DECIPHERING HYDROCHEMICAL INFORMATION PROVIDED BY SALINE SPRINGS IN THE CARPATHIANS BEND AREA: NO STRONG VRANCEA EARTHQUAKE EXPECTED TO OCCUR EARLIER THAN 2012

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Abstract. Several natural groundwater discharges in Vrancea seismic area were inferred to originate in the mixing between two distinct end-members: seasonally variable inflows of meteoric freshwater, and deep-origin saline fluids of a remarkably constant composition. However, prior to two rather strong Vrancea earthquakes (mb = 5.8 and 5.3 respectively), the composition of the saline end-members appeared to significantly change as well. The approximate durations of the corresponding anomalous precursory periods, of 18 months and 10 months respectively, were apparently directly correlated to the magnitudes of the ensuing earthquakes. Consequently, it has been assumed that an earthquake of magnitude 5.8 or larger was expected to occur no earlier than 18 months after a last series of "un-perturbed" samples; in particular, since the concerned springs samples collected on May 2010 exhibited no abnormal signatures, it seems unlikely that a strong Vrancea earthquake would occur sooner than 2012.

Key words: earthquake, precursor, groundwater, hydrochemical monitoring, saline spring, Vrancea

1. INTRODUCTION

There is an increasing number of reports (Tsunogai and Wakita, 1995; Toutain *et al.*, 1997; Yechieli and Bein, 2002; Skelton *et al.*, 2008; Liu *et al.*, 2010) about groundwater discharges which displayed unambiguous fluctuations of certain dissolved constituents before strong earthquakes. Nevertheless, mechanisms connecting phenomena occurring at focal depth with hydrochemical precursors recorded at ground surface continue to remain largely unknown.

Vrancea seismic area, at the Carpathians arc bend (Romania), is in principle outstandingly favorable for testing the usefulness of various hydrochemical parameters as earthquake precursors. Strong earthquakes (*mb* > 6) in that region are rather frequent, although their recurrence pattern is highly unpredictable. Alternatively, the corresponding seismogenic volume is quite narrowly confined (30 x 70 km lateral extent, 70-180 km depth range), therefore earthquake-forecast studies in that area are spared the question "*where?*", needing to answer instead only the questions "*when?*" and "*how strong?*".

The earliest attempt to detect hydrochemical signals related to the Vrancea earthquakes (Hartmann *et al.*, 2005) addressed a water-well at Turia, some 40 km outside the epicentral area. No connections were found between single hydrochemical signals and any of the Vrancea earthquakes - up to *mb* = 5.1 in magnitude - recorded during the monitoring time interval (1997-1999). Yet according to the complex statistical procedure developed by the authors, the analysed water significantly reacted to the *totality* of seismotectonic events which occurred during that period within distances up to 400 km away from the sampling point.

A more recent monitoring operation (launched in 2003) addressed saline springs at Slănic Moldova, some 35 km outside the epicentral area margin, and at Lepşa, near the middle of the epicentral domain (Fig. 1). The occurrence of only one strong Vrancea earthquake (*mb* = 5.8) during the time-interval 2003-2009 provided an unambiguous reference-moment for clearly distinguishing between pre-seismic and post-seismic periods. The above-indicated strong earthquake, on October 27, 2004, has been preceded by a persistent, more than 18 months long hydrochemical signature which was extensively documented in a spring ("No. 1 bis") at Slănic Moldova (Mitrofan *et al*., 2008; 2010).

The earthquake-forecasting ability of the considered saline springs in the Carpathians bend area is further explored in the present paper by taking into account a series of additional issues: the relatively recent occurrence, on April 25, 2009 of another significant, yet slightly weaker Vrancea earthquake (*mb* = 5.3), and the role that seasonal meteo-hydrological fluctuations might actually play in outlining the genuine seismotectonically-induced signals.

2. GEOLOGICAL FRAMEWORK

The focal region of the Vrancea earthquakes (Fig. 1) underlies a complex pile of nappes which consist of northward-trending successions of Cretaceous-Neogene flysch deposits. The emplacement of the nappes took place during the Miocene, in response to the subduction and the continental collision between the stable East European and Moesian foreland units, and the Alcapa and Tisia–Dacia intra-Carpathian microplates (Maţenco and Bertotti, 2000).

