The Quality of Underwater Supplies in Western Romania

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Over the last three decades, many scientist, national and international agencies were concerned about pollution of the Romanian environment, especially water and its impact on human health. This research includes studies and interpretations resulting from chemical and bacteriological analyzes of water samples collected from wells or underground springs from central north-western part of Romania. The water parameters were determined using standard analytical methods: pH, turbidity, oxidability, ammonium, nitrates, nitrites, chlorides, total hardness, conductivity, mesophilic heterotrophic microorganisms, coliforms, E. coli, intestinal enterococci. Regarding non-compliant samples, the main problem is the bacterial load of water, confirming domestic pollution sources of water. More than 50% of the analyzed samples, which had concentrations of nitrate over 10 mg/L were also found bacteriological inappropriate.

Keywords: water quality, ground water, nitrate, microbiology, public health

Water has been and will remain a central element in the life of human society. Water is perhaps the most important raw material of humanity. After the second half of the twentieth century, freshwater drinking becomes a critical issue due to continuous growth of the world population, the emergence of new industrial units and decreasing fresh water supply, especially by chemical and / or bacteriological contamination (this being a major cause of people's death all over the world).

In many places of the globe, even in developed countries, people consume water from private supplies [1] or unmonitored natural sources of water, as lakes [2], which are subject of no treatment, ignoring the in force water laws and rules, the advice from media or from local administrative institutions. This attitude has to be changed. The water qualities, both chemical and biological are important issues worldwide. The contamination of water supplies happens for many reasons. Some are related to human activities and population growth rate as: use of irrigation, agriculture, chemical fertilizers, rotation of crops [3-9], industrial sector [10,11], local activities as anthropogenic sources (transportation and highways) [12], water distribution networks [13], organic waste or infiltrations from sewage treatment plants [5,14-16], in a few words *mismanagement of water resources* [17,18]. Some are related to natural hazard: geochemical composition of the rocks [4,19], accidental weather phenomena [20,21].

Studies of chemical and biological characteristics of water and the correspondent treatment include not only standard analyses, but also multidisciplinary approaches: use of some agro ecosystems like the paddy rice field which can filter *coliforms* and chemicals [22,23], corrosion management of underground structures [20,24], electrocatalytic technologies [25,26], modelling tools for evaluation of some alternative ways of reducing water pollutants [27], technologies for removal and recovery of chemical pollutants [28, 29], enzyme based biosensors [30-32], satellite images technology to observe variations of land use change [33].

The consequences of chemical and biological water pollution are obviously not only on health of humans [34,35], but also on the *health* of earth ecosystem. They could vary from human disease as baby blue syndrome or hydric disease to poisoning and death of any living form. The use of water has to be done in order to minimize the effects on environmental and human health impact [3], which means also an integrated and sustainable watershed – based management of worldwide resources of water [17].

Total water resources of Romania are about 128 billion m^3/year, of which 40.4 billion in rivers and the rest from Danube. Romania has resources of about 9.62 billion m^3/year from underground water and an amount of 3,246 m^3/inhabitant/year. Over the last three decades, many scientists, national and international agencies were concerned about pollution of the Romanian environment, one of the problems being water and its impact on human health [35,36]. It was found that the soil fertilizers, used especially before 1989 were one of the main causes of nitrate contamination, situation which should have been changed after the implementation of European Union's Council Directive 91/676. It was shown that in Transylvania surface water sources are microbiological and chemical contaminated, not only because of management problems of wastes, but also because of municipal residual waters, which means absence or low efficiency of water treatment or damages of distribution networks [37-40].

This study includes interpretations of chemical and bacteriological test results of more than 100 water samples, collected from wells or underground springs of households at the request of private users from many places located in Cluj County, Romania. The samplings are not from any water company monitored sources. It should be emphasized that the samples do not meet the alarming drinkability. In the absence of feedback from the customer, i.e. a monitoring program of private sources of drinking water, the water situation in private households related study area is very critical. Similar conclusion – risk for

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human health [41], but related to the water of the river from almost the same geographic zone, sustained the results of this study.

Experimental part

We have processed the data from water samples collected according to the standards in force SR EN ISO 19458/2007 and SR ISO 5667/11/2002. For most of the samples the following parameters were determined: pH, turbidity, oxidability, ammonium, nitrates, nitrites, chlorides, total hardness, conductivity, mesophilic heterotrophic microorganisms, coliforms, *E. coli*, intestinal enterococci. Each parameter was determined according to the following standard method.

