

# 4.3. STÂNA DE VALE AREA, A LABOATORY FOR STILL WATERS (THE VLĂDEASA MASSIF)

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## Introduction

The excellent reputation of Stâna de Vale climate resort is due both to its exceptional tourism potential and to the outstanding qualities of the water of Izvorul Minunilor spring (Wonder spring). Known ever since the oldest times, due to their “pure air, very good water and shadow of the fir trees forests” (Familia, 1890, no. 19, p. 228), these places became an object of interest for the public starting with the year 1879. In the year 1886 Izvorul Minunilor was used for the supply of the “big shower”, also called the “cold bath” (Familia, 1886, no. 31, p. 376, in V. FAUR, D. CLUCIU, 1985, 1989).

The development of the resort has been favored by the completion of Oradea-Ceica-Beiuș-Vașcău railroad, commissioned in the month of June 1887, of Budureasa-Stâna de Vale road (1892), and of Valea Iadului-Stâna de Vale alpine railroad, completed in the month October 1934.

In the year 1928 Stâna de Vale is awarded the statute of “climate resort”, granted by the Ministry of Health and Social Protection, by the General Balneology-Climatic Inspectorate, as well as by the Bihor County Hygiene and Public Health Council.

## 1. History of the hydrogeological research

The first hydrogeological investigation of Izvorul Minunilor has been performed by the Institute of Studies and Research for Land Reclamation (ISPIF) during the period 1981-1982, and it has consisted in performing chemical and bacteriological analyses, the latter completed in the Preventive Medicine Laboratory in Beiuș, under the leadership of D. MOCUȚA. From the very beginning, there has been noticed the Izvorul Minunilor water exceptional microbiological purity, which had

not been met in the case of other sources, the results of these investigations naturally leading to awarding to the source at Stâna de Vale the still water statute (M. PASCU et al., 1984).

In the year 1995 I. Orășeanu installed a level recorder and collected water samples at Izvorul Minunilor, in order to outline the flow rates regime and the chemical and bacteriological character of the source. During the same period the source started being systematically investigated by A. Feru from SNAM (National Society of Mineral Waters, former RAMIN), investigations that still continue.

In between 1997-1998, M. GHIBIRDIC, ILEANA TIȚĂ and A. DRĂGĂNESCU from ISPIF undertakes hydrological, hydrochemical and bacteriological research on Cuciului (Hera), Pescăriei and Rampei water supplies.

In the year 1998, ILEANA TIȚĂ and V. MICULA published the results of the hydrochemical investigations that addressed the sources Izvorul Minunilor and Cuciului spring, by identifying in this way a second possible still water source in this area.

In the year 1998, I. ORĂȘEANU published the hydrogeological map of Stâna de Vale area and described the main hydrodynamic characteristics of Izvorul Minunilor.

A. FERU and RUXANDRA SLĂVOACĂ (1998), in a study addressing the assessment of the stability of the bottled waters based on the computation of the saturation indexes, have shown that over the temperatures range 0-50°C, the still water of Izvorul Minunilor spring is non-saturated with respect to all the minerals of its own paragenesis.

The results of the simulation of the behavior of the chemical composition of the water of the sources Izvorul Minunilor, Cuciului, Pescăriei and Rampei at temperatures up to 50°C, published by I. ORĂȘEANU (2000), indicate a very good stability of these waters.

## 2. Topography, hydrology and climate data

The climate resort Stâna de Vale is situated in the central-western area of Vlădeasa Massif, in the upper part of the catchment area of Iad river, a tributary of Crișu Repede river (Fig.1). The upper part of Iad catchment area (upstream of Băița brook confluence) has a circular depression shape, covering a surface of 8 km<sup>2</sup>, and it has 1233 m average elevation. It is bounded to the southwest by the catchment area of Crișu Negru river (Beiuș Basin), by the ridge Băița peak (1352.0 m)–Custurilor peak (1386.4 m) – Poienii peak (1626.8 m), while Baia Popii ridge, of 1400 m average elevation, separates it to the west with respect to Drăganului river catchment area (Fig. 2).

Across the depression there run the brooks Băița, Custuri, Trauri, Ariei and Fântâna Galbenă with its tributary Piciorul Galbenei and Rampei. We mention the fact that when reaching the Anisian dolomite substratum, the water of the last mentioned course sinks through several swallets that in terms of human exploration are impenetrable. During snow melt and heavy rainfall the absorbing capacity of these swallets is exceeded, and as a consequence, also the valley section that extends downstream carries temporarily water.

The climate of the area is of continental temperate type, in the domain of influence of the western circulation that carries wet and cold masses of oceanic air.



Figure 1. Location of study area.

The 1950-1999 multi-annual average of the rainfall recorded at the INMH meteorological station within the resort is 1563.3 mm/year. For 1970-2000 time interval, M. VLAICU and O. GAGEU, 2009, mention a value of 1632 mm/year. The most severe drought period has been recorded within the time interval 1959-1963, with rainfall in the year 1961 setting the lowest value (579.7 mm) of the so far recorded range. The 1982-1994 time interval has been also a quite dry one, with just two years within this interval, 1984 and 1985, slightly exceeding the multi-annual average (Fig. 3). The most rainy years, with rainfall exceeding 2000 mm, have been 1952, 1970, 1974, 1980 and 1995, the 2349.0 mm maximum having been recorded in the year 1974.