Simultaneously, at the western margin of the fold-and-thrust belt a subduction-related volcanic chain (Călimani-Gurghiu-Harghita) was developing. Igneous activity migrated in time along that chain from north to south (Pecskay *et al.*, 1995), to fade out only as recent as a few tens of thousands of years. The last active volcano was Ciomadul (in the South-Harghita mountains), positioned fairly close to the springs monitored at Slănic Moldova and at Lepşa (about 45, and 60 km respectively).

A mechanical strength transition boundary between the East-European/Scythian and the Moesian Platforms is delineated by a NNW–SSE oriented system of regional crustal-scale fractures (Peceneaga-Camena fault, Trotuş fault), which to a certain extent are presently still active (Cloetingh *et al.*, 2005).

The actual seismogenic volume of the Vrancea earthquakes corresponds to a sub-vertical lithospheric body, which is outlined by high seismic velocities. There are controversial opinions (e.g. Knapp *et al.*, 2005) concerning the relationships which exist between the previously discussed shallow geological structures and that deep lithospheric body.

3. GENERAL HYDROGEOLOGICAL FEATURES

A series of relevant characteristics of the saline springs at Slănic Moldova have been highlighted by a quite early hydrogeological study, which was conducted by Tschermak (1880):

- significant depth of origin has been assumed for those springs, by taking into account their water-temperatures, which exceeded by a few degrees Celsius the local average air-temperature; yet mixing with cold meteoric waters, and conductive cooling processes occurring during the fluid up-flow prevented a more precise assessment of the actual depth of origin values;
- all the saline springs were inferred to be supplied by a common, deep-origin end-member; the latter was subject to variable degrees of dilution, which were controlled by the actual amounts of meteoric freshwater that reached the up-flow path of each specific spring;
- the presence of a significant CO_2 gas phase was inferred to reveal a direct connection with a magma-body still subject to active degassing.

A more recent, extended and - inherently - more modern approach concerning the Carpathians bend area mineral water geochemistry has been provided by a study of Vaselli *et al.* (2002). The corresponding sampling domain consisted of a large section of the Carpathian flysch units, including also the highly seismic Vrancea region. Within that broad area, a large number of mineral waters, often associated with a gas phase (mostly CO_2 and H_2S, and only occasionally CH_4), discharge mainly along the volcanic-flysch borders and along the contacts between the overlapping nappes.

Among the multitude of groundwater outlets sampled by Vaselli *et al.* (2002) within the fold-and-thrust belt area, the discharges at Slănic Moldova were still the only ones to display a considerable amount of mantle-derived ^3He, which was detected in the gas samples associated to the saline fluids. The deep (regional) Trotuş and Peceneaga-Camena faults presumably favored access to the surface of those deep-seated waters, whose origin should be non-meteoric. The latter inference was supported by a noticeable O^{18} isotope enrichment relative to local meteoric waters, and by Na-K-Mg geothermometry diagnoses which indicated that the concerned saline waters were fairly "mature" and had been subject to deep-equilibration temperatures in excess of 150°C (Vaselli *et al.*, 2002).

4. MATERIALS AND METHODS

The geochemical monitoring of the two considered springs at Slănic Moldova locally designated as No. 1 bis and No. 10 began in April 2003. Water samples have been collected approximately once a month. Sampling frequency has been increased up to one series of samples per day during the two months that followed the significant Vrancea earthquake (*mb* = 5.8) of October 27, 2004. A total of 83 series of samples have been collected until May 2010.

