PHYSICAL AND BIOLOGICAL PROPERTIES OF BAZNA WATERS

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Abstract

The healing properties of Bazna waters and their therapeutic indications have been well known since the 18^{th} century. The objective of the present study was to characterize these waters from physical and biological points of view, and to further analyze the nitrogen compounds, especially NH4+. The following physical parameters of the water were analyzed: density (g/cm^3) , electric resistivity $(\Omega \cdot m)$, electric conductivity $(cm^3 \cdot o^2)$, salinity, The pH analysis of the biological component was performed on samples from 4 basins. Nitrogen compounds were dosed in the form of ammonium ion (NH^{5+}) . The physical and chemical proprieties are similar across the basins. Flora and fauna biological components were identified. Ammonium ions were identified in large quantities, but this did not lead to hygienically unclean waters.

Keywords: balneotherapy, spa treatment, spa water physical characteristics, spa water biological composition

Introduction

Bazna is one of the oldest resorts in our country, attested by documents in 1302. Natural spring waters were discovered, following natural gas reservoirs discoveries in 1671. The water healing proprieties were mentioned in the 18th century, followed by chemical and microbiological studies of the spring waters and therapeutic mud studies in the second half of the century. The first salty water exploitation was registered in 1814 and the first amenities consisting of 4 cabins and a water heating installation were made in 1835. The first balneal establishment was built in 1843, and two years later 637 people had been treated there. Ever since Bazna Resort has been visited annually by thousands of people who benefited from the marvelous effects of the resort salt waters and mud [1].

Therapeutic indications are similar to those of other thermal waters across Europe [2-5]:

- Degenerative rheumatic complaints (cervical, lumbar and dorsal spondylosis, arthrosis);
- Abarticular rheumatic complaints (bursitis, tendinosis, tendomyosis, tendoperiososis, fibrositis);
- Inflammatory rheumatic complaints (polyarthrosis, psoristic arthritis, ankylosing spondylitis);
 - Spondylosis and all kind of spondylitis;
 - Scapular-humeral periarthritis;
 - Gouty Rheumatism;
- Post operative conditions affecting the joints, muscles, bones, post traumatic conditions;
- Peripheral neurological diseases (post-traumatic paresis and paralysis, stiffness following polyneuropathy

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symptoms, poliomyelitis effects);

- Gynecological conditions (ovarian insufficiency, cervicitis) [1,6,7].

Bazna waters were previously characterized from a chemical point of view [1]. The objective of the present study was to characterize this water from physical and biological points of view, and to further analyze the nitrogen compounds, especially $\mathrm{Nh_4}^+$.

Materials and Methods

The following physical parameters of the water from the basins were analyzed: density (g/cm³), electric resistivity ($\Omega \cdot m$), electric conductivity (cm⁻¹ o⁻¹), salinity, pH.

Analysis of the biological component (flora, fauna) was performed in 10 samples from each of the four basins - basins no. 1, 2, 3, and the regeneration basin in two seasons, spring (May) and fall (September) as follows:

- Qualitative analysis of animal and vegetable organic material in the four basins' water
- Factors influencing the biological component: temperature, transparence, water dissolved oxygen, biochemical oxygen consumption (BOD5) of the substances that had been degraded biochemically in five days at 20°C (excluding those with slower biochemical degradation and the ones that degrade in other temperatures).

Nitrogen compounds were dosed in the form of ammonium ion (NH_4^+) . The chemical determinations of the ammonium ion were performed using ISO 5664/84 ISO. 7150/84 analytical method.

Results

The physical parameters of the Bazna waters are listed in table I. Their closed physical – chemical properties provide the posibility of using this water to the entire capacity in the Bazna Resort SPA.

Basin	Density g/cm ³	El. resistivity Ω m	El. conductivity cm ⁻¹ o ⁻¹	Salinity	рН
1 - Centre	1.0333	11.5455	0.0086	58.8	6.9
2 - Shore	1.0300	7.7300	0.0790	51.2	7.0
2 - Centre	1.0300	12.0138	0.0832	52.6	7.0
3 - Shore	1.0610	7.7369	0.1292	*	6.9
3 - Centre	1.0615	7.3737	0.1320	*	6.9
4 - Regeneration	1.0664	7.3135	0.1367	*	6.9

Tabel I. Basin water main physical indicators

1-4: Basin number; Analysis was performed at 26.09.2003; *: analysis not performed

The biological components identified were as follows: phytoplankton which consists of fifteen phytoplankton taxa belonging to the cyanophytes, chlorophyte and diatoms group, filamentous algae (Cladophora sp., Spyrogira sp., Enteromorpha clathatra) and zooplankton (which includes rotifers taxa, copepod, brachiopods bodies).

For Bazna mineral aquifer, the ammonium source with an abnormal level of concentration has two sources, both exclusively natural:

1. Primary, ionical ammonium, which enters the composition of Bazna mineral waters, results from ammonium salts dissociation, mainly carbons and ammonium chlorate, in the conditions of aquifer thermodynamical transition beetween underground geochemical conditions and emergence.

