**	
S1	0.12	$0.026 \cdot 10^{-4}$	All values are well below the allowed limit
S2	0.14	$0.030 \cdot 10^{-4}$	
S3	0.15	$0.033 \cdot 10^{-4}$	
S4	0.15	$0.033 \cdot 10^{-4}$	
S5	0.16	$0.035 \cdot 10^{-4}$	
S6	0.16	$0.035 \cdot 10^{-4}$	
S7	0.17	$0.037 \cdot 10^{-4}$	
S8	0.15	$0.033 \cdot 10^{-4}$	
S9	0.15	$0.033 \cdot 10^{-4}$	
S10	0.20	$0.044 \cdot 10^{-4}$	
Values range (Law 458/08.07. 2002)	**0.5**	**$0.109 \cdot 10^{-4}$**	

In Tables 5, 6 and 7, we see that the values of nitrate, nitrite and chloride in all analysed samples are below the maximum concentration allowed by law.

4. CONCLUSION

Taking into account the analysed parameters (nitrites, nitrates and chlorides), both Timiş and Bega rivers are within the limits stipulated by the concerning laws (Law 458/08.07.2002 for potable water).

Given that a high concentration of any of these parameters, especially nitrate, is an indicator of pollution, their low concentrations indicate no serious problems of pollution.

On the other hand, we can see that the difference between measurements obtained by spectrophotometric and potentiometric method, respectively, is below 5%, which indicates that potentiometry can be used to serial determinations of nitrate and chloride. This is very useful taking into account that the potentiometric method is less laborious than the spectrophotometric one.

Given the importance of the objective sought within this research, it is imperative to continue to monitor the surface water sources over a long period of time also considering other quality parameters.

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