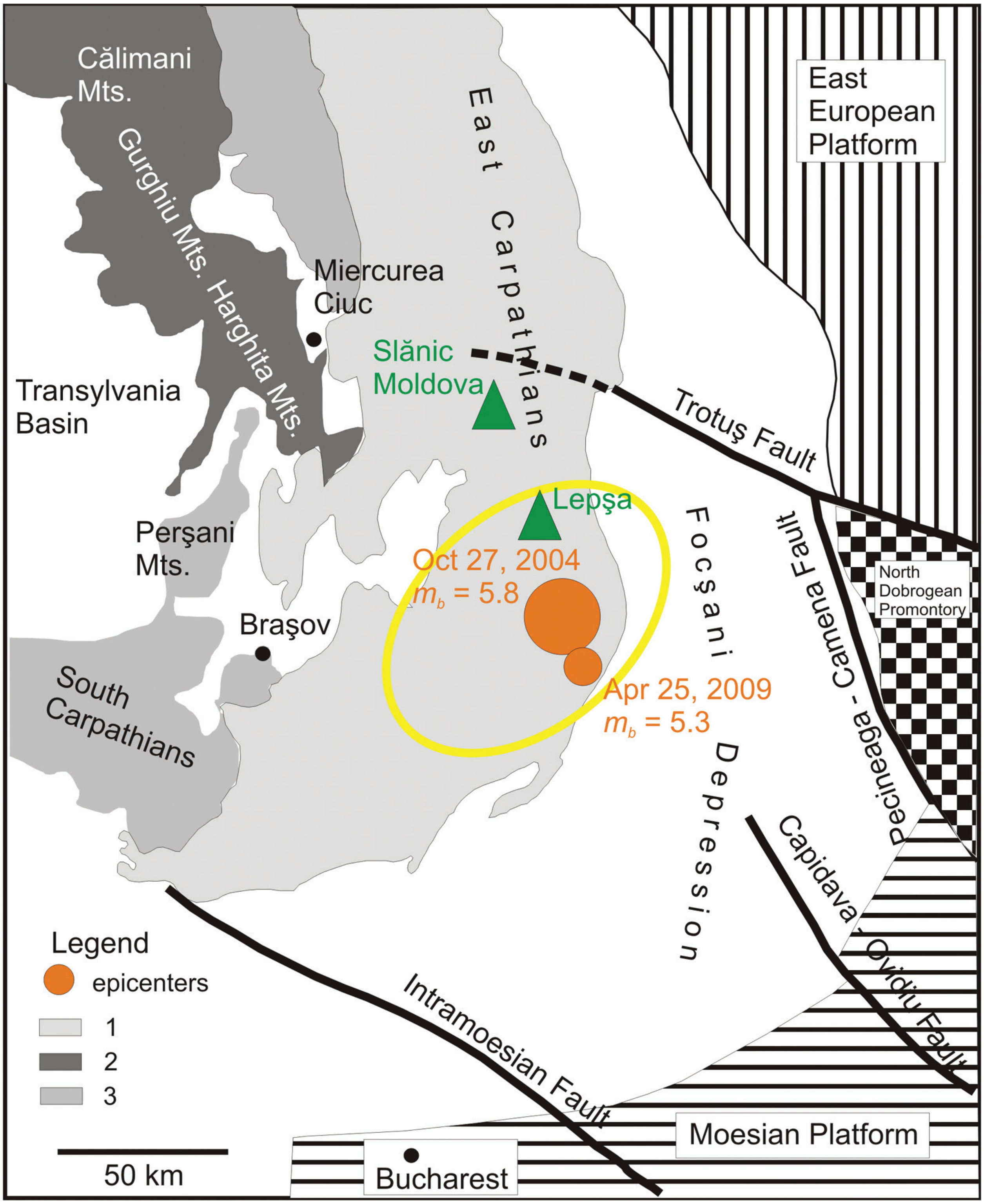


Fig. 1 Sketch map indicating the epicentral area of the strong, intermediate-depth Vrancea earthquakes (the yellow oval line) and the location of the hydrochemical monitoring sites at Slănic Moldova and Lepşa (the green triangles). Orange dots indicate the epicenters of the strongest Vrancea earthquakes occurred during the monitoring operation. Geological background after Dumitrescu and Săndulescu (1970): **1** - East Carpathians Cretaceous–Tertiary nappe system; **2** - Neogene-Quaternary volcanic arch; **3** - Crystalline basement and its Mesozoic cover (modified after Panaiotu *et al.*, 2007)

At the Sulfur spring of Lepşa, no systematic geochemical monitoring was initiated earlier than November 2006. Subsequently, groundwater sampling has been performed approximately once a month. A total of 33 samples were collected between November 2006 and May 2010, two additional samples having been collected on previous isolated occasions, in July 2003 and June 2004 respectively.

The laboratory of the Institute of Speleology „Emil Racovitza" of the Romanian Academy has performed the chemical analyses (pH, conductivity, TDS, major cations and anions) of all the collected samples.

The present study aimed to investigate whether, besides seasonal fluctuations, seismically-related signatures could also be detected in the hydrochemical time-series recorded at the Slănic Moldova springs, in the form of long-term evolution trends. Therefore, the spikes existing in the Cl^-, Na^+, K^+ and Mg^{2+} raw-concentration time-series have been smoothed, by using a running average algorithm previously described by Mitrofan *et al.* (2008; 2010). The obtained results are illustrated in Fig. 2.

