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ESTIMATION OF BORON CONCENTRATION IN SOME DRINKING WATER SAMPLES OF RURAL AREAS

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Abstract. Aim. Significant risks for human health may results from exposure to non pathogenic toxic contaminants that are often globally ubiquitous in waters from which drinking water is derived. In Moldova's rural areas (România) the wells are important water sources for the population. **Material and methods**. We have investigated the level of boron (B) in relation with other chemical parameters of water quality in 60 samples from 8 districts from Moldova (North-East România) in the period of 2005-2006 (nitrate, chloride, calcium, magnesium, total hardness, sodium, potassium, bicarbonate). **Results**. We have found out that the level of boron are below Romanian's sanitary norm, but there were noticed that well waters are polluted with nitrate. **Conclusions**. The presence of boron in drinking water sources in this territory is of natural origin. Thus, there is not a problem of aquifer pollution with boron.
Key words: boron, well water

Rezumat. Scop. Un risc semnificativ pentru sănătatea umană poate rezulta în urma expunerii la contaminanţi chimici nepatogeni care sunt, de multe ori, ubiquitari în sursele din care provine apa de băut. In zonele rurale ale Moldovei (România) fântânile sunt surse importante de apă pentru populaţie. **Material şi metodă**. Noi am investigat nivelul borului (B) în relaţie cu alţi parametri chimici de calitate ai apei în 60 de probe prelevate din 8 judeţe ale Moldovei (Nord-Estul României) în perioada 2005-2006 (nitraţi, cloruri, calciu, magneziu, duritate totală, sodiu, potasiu, bicarbonaţi). **Rezultate**. Am constatat că nivelul borului este inferior normei sanitare din România, dar am observat că apa din fântâni este poluată cu nitraţi. **Concluzii**. Prezenţa borului în sursele de apă din acest teritoriu este de origine naturală, astfel încât nu poate fi vorba despre o poluare a acviferului cu bor.
Cuvinte cheie: bor, apă de fântână

INTRODUCTION

Water quality of wells, important drinking water sources in rural areas is monitorized by Public Health Authorities.

Chemical and microbiological quality of these sources is often inadequate because water is not treated and/or the pollution sources, especially from agriculture and zootehny, are multiple. The hidro-geological condition and the climate changes can influence the quality of aquifers and, in strong connection, the population general health.

The Law 458/2002 (in conformity with Directive 98/83/ECC) stipulated Maximum Allowable Concentration for boron (B) which is present especially in ground water (1, 2).

As long as this aspect has not been well studied, we have proposed to investigate the level of boron from some individual sources (wells) from the rural areas in Moldova (Iaşi, Vaslui, Suceava, Bacău, Neamţ, Vrancea, Galaţi and Botoşani districts).

MATERIAL AND METHODS

The samples of water coming from wells have been sampled in glass bottles (1 liter) for the chemical parameters determinations and in polietylene bottles for boron determinations. The principle of spectrophotometric method with H-azomethine for determination of boron is the reaction of H-azomethine which is the product of acid H (8-amino-naftil-1-ol-3,6-pirosulfuric) and salicilice aldehide. In the presence of dissolved forms of borates, at pH=6, formation of yellow complex is take place, followed by the spectrophotometric measurements (λ = 415 nm).

For the calibration graph a stock solution of borate (H_3BO_4, 1 g/l) was used of which a calibration solution was prepared by dilution (1 ml = 0.1 µg borate). A linear calibration was observed, followed by the calculation of the slope factor. The results are exprimated in mg B/l. Regression equation: y = 1.6921 x + 0.0029. R^2 = 0.9998 (fig. 1).

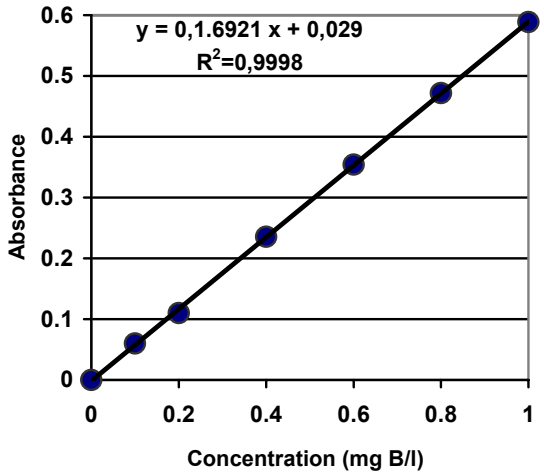

Fig. 1. The calibration graph – Boron

Calcium and magnesium were determined by EDTA titrimetric method, chloride by argentometric titration using standard silver nitrate as reagent with potassium dichromate as the indicators.