 $\mathrm{NH_4}^+\mathrm{CI}$ thermical dissociation from the aqueous solution is sustained by previous hydrolysis to a different pH from 7.4. The chemical hydrolysis results have the collision effect of mineral water pH change tendency in the emergence process, $\mathrm{NH_3}(g)$ leaving the system like an entropic solution, while HA remains in solution.

That is the reason why when the drilling is over, the mineral water has a slightly acid pH $(6.4 \div 6.6)$ favourable to NH₄⁺ ions (the pH variation domain in H₃BO₃ medium is $6.0 \div 7.4$).

We notice that the chemical analysis for dosing the chemical species resulted from $(NH_4)_2CO_3$ dissociation point up more bicarbonate (HNH_4CO_3) and carbonate $((NH_4)_2CO_3)$ stages and less thermical dissociation step, represented by the ammonium carbonate acid (NH_2COONH_4) .

The NH₄⁺ ion results from the migration in hydrated phase (NH₄OH) and partially absorbed on the hydrolyzed fraction entrained from the aquifer capitation together with iron hydrated micelles oxides, at an isoelectric level and a mycellar proportion which favors dispersion [4].

2. To bring NH₄⁺ into the Bazna mineral water [4] another geochemical method is used, based on NH

neutralization. NH₄⁺ results in splitting, amination and decarboxylating processes (in the catalytic presence of Sarmatian clay) with a weakly dissociated diprotical acid, such as:

$$Nh_3 + HOH \leftrightarrow NH_4^+ + HO^+$$

Disscussion

The physical determinations of density, conductivity and resitivity complete the chemical ones, so that we could understand the therapeutical proprieties of Bazna waters. Their therapeutical action does not depend only on different types of ions, but on complex action where the raport beetwen mineral water ions mixtures and exchange play an important rol [9].

Basins pH water variation is influenced directly by equilibrium changes C0₂/HCO₃/CO₃². CO₂ absence in the surface layers, after photosynthesis intensification, temperature increases, lead to displacement of this system favoring carbonates and dicarbonates. This hydrolysis releases OH, which further contributes to pH increases.

Basins pH water variation is influenced directly by equilibrium changes in C0₂/HCO₃/CO₃². CO₂ absence in the surface layers, after photosynthesis intensification, temperature increases, lead to displacement of this system favoring carbonates and bicarbonates. This hydrolysis, releasing OH, contributes to pH increases.

Salt lakes biological characterization

Factors influencing the biological component:

<u>Temperature</u> is an important abiotic factor of the biotope, because it influences the intensity of chemical and biochemical reactions in the lake. Surface water temperature is influenced by the ambient temperature, which is why the four Bazna's basins presented seasonal thermal oscillations in 2003.

Temperature variation also explains phytoplankton dynamics, algal biomass reaching a maximum in May, and possibly a new high in late summer.

<u>Transparence</u> of the lake water is another important environmental factor because light penetration affects complex biological processes that occur in the water, especially photosynthesis.

Thus, in samples from May, when because of the high temperature, algal development was remarkable, transparency varies between 1÷40 cm for Basin 3 (Regeneration basin), while in samples taken in late September, when the cycle of phytoplankton evolution almost concluded, transparency recorded higher values, between 1.80 cm (Basin 3) and 60 cm (Regeneration basin).

<u>Water dissolved oxygen</u> is also a biotope factor which is limiting aquatic life; values recorded in water samples were disparate and inconclusive.

It varies considerably between 1.76 mg/l (Basin 1) and 17.25 mg/l (Basin 2). Oxygen saturation is the average between 26.5÷60.4%, these results characterizing the four basins as mesotrophic lakes.

<u>Biochemical oxygen consumption</u> - BOD_5 - The recorded values for this indicator correspond to the evolution of life in lakes, being higher in September.

All these parameters characterize lacustrine ecosystems under study at a time. It can tell about water quality variation from natural causes, which can be significant over time, periodic or non-periodic, biotic or abiotic cause, internal or external to these water masses.

That is why it is absolutely necessary to monitor the physico-chemical changes because it can detect variations induced by hydrological regime of the analyzed basins, the origin and physico-chemical-biological behavior of various constituents of studied salt lakes. In lakes, if the water time resident is over a year, the most variations of water quality in time are due to internal processes, climatic and biologically determined [8].

Biological caracteristics

From the qualitative point of view, the <u>phytoplankton</u> consists of fifteen phytoplankton taxa belonging to the cyanophte, chlorophyte and diatoms group. The development is increasing from spring to autumn in all four basins: Basin 1, 2, 3 and Regeneration basin, phytoplankton production being influenced by the abundance of nutrients, sunlight, dung hole depth, turbidity (water transparency), water temperature, zooplankton abundance and degree of water pollution. The phytoplankton is dominated in May by <u>chlorophyll</u> and in September by <u>diatoms</u> (hydrobionts that develop mainly in lower temperature and when the quantity of iron is greater) in all four basins. Phytoplankton dominated in number and biomass intake by diatoms, most species been located in Basin 1, especially during harvesting in May-June.