In the case of the Sulfur spring of Lepşa, just the raw-data evolutions are illustrated (Fig. 3). The rationale for this approach is that, obviously, only such raw-data were unequivocally suitable for being compared with the isolated, pre-seismic values obtained in 2003 and 2004.

The seismic events potentially relevant in terms of earthquake-related hydrochemical signals have been retrieved from the Harvard CMT catalog (available at http://www.globalcmt.org/). Specifically, during the concerned time-interval, only 3 events with body-waves magnitudes $mb > 5$ have occurred in the Vrancea area. Since the weakest of those 3 events ($mb = 5.1$, on May 14, 2005) appeared to display no hydrochemical signature, our further interpretations have considered only the October 27, 2004 ($mb = 5.8$) and the April 25, 2009 ($mb = 5.3$) earthquakes (Fig. 1). For each of those two latter events, the computed focal depths were approximately 100 km.

The subsequent processing step has been to separately address the Cl^- anion, which is considered a quite robust indicator of the saline-water/fresh-water mixing regime (Tsunogai and Wakita, 1995; Toutain *et al*., 1997, 2006). Figs. 2 and 3 indicate that, for the monitored springs, the Cl^- concentration variations display no obvious seismotectonically-related deviations, being instead modulated essentially by seasonal, meteorically-induced processes.

Simultaneously with the Cl^- anion evolutions, each of the Na^+, K^+ and Mg^{2+} cations time-series have been plotted, by using appropriate scales (Figs. 2 and 3). In the resulting diagrams, the periods when cations variations closely followed the meteo-hydrologically controlled fluctuations of the Cl^- anion are readily discernible from other periods, when certain cations displayed notable long-term deviations, assumedly related to the Vrancea seismogenetic processes.

5. RESULTS AND DISCUSSION

5.1. Delineation of specific features associated to the monitored springs

All the monitored springs share several common characteristics: they are cold (9-10°C on the average), H_2S-rich, and they discharge NaCl type water of rather high concentration. Their average TDS values are comparable as well (11 and 9 g/kg respectively for the springs No. 1 bis and No. 10 of Slănic Moldova, as compared to about 7 g/kg for the Sulfur spring of Lepşa). However, the corresponding TDS fluctuation ranges (expressed as standard deviations normalized against the averages) are highly contrasting: 50 % at Lepşa, against only 2-3 % at Slănic Moldova.

Another significant difference derives from the recorded B/Cl^- mass-ratios. The 0.002 average B/Cl^- value computed in the case of the Sulfur spring at Lepşa is characteristic for a fossil water of marine origin. Alternatively, both monitored springs at Slănic Moldova display average values which are almost one order of magnitude higher (0.014). The boron enrichment thus suggested for the Slănic Moldova springs may be a result of direct magmatic volatile inputs (Arnórsson and Andrésdóttir, 1995; Foustoukos *et al.*, 2004). This interpretation is further substantiated by the fact that the springs at Slănic Moldova contain significant amounts of CO_2, a gas associated to ongoing magma degassing, and which on the other hand is virtually absent in the Sulfur spring of Lepşa.

5.2. Seasonal versus earthquake-related fluctuations of the chemical constituents

As previously mentioned, both at Slănic Moldova and Lepşa the monitored springs discharge high-concentration water of sodium chloride type, which comes from large depth. Close to the ground surface, this concentrated, deep-origin fluid is diluted by low-mineralized meteoric water. As the intensity of the meteoric influx has time fluctuations, seasonal variations of the main anion (Cl^-) and of the main cations (Na^+, K^+, Mg^{2+}) are recorded in the spring water.

In fact, attempting to document possibly existing correlations between rainfall and the ion concentration variations of a spring-water proves to be, in most instances, quite awkward: not only is the interplay between precipitation, runoff, evapo-transpiration, snow-melt and the amount of groundwater existing in the soil extremely intricate (see, for instance Toutain *et al.*, 2006), but also the surface-infiltration area associated to the concerned spring may occur tens of kilometers away from the nearest meteorological station - hence even the rainfall data utilized as input may be quite inadequate. Daily-rainfall data collected by a meteorological station operating at Slănic Moldova were available, although only between June 2005 and September 2007.