Bicarbonate (HCO_3^-) was estimated by titration to pH = 4.5 with 0.10 M HCl,

nitrate by collorimetry using phenolic-disulfonic acid and sodium and potassium using flam photometry.
Were collected and analyzed the well waters from 8 districts of Moldova (Romania) rural territories between 2005 and 2006 period. Each sample was run in duplicate and the mean of two successive results at the relative standard deviation not exceeding 5% were accepted as an estimation value.
Statistical analysis was performed using Statistical Functions for Excel packages.

RESULTS AND DISCUSSIONS

General aspects regarding boron and its compounds

Boron (B) is a ubiquitous element in rocks, soil and water. Boron forms compounds with oxygen, hydrogen, the halogens, nitrogen, phosphorus and carbon. It also forms organic compounds. It is most commonly used in its compounds, especially borax ($Na_2B_4O_7$ x 10 H_2O) and boric acid (H_3BO_3). Borate - mineral concentrates and refined products and sold worldwide.
Agriculturally, borates are used in fertilizer (4% of BO_3) to correct trace boron deficiency in certain crops. Boron is one of the more important essential elements on plant growth high concentrations can be toxic to certain species. Borates and combinations of borates, with organic herbicides are used to control weeds. Insecticidal use of borates is attractive because of their low mammalian toxicity and lack of insect resistance compared with organic insecticides. Sodium perborates [$NaBO_3$ x H_2O or 4 H_2O] are true per salts traditionally have been blended into powdered detergents in Europe as bleadring agents (3).
Boric acid and borax were widely used in medicine the beginning of the century for therapeutic purposed locally as well orally (4).
A small group of boron (containing antibiotics), contain a single tetrahedral boron atom in the center of the structure, complexed with two vicinal dial groups. The first to be isolated and identified was *Bromicyn* from *Streptomyces antibioticus* (fig. 2).
From humans, boron exposure occur primary through the diet and drinking water. The mean global boron concentration in drinking water was considered to be between 0.1 and 0.3 mg B/l (5).
It is known biochemical and pharmacological effects of boron in plants, animals and humans. Zang and col. studies suggest that boron has a very important function in humans that involve macromineral and cellular metabolism at the cell membrane level (6).
Still another study today that boron compounds, while not carcinogenic or mutagenic, are poisonous to both animals and humans when ingested in highest concentrations.
On the other hand, it is also been shown that boron is essential to the body for a number of processes, including effective bone, lipid and mineral metabolism, proper immune system and brain function (7).

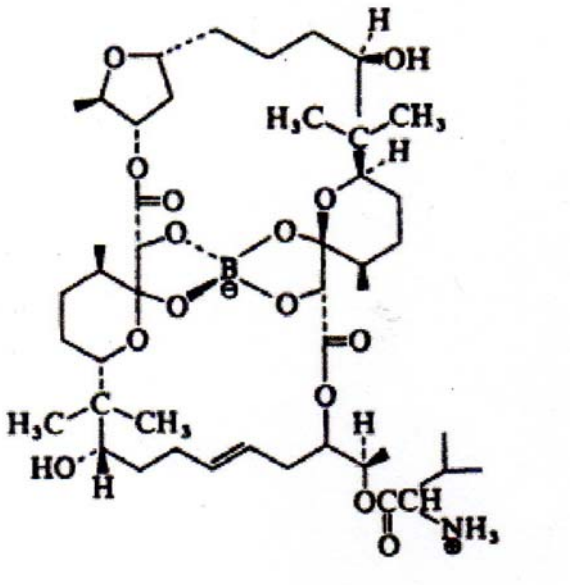

Fig. 2. Bromicyn

Findings from human experiments show that B is a dynamic trace element that can affect the metabolism or utilization of numerous substances involved in life processes, including calcium, cooper, magnesium, glucose, triglicerides, reactive oxygen and estrogen (8).