Among the <u>filamentous algae</u> the following were identified: Cladophora sp., Spyrogira sp., Enteromorpha clathatra. The above mentioned species had a remarkable development in May in all basins. Filamentous algae were identified especially in high densities, in the regeneration basin, Cladophora sp. occupying about one-third of the basin

[8].

The cyanophytes are represented by a few individuals of the species *Oscillatoria tennuis* and *Anaeba planetonica*, in spring samples from Basin 1, not identified in other basins.

Zooplankton includes rotifers taxa, copepod, brachiopods bodies, their quantitative and qualitative contribution to biomass of Basins 1, 2 and 3 been insignificant in May and June months, except for the Regeneration basin, where the whole plankton is dominated by Brachionus urceolaris - rotifer identified with great frequency, so water gained a particular aspect and color (green-brown).

Rotifers are microscopic animals with a diet which must contain small enough particles to be ingested during filtration feeding. These round animals are primarily omnivores that eat mostly dead or decaying organic matter such as unicellular algae and other phytoplankton components representing primary producers in aquatic biocenosis.

Rotifers are primary consumers. In September, the zooplankton organism's density remains low in Basins 1, 2 and 3: in these basins, during September 2003 the following were identified: Urceolaris Brachionus, Artemia salina, Arctodioaptomus salinus.

The regeneration basin presents again a particularity: the zooplankton is dominated this time by the specia Artemia salina – a crustacean commonly found in salt lakes due euryhalinity that characterizes it.

Artemia salina has an important role as an organic meal intake in peloidogenesis (by high frequency, but also by the large amount of biomass).

Macrophytes that form the lakes (basins) riparian vegetation are species adapted to the salty and clay fields conditions that surround the four basins as follows: *Aster tripoium*, *Ateriplex hastate*, *Salicornia europaea*, *Phragmites australis*, *Daucus carota*, *Agropyron repens*, *Plantago mayor*, *Ranunculus repens*.

Analysis of amonium compounds

Because they are reservoir water, the contain ammonium ions in big quantities without being hygienicaly unclean. It is good to mention the fact that ammonium ions are toxic only for high alcalinity pH waters, when they are delivered as ammonia. Well Drill 2 (114 mg/l) has the biggest amount of NH₄⁺ ions. For a water pH=7.35, only 1% of 100% NH₄⁺ mg is transformed in ammonia. Nitrates are present in this wells in limited quantities. They result in the NH₄⁺ process of oxidation, the reduce form [8].

Nitrites are an intermediary stage for $\mathrm{NH_4}^+$ ions conversion in nitrates. Their values are small, like "trace" elements. Among undissociate elements the soluble metasilicic acid is evidenced. This acid is a part of weak acid category which is hydrolysing in solution, realizing OH ions.

Ammonia and ammonium are present in the mineral water in an accentuated disproportion for $\mathrm{NH_4}^+$ corresponding to a pH=6.5, ionical strength (hypertonic solution with >50 g/l concentration in dissociated salts) and source temperature $(10\div12)^\circ\mathrm{C}.$ The disproportion is more accentuated in the Basin. An ammonia percentage is transformed in a NO₃ assimilable form as a result of O₂ presence in the water by dehydrates reactions.

The syngenetical characteristic of organic nitrogen conversion process is significantly relevant both in the superficial area of Bazna aquifer [8] where deamination has a strong hydrolythic, partial oxidative, intramolecular character, forming NH₃, oxyacids, aldehydes, and CO₂, and in the profound areas where dehydrogenation process and cycloparaffin and cicloolefin nucleus splitting are running simultaneously, essential processes in the hydrocarbons genesis.

Nitrogen passes through different association phases during the natural labor from genetic processes, capture and delivery points.

$$NH_3 \rightarrow NH_4OH \rightarrow NH_2OH \rightarrow HNO \leftarrow NH(OH)_2 \leftarrow HNO_2 \leftarrow HNO_3$$

$$I$$

$$R - NH_4$$

Conclusions

The mineral water from Bazna has such a complex mixture that the total action is formed from the interplay of multiple factors. Because it is reservoir water, it contains ammonium ions in big quantities without being hygienically unclean; ammonium ions are toxic only in high alcalinity pH waters, when they are delivered as ammonia, which is not the case of Bazna basins.

Natural mineral water, captured by drilling to exploit the aquifer hydro Bazna has an abnormal ammonium content in relation to background concentrations hydro for this component, such as the global value of Clarke and the regional background value. Ammonium content is anomalous in relation to the mineral waters genetic similarity (accumulations of hydrocarbons from gasstructures in Romania).

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