Measurement of pH, conductivity, was done using laboratory multiparameter InoLab WTW 740, according to SR ISO 10523/1997, respectively SR EN 27888/1997.

Turbidity measurement was made in the laboratory by nephelometric technique using a portable HACH 2000 turbidimeter, according to SR EN ISO 7027/2001.

Oxidability - $KMnO_4$ index values were obtained by using the titrimetric method for determination of the oxidability SR EN ISO 8467/2001.

Chlorides were determined by titrimetric method using silver nitrate chromate as indicator - Mohr method, according to SR ISO 9297/2001.

Ammonium, nitrite and nitrate were determined by spectrophotometric method specific to each parameter with spectrophotometer UV/VIS Perkin Elmer, according to SR EN ISO 7150-1/2001, SR EN ISO 26777/2002, respectively SR ISO 7890-3/2000.

Overall water hardness was measured by EDTA titrimetric method according to SR EN ISO 6059/2008.

Colony forming units (CFU) representing *mesophilic heterotrophic microorganisms* were counted after inoculation in culture medium and incubated at 37 °C for 48 hours, according to SR ISO 5667-11/2002.

The number of coliforms and of *E.coli* were determined according to SR EN ISO 9308 -1/2004/AC2009. Intestinal enterococci were determined by the membrane filter method, according to SR EN ISO 7899-2/2002.

All chemicals used in the preparation of specific solutions were of p.a. purity, Merck.

Graphics and statistical calculus were obtained using OriginLab 8.0.

Results and discussions

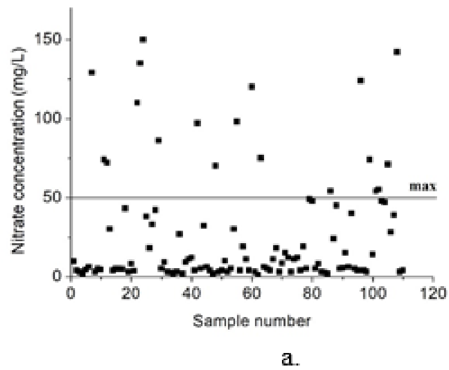
The values of the chemical and biological parameters of the studied water samples are presented in accordance with the maximum admissible limit.

After analyzing the compliance with legislation it results that only 10% of the samples fall entirely within the allowable range, so that the drinking water can be declared under the standards. Regarding non-compliant samples, the main problem is the bacterial load of water, confirming domestic pollution sources of water. These contamination indicators are *Escherichia coli* and intestinal enterococci, which suggests the possible presence of pathogens that can be a health threat to consumers, especially children, older people or individuals with impaired immune system. A total of 63 samples analyzed had more than 100 colony forming units per milliliter of water at 37°C (CFU 37°C) and the parameter coliform bacteria indicate recorded samples at 93 different values. A major problem is represented by microbiological parameters contamination with *E. coli* - 90 positive samples, respectively intestinal enterococci - 75 positive samples.

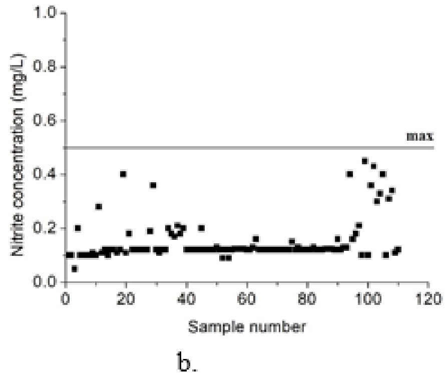
Also a major problem is the presence of nitrates, their concentration in the analyzed samples is frequently above the permissible limits. From the total of 110 analyzed samples, 21 samples had nitrate concentrations above 50 mg/L, 16 samples between 20-50 mg/L and 14 samples between 10 to 20 mg/L. In conclusion, in 46.4% of samples the nitrate concentration was over 10 mg/L (fig. 1a).

These results indicate that the population that uses for daily consumption these sources of water is exposed to a real risk. No sample had exceeded the maximum allowable value for nitrite (fig. 1b) and only 3 samples exceeded the parameter ammonium (fig. 1c).

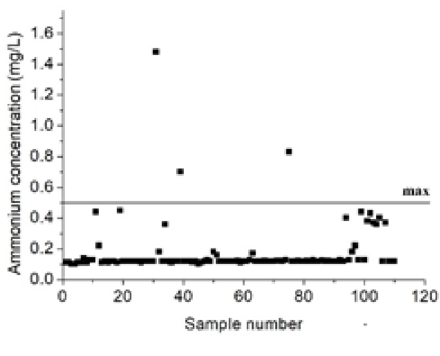
From the 110 analyzed samples, 22 had total hardness above 30 German degrees and 2 showed 100 degrees German hardness, characterizing a very hard water (fig. 2).



a.



b.



c.