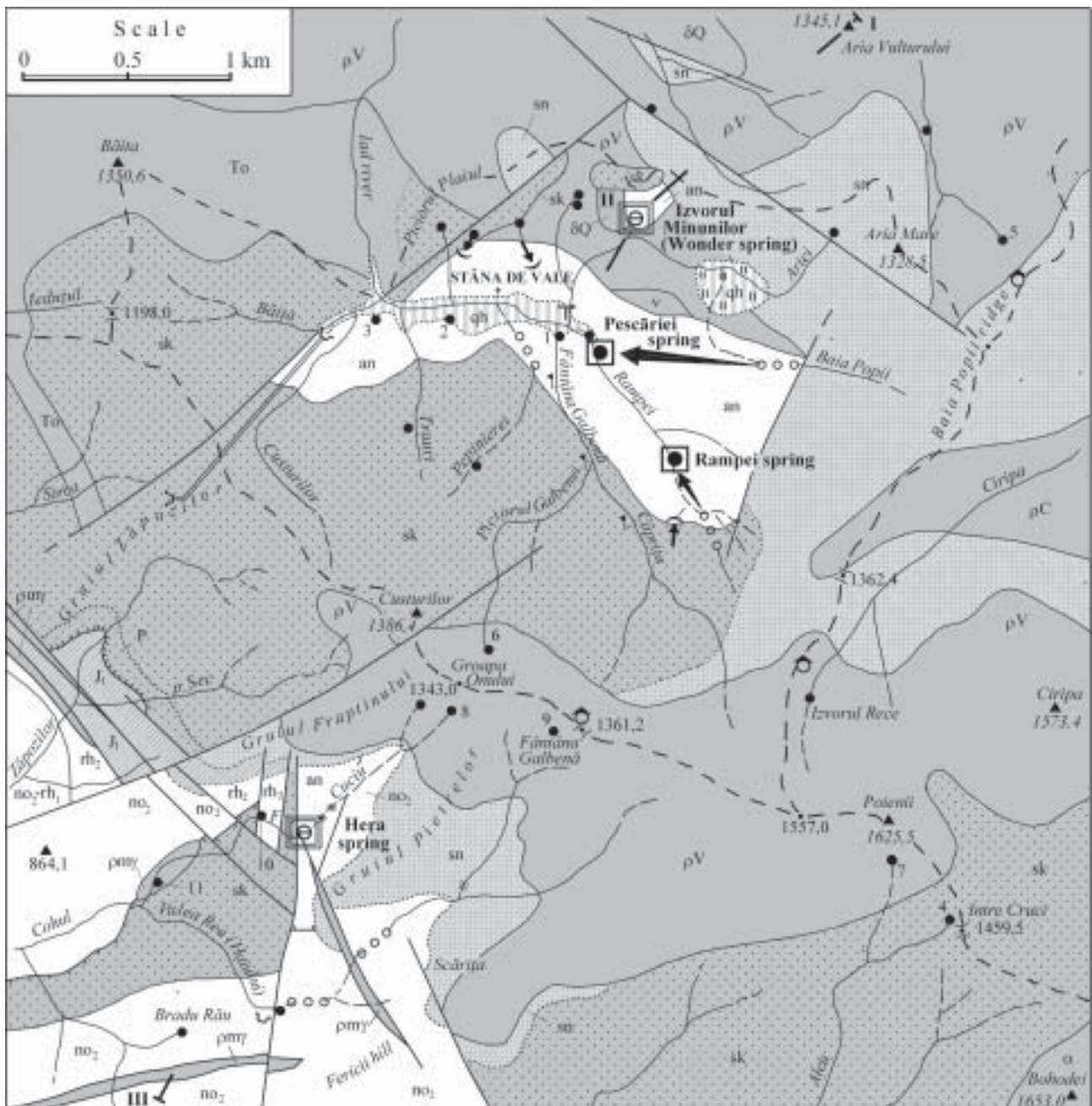
June is the most rainy month at Stâna de Vale (data over the 1950-1999 period), with 12.6% (197.2 mm) of the multi-annual average rainfall occurring during this month. The most dry months are February and March, with 6.7% (104.5 mm) and 6.0% (93.97 mm) respectively of the multi-annual average. The multi-annual average rainfall amounts, distributed as a function of the warm and the cold seasons, namely over the time interval May-September and October-April respectively, are relatively similar (47.8%, and 52.2% respectively).

The multi-annual monthly average distribution of rainfalls for 1978-1997 period is presented in Fig. 4, at the left. The maximum is recorded in June (197.6 mm), while minimum is recorded in February (108.8 mm). The multiannual average for this period is 1668.2 mm. The layer of snow is present from October to May. During the above-mentioned interval, the maximum of the snow layer was 194 cm (Fig.4, right). The absolute maximum was 310 cm, recorded in January 2000 (MARIA CRISTEA, 2004).

The multi-annual average (1978-1997) air temperature at Stâna de Vale is 3.9°C, the maximum mean values being recorded in the months of July (13.2°C) and August (12.7°C), and the minimum ones in the month of January (-5.3°C), (MARIA CRISTEA, 2004, Fig. 4 left).

The vegetation that prevails in the domain consists of fir tree, spruce and beech forests, that on the ridges are replaced by alpine grasslands.

In Stâna de Vale area, due to the steep and large elevation range topography, the runoff regime closely mirrors the rainfall regime. The heavy



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<table border="1" style="border-collapse: collapse; width: 100px; height: 150px;"> <tr> <td style="text-align: center;">a</td> <td style="text-align: center;">b<sup>1</sup> b<sup>2</sup> b<sup>3</sup></td> </tr> <tr> <td style="text-align: center;">P<sub>g1</sub></td> <td style="text-align: center;">P<sub>g1</sub></td> </tr> <tr> <td style="text-align: center;">ma-P<sub>g1</sub></td> <td style="text-align: center;">P<sub>g1</sub></td> </tr> <tr> <td style="text-align: center;">P<sub>g1</sub></td> <td style="text-align: center;">P<sub>g1</sub></td> </tr> </table>	a	b <sup>1</sup> b <sup>2</sup> b <sup>3</sup>	P <sub>g1</sub>	P <sub>g1</sub>	ma-P <sub>g1</sub>	P <sub>g1</sub>	P <sub>g1</sub>	P <sub>g1</sub>	<p>Quaternary alluvium (a) and deluvium (b)</p> <p>Laramian magmatites:</p> <p>Microgranite rhyolite;          Granodiorites          Quartz diorite          Tonalite          Vlădeasa rhyolite          Ciripa rhyolite          Dacite          Quartz andesite</p> <p>Senonian in Gosau facies          Jurassic limestones and marls          Triassic limestones and dolomites          Shales intercalations in upper terms          Permo-skithian sandstones</p>	<p>Losses in flow along the riverbed          Ponor (swallet hole)          Spring          Spring developed for potable water supply          Still water spring          Proved groundwater flow direction          Watershed          Tunnel for water pipe          Waterfall          Weather station          Water level recorder          Hydrogeological cross section</p>
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Figure 2. Hydrogeological map of Stâna de Vale.  
 Geological data after S. BORDEA, 1999 and G. ISTRATE, 1978.



rainfall or the fast snow melt periods are accompanied by significant increases of the stream courses discharges, while drought periods lead to severe reductions of these flow rates.

The catchment area of Fântâna Galbenă and Ieduț brooks belongs to the category of representative basins of the National Institute of Hydrology and Water Management, being subjected to a close monitoring of the hydrologic events evolution (P. MIȚĂ, 1996).

### 3. The geological structure

The geological structure of Stâna de Vale area is extremely complicated, with sedimentary deposits in overthrust structures belonging to the Codru Nappes System (the Ferice and Arieșeni nappes), pierced or overlain by the Vlădeasa igneous body rocks (Figure 2). Areas of significant extent are occupied by sedimentary and volcanogene-sedimentary deposits of Senonian age, transgressively deposited over the older sedimentary structures and igneous formations, being synchronous to, or overlain by the upper terms of the Banatitic eruptions.

#### 3.1. Sedimentary deposits

**Ferice Nappe.** This tectonic unit consists of Triassic and Jurassic formations, that include the following lithologic succession (S. BORDEA, 1999):

Skythian. Deposits of this age consist of very hard, bedded, gray or greenish quartzite sandstones, having a thickness of about 200 m.