Boron aids in the body's inflammatory functions and may therefore help to control and normalize the discomfort associated with unhealthy joints (9). Now, studies also conclude that boron may be the single most important in the prevention of prostate cancer (10).

Analytical methods used for boron determination

In water, boron can be determined by several methods including the curcumin method: boron has to be transferred to boric acid or borates on reaction with curcumin (diferuloylmethane – $C_{21}H_{20}O_6$) in acidic solution, a red colored boron – chelate complex rosoeyanine $[B(C_{21}H_{19}O_6)_2Cl]$ is formed.

Carmine method, which involve combination with carmine or carminic acid in sulphuric acid are followed by photometric measurement. The curcumin method is recommended for water with boron concentrations between 0.1 and 1.0 mg/l whereas the carmine method is optimum for determination of boron level in the range of 1 – 10 mg/l (11).

Other analytical method includes spectrophotometric determination with azomethine – H and volumetric determination following distillation, for waters that contain more 0.2 mg/l boron and that are colored (12).

In Romania, it is appreciate that approximately 7.4 millions of habitants (34.4%) from the century's population are using drinking water from their own sources (wells and springs). Frequently, the hygiene norms for these sources are not according to the conditions stipulated in Law 458/2002 (1).

We should stress that even now, the water contamination of wells with nitrate and other chemical compounds toxic potentially is taking place.

A total of 80 wells were sampled and examined for boron content and other quality parameters (chloride, alkalinity, calcium, magnesium, sodium, potassium, bicarbonates, nitrate, total hardness).

Several regulatory agencies from world have set or plan to set drinking water guidelines or standards for boron (13).

Table 1 shows the limits for this non metallic element in comparison with Romanian sanitary norm.

Table 1. Norms for boron in drinking water

Boron concentration in drinking water (mg/l)	WHO	European Community	USA	Canada	Australia	Romania
	0.5	1.0	NL	5.0	0.3	1.0

NL – no limit listed

Our investigations revealed that, in the Moldova territory, the boron concentration was situated, in generally, below at the Maximum Allowable Concentration (minimum value 0.02 mg/l and maximum value 1.55 mg/l) (tab. 2).

Table 2. Descriptive statistics for boron in the well waters

Districts	Min	Max	Mean	SD	SE	Variance	Mediane	Range
Botoşani	0.020	1.10	0.327	0.368	0.116	0.136	0.20	1.08
Suceava	0.050	1.10	0.500	0.436	0.138	0.190	0.28	1.05
Iaşi	0.020	1.55	0.540	0.470	0.119	0.326	0.40	1.53
Bacău	0.030	1.10	0.390	0.454	0.143	0.206	0.08	1.07
Vaslui	0.035	1.21	0.294	0.349	0.110	0.122	0.16	1.17
Vrancea	0.025	1.20	0.650	0.426	0.134	0.182	0.77	1.12
Neamț	0.131	1.25	0.380	0.409	0.123	0.168	0.14	1.22
Galați	0.133	0.45	0.159	0.132	0.040	0.017	0.11	0.41

Well waters with high mineral content and highest concentration values of boron have been taken into consideration.

Because water is an excellent solvent it can contains lots of dissolved chemicals. Since ground water moves through rocks and substance soil, it has a lot of opportunity to dissolve substances as it moves, such as magnesium, calcium, chlorides, other macro and microelements. The quantity of minerals found in water supply, depend mainly on the types of rocks or soil the water comes into contact with, and the amount of water lost to evaporation relative to precipitation addition.

A high mineral concentration can restrict the use of water, depending on the specific mineral present and their individual concentration.

Also, the quality of ground water can register changes as the result of the mixing of water different aquifers. In aquifers affected by human activity, the quality of water can be directly affected by the infiltration of anthropogenic compounds or indirectly affected by alteration of flow paths or geochemical conditions.

In the water with high concentrations of boron were revealed nitrates (NO_3^-) of anthropogenic origin, probably because of intensive agriculture in this territory. In the water samples, of rural areas, the concentrations of nitrate ranged between 6.8 and 344.5 mg NO_3^-/l (Neamț district). The nitrate values were prepared by box-plot method (9).

Figure 3 shows the levels of this pollutant in investigated well waters of six districts of Moldova.