Fig.1. Nitrates (a), nitrite (b) and ammonium (c) concentration of the water samples

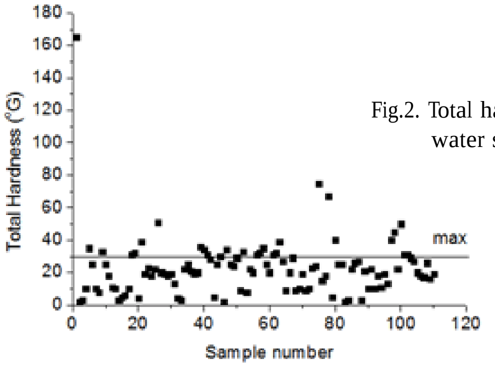


Fig.2. Total hardness of the water samples

A percentage of less than 5% of the total number of non-conformities had the following parameters: *p*H (fig. 3), chlorides (fig. 4), conductivity (fig. 5), turbidity (fig. 6), and oxidability (7).

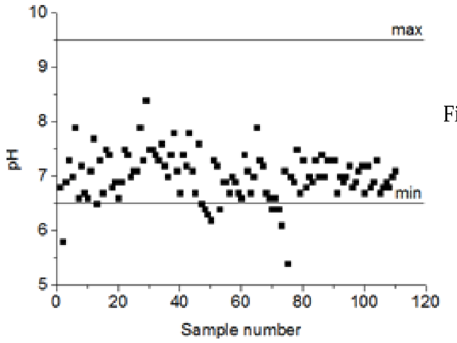


Fig.3. *p*H of the water samples

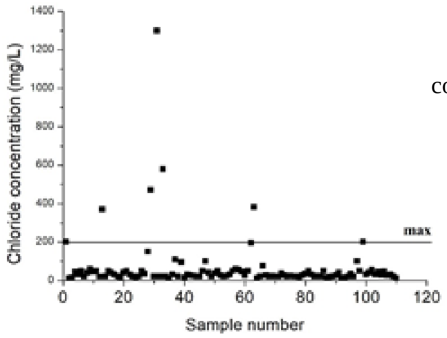


Fig.4. Chlorides concentration of the water samples

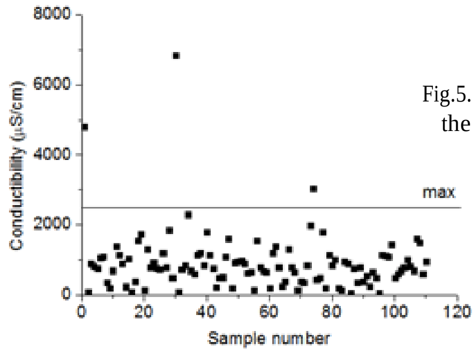


Fig.5. Conductibility of the water samples

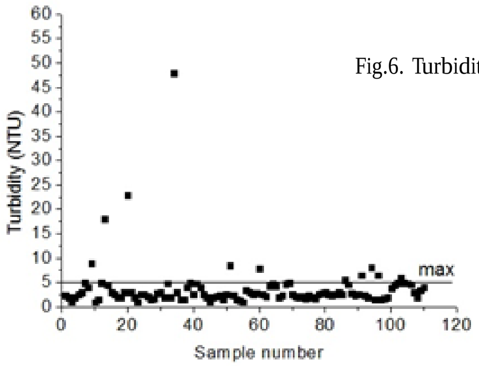


Fig.6. Turbidity of the water

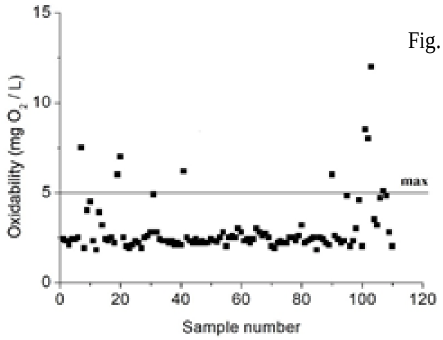


Fig. 7. Oxidability of the water samples

The main concern in terms of human health on the ingestion of nitrates is juvenile acute methemoglobinemia - *blue baby* syndrome. Healthy adults do not develop methemoglobinemia at concentrations of nitrates in drinking water that puts infants at risk.