Anisian formations consist of gray dolomites, well bedded in sub-metric beds, similar to those of

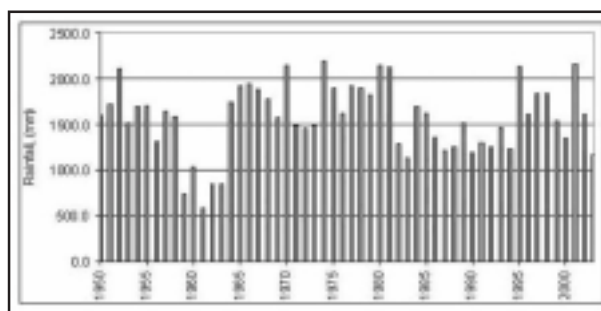


Figure 3. Annual rainfall recorded at Stâna de Vale over the period 1950-2003.

the Arieșeni Nappe. The deposits are about 150 m thick.

Late Norian – The Codru Formation – consists of gray shales alternating with siltstones, in which dolomitic limestones with brucite occurs. The estimated thickness of this formation is 250 m.

Early Rhaetian – The Valea Frunzei Formation – includes beds of dolomitic limestones with megalodonts, carbonate sandstones, siltstones, carbonate conglomerates and clays, the entire series having a thickness of about 350 m.

Late Rhaetian – The Kossen formation – consists of a black, layered limestone, that hosts a rich fauna of brachiopods and corals. 25 m maximum thickness.

Early Jurassic, consists of marly clays alternating with spatic carbonate sandstones and marly limestones with belemnites. About 250 m thickness.

The Ferice Nappe deposits outcrop in the south-western part of the domain, in the catchment areas of Zăpozilor, Cuciului and Valea Rea brooks. Deposits of the same overthrust also occur in Aleu stream upper catchment area. They lay over the Banatitic body or over the Jurassic or Cre-

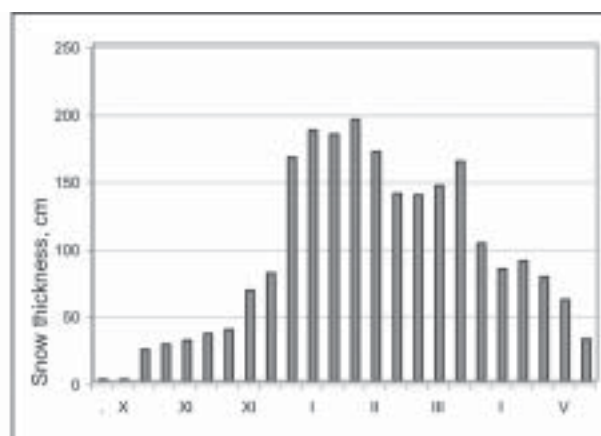
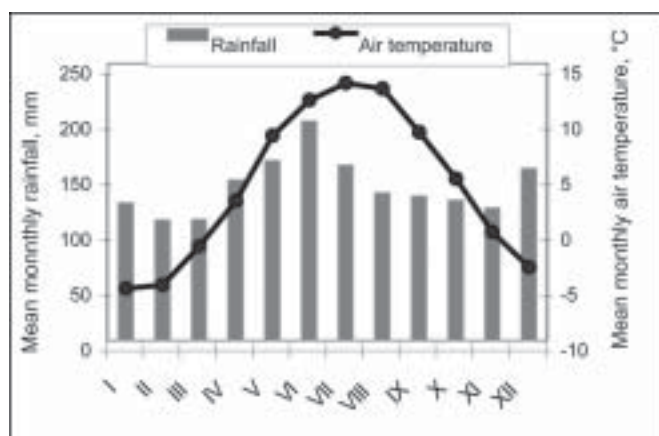


Figure 4. The multi-annual monthly average (1978-1997) of rainfall and air temperatures (left) and of snow layer thickness (right). After MARIA CRISTEA, 2004.

taceous deposits of the Bihor Unit, and they are partly overlain, in an overthrust setting, by the quartzite sandstones of the Arieșeni Nappe or by the Vlădeasa rhyolites.

**The Arieșeni Nappe.** Permian and Early Triassic formations have been distinguished within this tectonic unit.

Permian formations include detritic, continental streambed deposits of red color, with feldspar (the Feldspat Formation) or with worms imprints (the Vermicular Formation). 200 m thickness.

Skythian formations include well bedded quartzite sandstones and conglomerates, with sparse intercalations of red or greenish shales. 150-500 m thickness.

Anisian formations consist of gray dolomites and dolomite breccias, with a thickness of 150 m.

### 3.2. Alpine subsequent igneous rocks (Banatites)

Vlădeasa igneous complex occurs in a subsidence area of graben type, the ascending magmas following the fractures systems of the Crystalline-Mesozoic basement. The igneous activity resulted in the emplacement of a sequence that includes a multitude of intrusive rocks, consisting of andesites and of a series of dacites and rhyolites solidified subject to sub-volcanic conditions. Subsequently, there have been emplaced intrusions of micro-diorites, diorites, porphyric granodiorites, granodiorites, granophires, microgranites and granites.

Rhyolitic rocks of Vlădeasa Massif, designated by D. GIUȘCĂ (1950) as the “Vlădeasa rhyolites”, and by G. ISTRATE (1978) as the “ignimbritic rhyolites formation”, occur under various facieses, that range from eutaxitic (flow textures, ribbon-like) to compact, vitrophiric, up to pyroclastic with volcanic tuffs and many xenoliths, depending on the way the rhyolitic magma solidified, namely beneath the Senonian sedimentary cover or at the surface.

The Banatites intrusion has generated contact phenomena within the sedimentary deposits it crossed. At the contact between Banatites and limestone, there have been generated marbles and various types of calcic skarns, while at the contact with detritic and pelitic rocks there have been generated hornfels, skarns with garnets, etc.

Within Stâna de Vale area, the most frequent igneous rock types are as follows:

- the Ciripa rhyolites, are ribbon-like rhyolites displaying an eutaxitic structure and a broad crystallization of the main mass;
- the rhyolites with ignimbritic structures, the Vlădeasa rhyolites, occur subject to a variety of structural and textural appearances. They are gray colored and their facies is massive or eutaxitic (finely vesicular and non-homogeneous magma), less frequently pyroclastic or of breccia type (of explosion);
- the tonalites are intrusive rocks, representing the transition between granodiorites and diorites. They have a holocrystalline structure and massive texture, a dark color and they form a large extent body, with deep “roots”, in the area of Băița peak, in the north-western part of the domain.

### 3.3. The post-tectonic cover

Senonian deposits, occurring in a Gossau facies, form the Late Cretaceous post-tectonic cover of the Bihor Unit and of the Codru Nappes System. These deposits outcrop on relatively large areas east of Stâna de Vale resort.