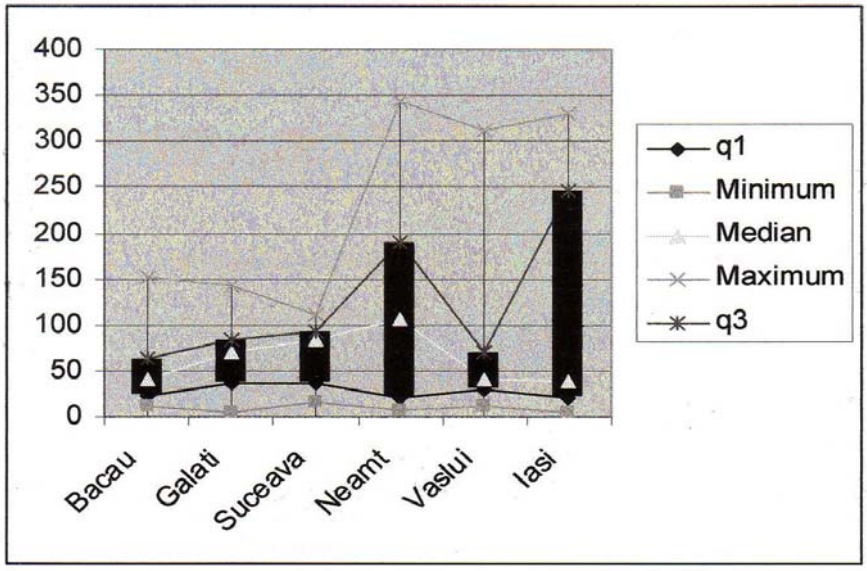

Fig. 3. Interquartile range of nitrate (mg/l) in well waters from rural areas

In Iaşi district there was registered a concentration of about 50 mg NO_3^-/l within a lot of 75% (q3) of water samples.

The following concentration criteria were used to identify if nitrate in well waters could be of anthropogenic origin or not:

- nitrate in concentration less than 0.9 mg/l indicated background level;
- nitrate concentration between 0.9 and 13.5 mg/l representing transition level;
- nitrate concentration > 13.5 mg/l showing an eventual human influence on water quality.

The high chloride content is generally considered as an index of impurity of ground water. In some wells, the matter contains chloride in high concentrations that exceeded Romanian's norm (250 mg/l).

Correlation analysis between the principal components was examined to find out possible relationships among these parameters of ground water samples. Table 3 shows the concentrations between the water quality parameters for well waters from rural localities (Prisecani, Iaşi district).

Table 3. Correlation analysis between water quality parameters

	Boron	Nitrate	Chloride	Total hardness	Calcium	Magnesium	Bicarbonates	Fluorine
Boron	1							
Nitrate	0.871	1						
Chloride	-0.354	-0.294	1					
Total hardness	0.607	0.304	0.157	1				
Calcium	-0.183	-0.247	0.286	0.350	1			
Magnesium	0.875	0.555	-0.287	0.678	-0.060	1		
Bicarbonates	0.374	0.153	-0.882	0.044	-0.079	0.425	1	
Fluorine	0.296	0.282	0.042	-0.199	-0.786	0.332	-0.122	1

The boron is high correlated with nitrate ($R^2 = 0.871$), total hardness ($R^2 = 0.607$) and magnesium ($R^2 = 0.875$). No significant correlations between boron and bicarbonates, boron and fluorine, nitrate and bicarbonates, calcium and chloride we founded.

CONCLUSIONS

- Well waters are used for drinking purpose in many rural localities in rural areas of Moldova territory.
- The analytical results of chemical water analysis revealed the presence of boron in the limit of Law

458/2002, with a variation between 0.002-1.55 mgB/l.

- Another important aspect is the high concentrations of nitrate that exceed 50 mg/l in more than half of the well sampled.
- In general, well waters within the investigated areas, are highly mineralized. They contain chloride, bicarbonate as total hardness. Calcium and magnesium registered high levels in some wells.
- The correlation analysis revealed the strong positive association between boron and some chemical compounds in drinking water.
- Access to safe drinking water is essential to human wellbeing and is a key public health issue.

The maintenance of good quality of drinking water is achieved both by protecting the raw water supply and water treatment. It is possible to protect the raw waters supply by means of pollution control measures that prevent undesirable constituents from entering the water and by good watershed management practices.

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