Pregnant women are more vulnerable to the effects of nitrates due to the increase in the natural level of methemoglobin in the last weeks of pregnancy. The only well-known non-carcinogenic effect is methemoglobinemia, caused by nitrates. No other non-carcinogenic effect due to chronic exposure has been shown.

Studies performed in Romania highlight the broad range of coverage of this type of pollution in the country and the impact on the population. In most of the country's counties (including those in Moldavia) in southern and central regions, due to high concentrations of nitrates are registered most cases of blue baby syndrome. Reporting of cases of acute infantile methemoglobinemia nationwide began in 1984: the number of cases decreased, steadily being placed at below 50% of baseline. Although regulations and drinking water standards indicate allowable concentration of 40-50 mg/L, it is recommended that drinking water have a nitrate concentration of 10 mg/L. Among the analyzed parameters were recorded significant correlations at different levels, always in the same direction (table 1).

Table 1
SIGNIFICANT CORRELATIONS BETWEEN CHEMICAL AND BIOLOGICAL PARAMETERS OF WATER SAMPLES

Parameters	Correlation coefficient	Correlation
Total coliforms + E. coli	0.84	Very good
Ammonium + conductivity	0.63	Good
Total coliformes + intestinal enterococci	0.62	Good
E. coli + intestinal enterococci	0.61	Good
Oxidability + nitrite	0.57	Good
Total hardness + conductivity	0.52	Good
CFU 37ºC + *total coliforms*	0.36	Weak
CFU 37ºC + *E. coli*	0.35	Weak
CFU 37ºC + *intestinal enterococci*	0.31	Weak
Ammonium + nitrite	0.30	Weak
Nitrate + *E.coli*	0.28	Weak
Oxidability + nitrate	0.27	Weak

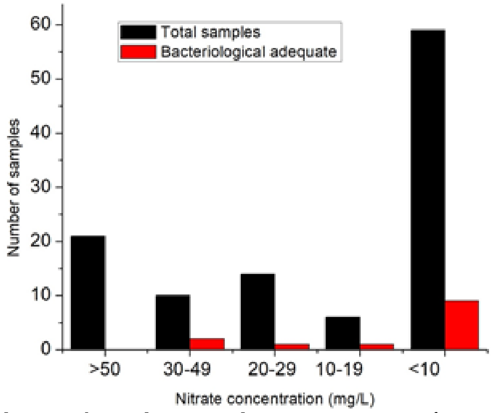


Fig. 8.The correlation between the concentrations of nitrates and bacteriological quality of water samples

The correlation between nitrate concentration and bacteriological quality of water samples revealed that all samples in which the nitrate concentration was over 50 mg/L were entirely bacteriological inadequate for all monitored parameters (fig. 8).

As a result, over 50% of the analyzed samples that had concentrations of nitrate above 10 mg/L were also bacteriological inadequate demonstrating that the main cause is the improper positioning of the wells in households [42]. As an unfortunate confirmation of these results are the 2000-2011 cases of infant acute methemoglobinemia - baby blue syndrome [43].

Parameters with exceeding values above the maximum permissible in private household wells in Cluj County are: nitrate, total hardness, turbidity, pH, oxidability, chlorides, ammonium, and conductivity. Positive samples indicated: total coliforms (93 samples), *E. coli* (90 samples), intestinal enterococci (75 samples), CFU 37°C (63 samples had over 100 units).

The health risk is even higher if the wells examined present elevated nitrate concentrations correlated with bacteriological contamination risk, in this case being both toxicological and infectious.

Conclusions

Only 10 % of a total of 100 analyzed wells in Cluj County over a period of two years proved to have drinkable water. This percentage suggests an alarming urge to inform and educate the public on how to construct and use wells, monitoring water quality from private wells and implement the measures recommended by the World Health Organization. In order to protect water quality the following measures are recommended: the well location to be at least 30 meters upstream of latrines and other sources of pollution, drainage wells downstream animal manure, waste and stagnant water, sealing the fountain wall tube with cement and cementing a zone of at least 2 meters around the fountains, proper maintenance of pumps, storage buckets in hygienic conditions and avoid their contamination, location of filters and softeners, where necessary to their proper functioning, conducting sanitary inspections of water quality twice a year, once in the rainy season and once in the dry season. In Romania it is estimated that nearly half of the population is drinking water from wells contaminated with nitrates, bacteria or pesticides.

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