G. ISTRATE (1978), in his work dedicated to the petrographic study of Vlădeasa Massif (their western section), distinguishes within the Senonian deposits a lower sedimentary complex and a volcano-sedimentary formation. The lower sedimentary complex - the Gossau formation - is largely represented in the northern part of the mountains body, where crystalline schists are overlain by a succession that includes three horizons: a conglomerate one at the bottom, a marly-sandy, micaferous one in the median position, and a micro-conglomerate one at the top.

The volcano-sedimentary formation deposits consist of a variable ratios mixture of sedimentary and igneous material, including tuffites, tuff-breccia and volcanic conglomerates, sometimes reaching thicknesses of 100-150 m.

### 3.4. Tectonics of the area

The Anisian dolomites of the Arieșeni Nappe occur in Stâna de Vale area within a syncline structure, with Skythian quartzite sandstones at the bottom, and with the micro-conglomerate sandstones

and clays of the Senonian transgression covering it in the north-eastern part. In the south-western part of the area, the continuity of the Arieșeni overthrust deposits is broken by the fault of Custurilor peak, that strikes approximately NE-SW and has its south-eastern compartment down-thrown, with Anisian dolomites on Cuciului stream outcropping in it (Fig. 5).

The deposits of the Arieșeni Nappe are pierced by the tonalites rooted body of Băița peak and by the quartz diorites in the area of Izvorul Minunilor. Within the ridge Custurilor peak - Poienii peak and north of Stâna de Vale resort, they are covered by the Vlădeasa rhyolites, the contact between the Triassic deposits and the igneous formations being frequently marked by the Senonian deposits that rhyolites overlie. The contact between the Anisian dolomites in Stâna de Vale area and the Vlădeasa rhyolites occurring to the north, is a tectonic one, consisting of a NW-SE striking fault, with its north-eastern compartment down-thrown.

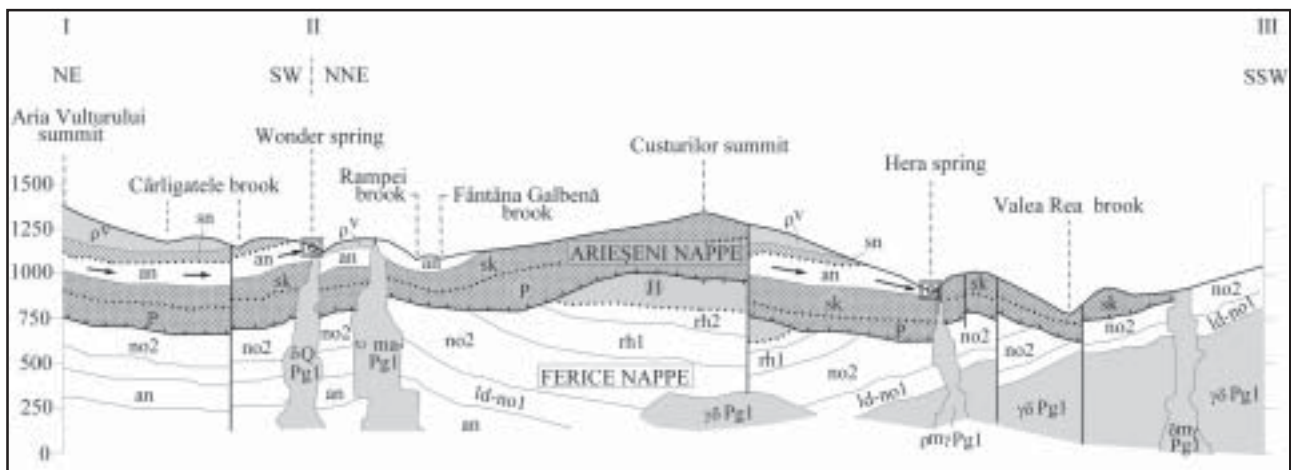
## 4. The hydrogeologic setting of Stâna de Vale area

The important tectonic actions to which the formations included in the geological structure of the south-western part of Vlădeasa Massif body had been subjected, have resulted in of a kaleidoscopic distribution of rocks, in which formations with distinct lithology compositions are brought into direct hydrogeological connections, generating aquifers with specific groundwater recharge, flow and discharge conditions.

The genesis of the main springs in the south-western part of Vlădeasa Massif (Izvorul Minunilor, Pescăriei, Rampei and Cuciului), is related to the occurrence of carbonate rocks, the latter behaving as drains for the water accumulations located in the other rock types. Limestones and dolomites are largely developed in the basement of the area, yet they outcrop over restricted surfaces, because both Senonian deposits and Vlădeasa rhyolites cover them to a large extent. The entire rocks series is pierced by intrusive rock bodies having penetrated along fractures.

The dolomite plate in Stâna de Vale area (Fig. 2), being positioned below the mountain ridges that surround it, concentrates the runoff from the adjoining, non-karst hillslopes. The recharge of the karst aquifers is derived both from surface stream courses, whose water sinks in the underground either fast, through swallets, or in a diffuse manner, through the alluvia in their stream-beds (Fântâna Galbenă, Pepinierei and the brooks in the upper catchment area of Rampei), and by the underground flow occurring within the entire contact zone between dolomites and adjacent rocks. Aquifers hosted by the Senonian deposits and/or by Vlădeasa rhyolites overlie the karst aquifers, and as a consequence the latter are warranted both a constant recharge, and a protection resulting from filtering of the superficial, rainfall derived waters.

The groundwater accumulations in the Anisian dolomites in Stâna de Vale area discharge via three main outlets: Izvorul Minunilor, Pescăriei and Rampei springs. Beside these ones, there are a few other springs with small flow rates, such as Păcii (Fig. 2, no. 1), Radu (no. 2) and Pavel (no.



**Figure 5. Hydrogeological cross section of Stâna de Vale area.**

After S. BORDEA, 1999, modified. (Legend as in Figure 1. Line of section shown in Figure 1.)

3) springs. Finally, the karst aquifer is drained by Iad riverbed on the slot placed upstream the junction with Băița stream.

The Skythian quartzite sandstones display groundwater accumulations in their weathering zones, marked by a multitude of springs with flow rates up to 1 l/s, such Brăesei spring (Fig. 2, no. 4) and as those along Ariei, Trauri, Pepinierei brooks. The crushed zones that accompany the main faults occurring within the Skythian sandstones may act as drain for the groundwater in their weathering zone and in the adjacent deposits. In this respect, one example is met in the tunnel excavated for setting the pipes required in order to convey the water from Stâna de Vale to Sudrigiu and Rieni bottling factories.

Rhyolite rocks host groundwater accumulations as well, as indicated especially by the springs occurring in the upper reaches of the valleys excavated in these rocks: Ariei (Fig. 2, no. 5), Groapa Onului (no. 6), Plodul Babei (no. 7), spring of Cuciului brook (no. 8). These springs have average flow rates that may reach 1-3 l/s, a generally neutral, yet occasionally acid pH, the latter instance occurring as a consequence of the oxidation undergone by pyrite strewn within the rock mass (e.g. Fântâna Galbenă spring, pH=3.6, Fig. 2, no. 9). The water of these springs is of calcium bicarbonate type, with 60-80 mg/l TDS contents.

The electric conductivity (EC) is a global geochemical parameter, that is quite easily obtained in the field, with good accuracy and excellent reproducibility, its distribution diagrams outlining both the differences in the behaviour of the different aquifer types, and the degree of structuring of the karst aquifers (M. BAKALOWICZ, A. MANGIN, 1980). The electrical conductivity of water for Rampei spring was weekly monitored in between X.2004- IX.2005. We have used daily recordings undertaken by SNAM for Izvorul Minunilor in between VII.2001- V.2002 (A. FERU, 2007).

The distribution diagrams hence provide a more or less distorted image concerning the ways in which the flooded zone is recharged (Fig. 6).

The water at Izvorul Minunilor have low temporal variations of EC, 84% of the values being in placed in the 115-125  $\mu\text{S}/\text{cm}$  slot. The diagram, homogenous, with a clearly developed maximum, points a mainly feeding from a granular/cracked or

non-karstified carbonate aquifer. The flooded karst is less organized and has a low capacity.

The diagrams of the distribution over a hydrological cycle of water conductivity frequency values for the carbonate aquifer drained by Rampei springs, show the presence of an well structured and organized karst aquifer, with a functional main flow axis that facilitates to the water sunk in shallow holes, each one having its own geochemical evolution and own hydrogeological history, a fast arrival to the springs without significantly mixing with the water stored in the annex systems of the karst aquifer.

The time series of mean daily debits of main supplies in Stâna de Vale and rainfalls recorded at the meteorological station between 2001-2008 were analysed based on a correlating and spectral analysis proposed by A. MANGIN (1981, 1984). The method allows to know the structure of that data and identification of the relationship between rainfalls and debits.

The seasonal distribution of rainfalls recorded at Stâna de Vale is relatively quantitatively uniform along one year: 23.3% in winter, 24.9% in spring, 29.3% in summer, 22.6% in autumn (MARIA CRISTEA, 2004), while rainy intervals do not correspond from one year to the next one. Due to this fact, the entrance function (rain) could be seen as random, a fact clearly marked by the spectrum in Fig. 7, left.

The variance density spectrum of debits translates the presence of periodically events participating to their formation. The lower frequency values of the spectrum, shown a high inertial of the system. The scale of frequency may be expressed in days (1/f), being known as time of regulation and being connected to the duration of the impulse reaction.

The long terms variance density spectrum of sources discharge exhibits a succession of peaks corresponding to the periodicity of cold seasons (with solid precipitation and lack of infiltration), of snow melting period and of warm seasons, among which those at 357.1, 192.3 and 125 days are discernible in the spectrum of all spring as well. In Figure 7 right is presented the spectrum of Rampei spring.

The short term variance density spectrum of Izvorul Minunilor and Rampei supplies (Fig. 8, left) have very different truncation frequency (0.028 and 0.204), and then higher frequency is

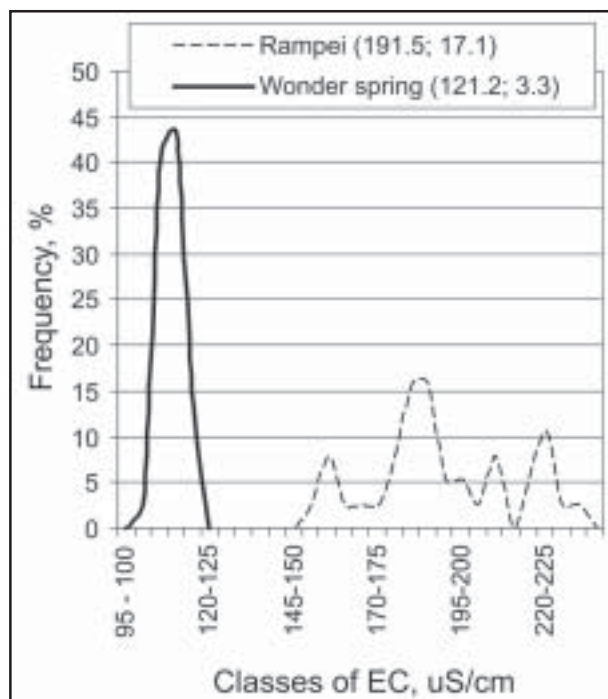


completely filtered. The spectral bandwidth of Izvorul Minunilor is narrow. The regulation time for the above-mentioned spring has 62.5 days value.

The correlogram of Izvorul Minunilor time series debits shows a gradual decline and reaches 0.2 for  $k=58$  days (Fig. 9, left), suggesting the inertia and high memory effect of the system; these features are confirmed also by the presence of a single maximum on the annual hydrogram of debits (April-May).

The long term correlogram of Izvorul Minunilor (Fig. 9, right) indicates the annual periodicity of precipitations, while other periodicity of the long term variance density spectrum are lightened by the high regulation power of the system. The correlation coefficient for 360 days for this spring has a very high value,  $r_k=0.43$ , much higher than for other supplies.

Crossed rainfalls-debits correlograms provide a good image of the unitary hydrographs of sources, an essential estimator of the quality of drainage and of the importance of the reserves in the karst system. Izvorul Rampei shows a narrow and pointed hydrograph (Fig. 8, right), the reaction of the karst system is swift and clear. The organization and the drainage abilities of the karst



**Figure 6. The distribution diagrams of frequency classes of the water electrical conductivity for two sources in Stăna de Vale area (in brackets mean EC and mean deviation of EC measured values).**

system are well developed, being mainly transmissive and less capacitive.

The shape for the impulsive response for Izvorul Minunilor is smooth and well spread out (Fig. 8, right). The direct and immediate relation rain-debit has a reduced role since the system has a high regulatory role and is low drained.

The interpretation of the recession curves of the debits of supplies recorded between 2001-2008, in periods with no recharge of the aquifer, provides average values of 0.008 - 0.01 for recession coefficients for Izvorul Minunilor spring and 0.017-0.026 for Rampei spring.

Data for multiannual average debits and temperatures of supplies, as well as results of handing out the temporal series of debits recorded for 2001-2008 are presented in Table 1.

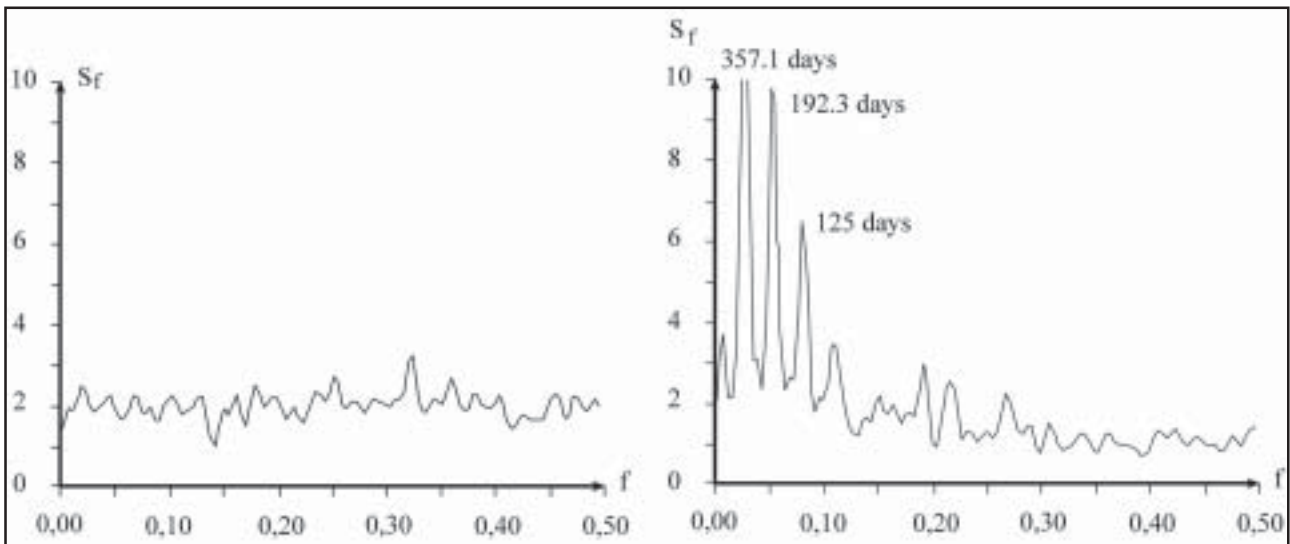
#### 4.1. Izvorul Minunilor spring

Izvorul Minunilor spring emerges from a small outcrop of Anisian dolomites, surrounded by Skythian and Senonian deposits and by Vlădeasa rhyolites (Figures 2 and 5). Although in the area of Izvorul Minunilor spring the dolomites outcrop over a very small surface, they are largely developed within the basement, acting as a drain for the groundwater accumulations located within the overlying formations, that prevalently consist of Senonian deposits (sandstones, clayey sandstones, conglomerates, marls) and of Vlădeasa rhyolites. These formations exert a twofold hydrogeological role, both by securing a strong and constant supply to the carbonate aquifer, and by providing it with a protection against fast recharge with surface-derived water, that is likely to be charged with mineral suspensions and with bacteriological loads.

The aquifer drained by Izvorul Minunilor spring has a high memory effect (58 days), a narrow spectral bandwidth (the filtration of rainfall information beginning with 0.028 frequency), while the regularization time is high. The unitary impulsive response of the system is smooth and well spread out and has a low value for the recession coefficient (0.009), specific for features of the aquifer with major reserves, capacitive and low transmissive, with no direct and immediate relation for rainfalls.

The water of Izvorul Minunilor outlet is of calcium bicarbonate type, with a very low TDS





**Figure 7.** The long term variance density spectrum of rainfall in Stâna de Vale (left) and of Rampei spring discharge time serie (right) for 2001-2008 time interval. ( $n = 10$ ,  $m = 1250$ ).

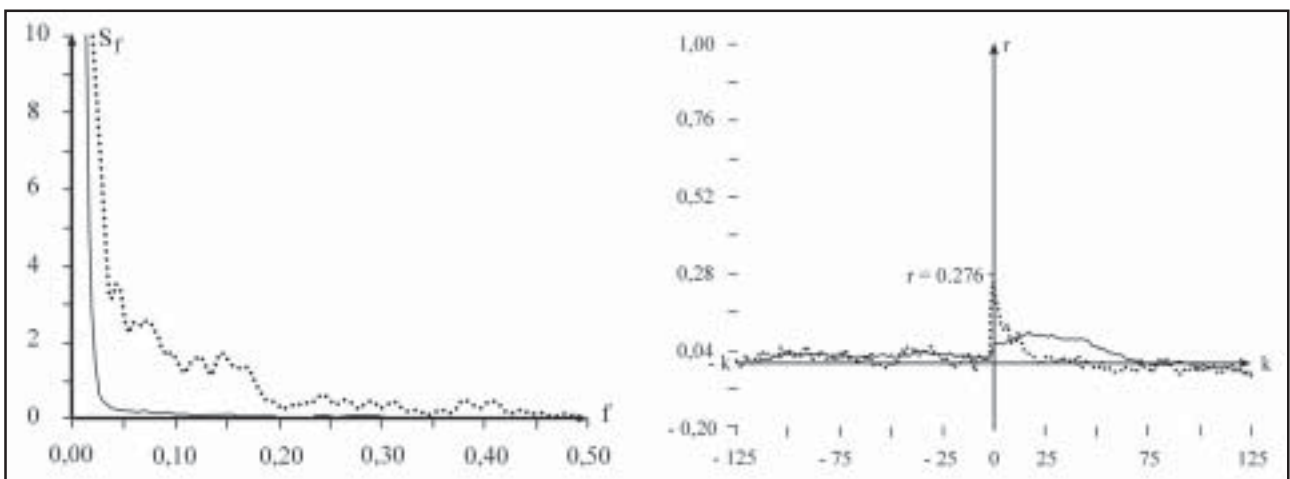
content (Table 2), having a neutral - slightly alkaline character, it is non-radioactive, pure from a bacteriological point of view, colorless and it tastes good.

The investigations addressing the behavior of Izvorul Minunilor outlet water chemical constituents, performed both on water samples collected from the spring and stored during 5 months in the laboratory (M. PASCU et al, 1984), and by geochemical computer modeling which has simulated storage temperatures as high as 50°C (A. FERU., RUXANDRA SLĂVOACĂ, 1998, I. ORĂȘEANU, 2000), have indicated a very good stability of the water chemical composition.

As a consequence of the outstandingly constant values of its physical-chemical parameters,

and of the permanent absence of any bacteriological load, Izvorul Minunilor at Stâna de Vale ranks as one of the best sources of non-carbonated natural mineral water (still water) in Romania.

Izvorul Minunilor outlet has been certified as still water in the year 1984. In the year 1990 RAMIN (SNAM) has been appointed its administrator. This company has subsequently financed the building of the present-day intake, based on the design of I. VERNESCU. During the period 2000-2001, the company European Drinks S.A. has built a 27 km long stainless steel pipe line, down to the bottling factories at Sudrigiu and Rieni. In the year 2001 the spring has been once more certified by National Agency for Mineral Resources (ANRM).



**Figure 8.** The variance density spectrum of Wonder spring (solid line) and Rampei (dotted line) springs (left). The cross correlograms between rainfall at Stâna de Vale and Wonder spring (solid line) and Rampei spring (dotted line) discharges time series (right). Data for 2001-2008 time period, ( $n = 1$ ,  $m = 125$ ).

## 4.2. Rampei spring

Rampeï spring emerges from Anisian gray dolomitic limestones, in the upper reaches of the valley that bears the same name. The spring water is clear for most part of the year, yet it violently turns into muddy during high rainfall and fast snow melt periods.

Excavations performed in the autumn of the year 2000 in order to tap the spring have outlined the presence of a wide cavern developed in dolomitic limestones, the most part of which was plugged with pebble consisting of rhyolites and of Senonian sandstones. The stream cave thus discovered has been explored on a distance of 14 m, up to a sump.

Rampeï spring is supplied by the rainfall water collected in Rampei brook upper catchment area. This water supplies the karst aquifer on the boundary between the Skythian sandstones and the dolomites, such a process being indicated by the diffuse or concentrated sinks that occur on the streamlets in the upper catchment area of Rampei stream, most of these water losses being of temporary character. The water of one such total losses has been traced with fluorescein on 16.06.1999. The tracer has reached Rampei spring 2.5 hours later, attaining the maximum concentration after 8 hours.

During the period 2001-2008, the daily average flow rates of Rampei spring have fluctuated between 1.2 l/s and 442.5 l/s, for an annual average value of 19.6 l/s. The Rampei spring water temperature has fluctuated within the range 5.1-6.8°C, with an average value of 5.3°C.

The spring water has a neutral - slightly alkaline character, a calcium bicarbonate type, and a TDS content that ranges around 170 mg/l with large fluctuations.

## 4.3. Hera (Cuciului) spring

Hera spring is the most important outlet in the upper catchment area of Nimăiești stream. It emerges from Anisian dolomites, on the median course of Cuciului brook, at 907 m elevation.

The water of Hera spring is permanently clear. Information provided by local people indicate that the water of this spring has never been seen to turn muddy. The water tastes good, renders a sensation of satiation, it does not have smell and no sediments. The chemical character of spring water is neutral-slightly alkaline (Table 2), calcium bicarbonate type with low mineral content, with TDS ranging around 140 mg/l.

The contents in terms of indicators considered as toxic substances and in terms of pesticides, as well the radioactivity of the water discharged by Hera spring range within the limits imposed by the standard of natural mineral waters (HG 1020/2005).

As a consequence of the outstandingly better qualities, the Hera source has been certified as still water in 2005 by ANRM.

## 4.4. Chemical stability of water sources

Saturation state of a water solution towards a mineral can be appreciated by comparing the solubility product value of the mineral (equilib-

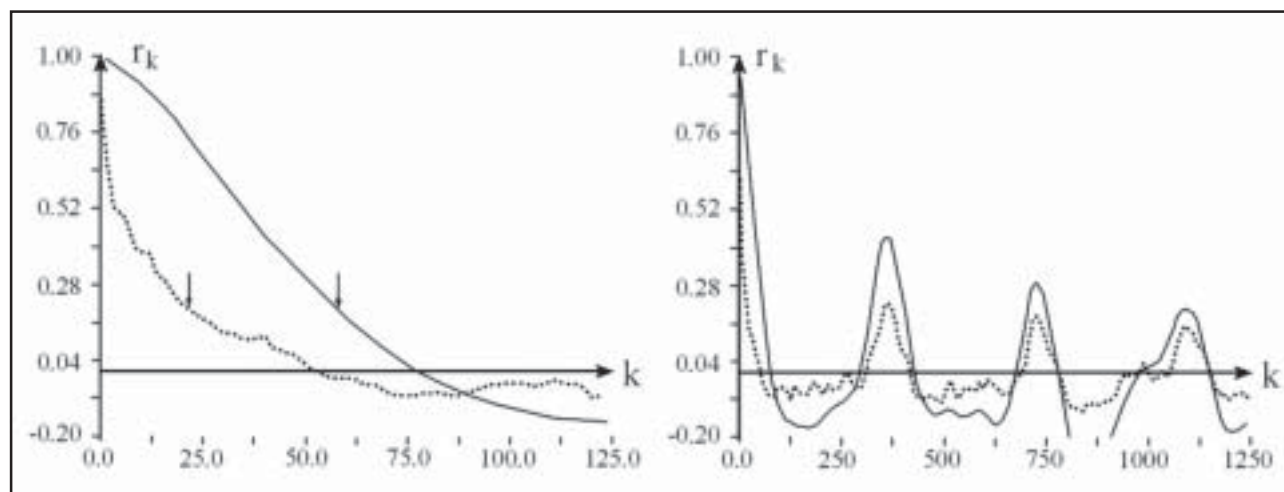


Figure 9. Short term (left;  $n = 1$ ,  $m = 125$ ) and long term (right;  $n = 10$ ,  $m = 1250$ ) correlograms of mean daily discharges series of Izvorul Minunilor (solid line) and Rampei (dotted line) springs over the period 2001-2008.

rium constant, K) with the same product of the existing ions in the water sample (IAP or Q). Saturation index (or stability ratio) has the following formula  $IS = \log(IAP/K)$ .  $IS=0$  value shows an equilibrium between the mineral and the solution, the last one is saturated towards the mineral.  $IS<0$  value describes non-saturated situations of the solution towards the mineral species, and its probability of dissolving.  $IS>0$  value shows over the limit saturation states of the solution, with a tendency of exit the mineral species from the system (C. MARIN, 1999).

The simulation of variation with the temperature of the saturation index of the Wonder spring, Hera, Pescăriei and Rampei water sources, respect to the aragonite, calcite and dolomite, made with the help of the program WATEQ (Truesdel, Johnes, 1973) shows that these have negative values for the interval of temperatures between 0 and 50°C, and the minerals mentioned don't have tendencies of crystallization (I. ORĂȘEANU, 2000). In Figure 10 we present the temperature variation of the saturation index respect to the calcite (c) and aragonite (a).

During a year, the chemical composition and the quantity of mineral species dissolved in the water of some natural sources changes. During the periods with high flow, the waters of these sources are less mineralized and less saturated respect to other mineral species, while during recession periods, characterized by longer values of time of water residence in the underground, the quantity of dissolved minerals augments, and some of these may crystallize. These evolutions are better shown off by calculating the saturation values for samples thaken and analyzed monthly.

The water of Hera, Wonder spring, Pescăriei and Rampei water sources is very unsaturated re-



spect to these minerals during the whole period of investigation, the apparition of crystallization phenomena of the mentioned minerals being excluded (Fig. 11).

## Conclusions

The geological-structural setting of Stâna de Vale area, with carbonate deposits embedded in a "mosaic" next to other sedimentary deposits (sandstones, marls, shales, conglomerates) and igneous rocks (rhyolites, tonalites, etc.), have created an outstandingly favorable substratum in terms of very good quality water aquifers. By adding to this the favorable opportunity of a basement including an established reservoir rock, the limestones, highly efficient in transmissive terms and less in storage terms, and of an overlying aquifer, potentially efficient in storage terms, yet not very conductive, the Senonian deposits and the Vlădeasa rhyolites, we get the picture of the retort where the wonder water of Izvorul Minunilor was elaborated.

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Spring	T mean °C	Cv	ME, days	RT, days	TF	a
Rampei	5.3	0.7	22	21.5	0.204	0.017-0.026
Hera	7.2	0.4	35	31.2	0.088	0.035
Pescăriei	5.7	0.5	42	47.6	0.092	0.005-0.013
Minunilor	5.9	0.25	58	64.3	0.028	0.008-0.01

Cv - index of discharge time series variability, ME - memory effect, RT - regulation time, TF - truncation frequency, a - recession coefficient

**Table 1. Main characteristics of discharge time series of springs in Stâna de Vale area in 2001-2008 time period.**



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Spring	t	ph	Cl	NO <sub>2</sub>	NO <sub>3</sub>	SO <sub>3</sub>	HCO <sub>3</sub>	Na	K	Ca	Mg	DR	DT	TDS
	°C		ppm										°ger	ppm
Izvorul Minunilor		7.6	8	0.02	3.9	27.3	122	1.1	0.8	22	4.9	80	3.9	
Pescăriei	5.4	7.67	3.5	0	1.7	0	122	0.8	0.4	28.1	8.5	140.8	5.9	202.8
Rampeii	5.2	7.81	3.5	0	2.7	0	109.8	0.4	0.4	20.0	10.	125.7	5.3	172.3
Cuciului	6.5	7.98	3.5	0	2.7	0	73.2	0.6	0.5	26.1	0.0	101.8	3.6	136.4
Tunnel, m. 900	7.4	6.2	1.8	0	0	19.1	27.21	0.7	0.8	9.9	2.7	61	2	92.0
Podu Cuciului, no. 10	9.2	7.1	3.5	0	0	0	106.2	0	0.2	33.1	2.3	93.5	5.2	166.9
Fântâna Galbenă, no.8	6.0	3.64	3.5	0	0	sld	11.6	0	0.4	5.2	0.2	15.6	0.8	36.1
Izvorul Rece	5.0	4.39	1.8	0	0.1	2.4	6.1	0	0	4.0	0.0	15.7	0.6	35.1
Ob. p. Cuciului, no. 9			3.5	0	0.6	9.6	20.7	1.6	1.1	8.6	0.0	45.7	1.2	110.3
Izvorul Nou, no. 11	8.6	7.5	3.5	0	0	0	146.4	0	0	38.0	7.3	158	7	214.5

**Table 2. Chemical composition of sources in Stâna de Vale area (Fe) is absent in all analyses).**

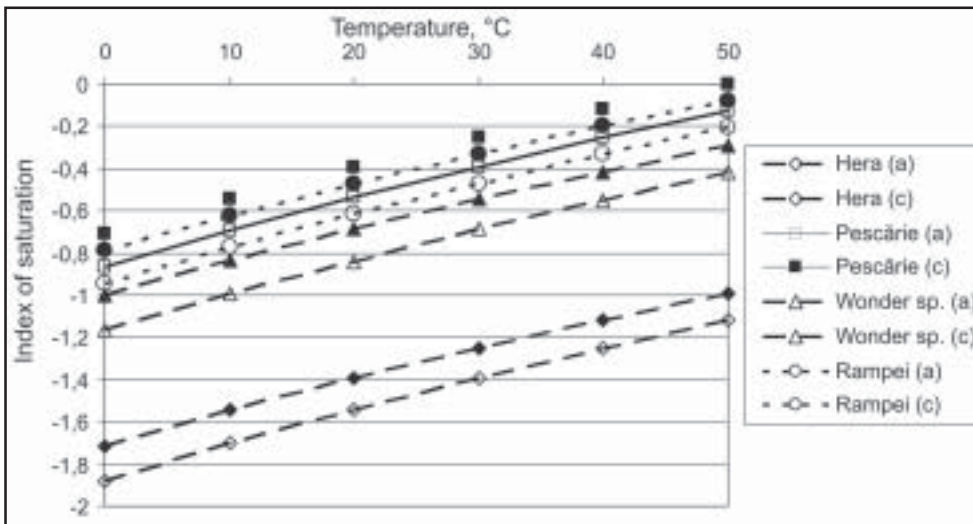


Figure 10. The temperature variation of the saturation index respect to the calcite (c) and aragonite (a) for Hera, Wonder spring, Pescăriei and Rampei water sources.

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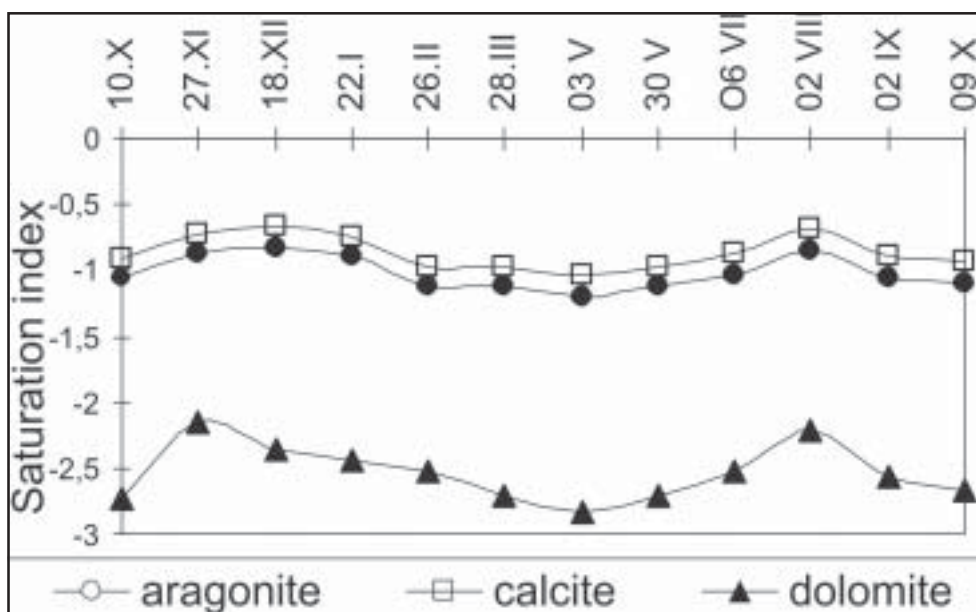


Figure 11. The monthly fluctuation of the saturation index values respect to the aragonite, calcite and dolomite, of the Hera source, between October 1997- October 1998.