Relying on those records, the total amount of precipitation fallen between two consecutive hydrochemical sampling dates has been divided by the corresponding time-

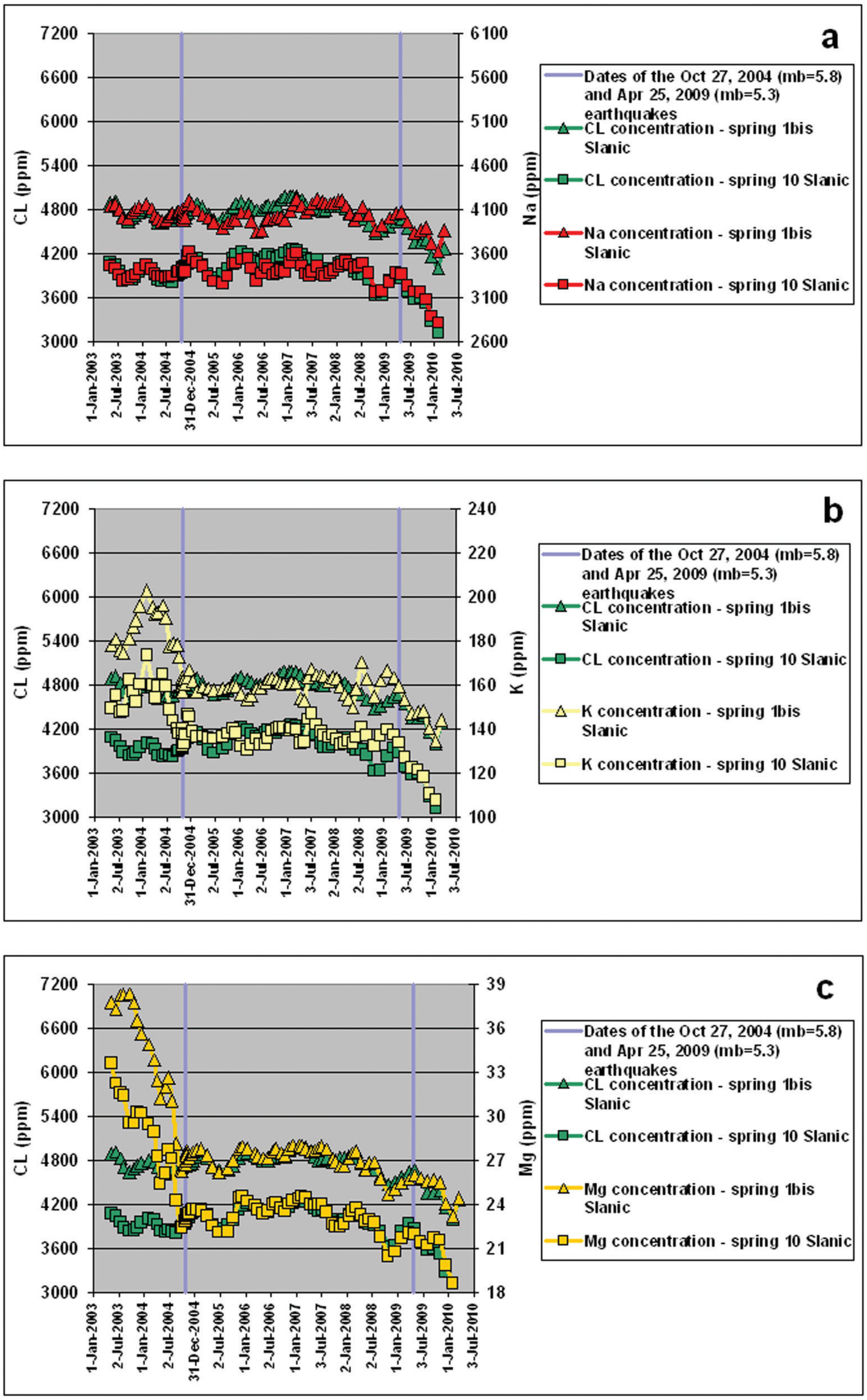


Fig. 2 Springs No. 1 bis and No. 10 of Slănic Moldova. Time-series of the averaged concentrations of the main anion (Cl^-), appropriately plotted in correlation with the time-series of the averaged concentrations of the main cations: Na^+ (**a**); K^+ (**b**); Mg^{2+} (**c**). The blue vertical bars indicate the strongest Vrancea earthquakes having occurred during the monitoring operation.

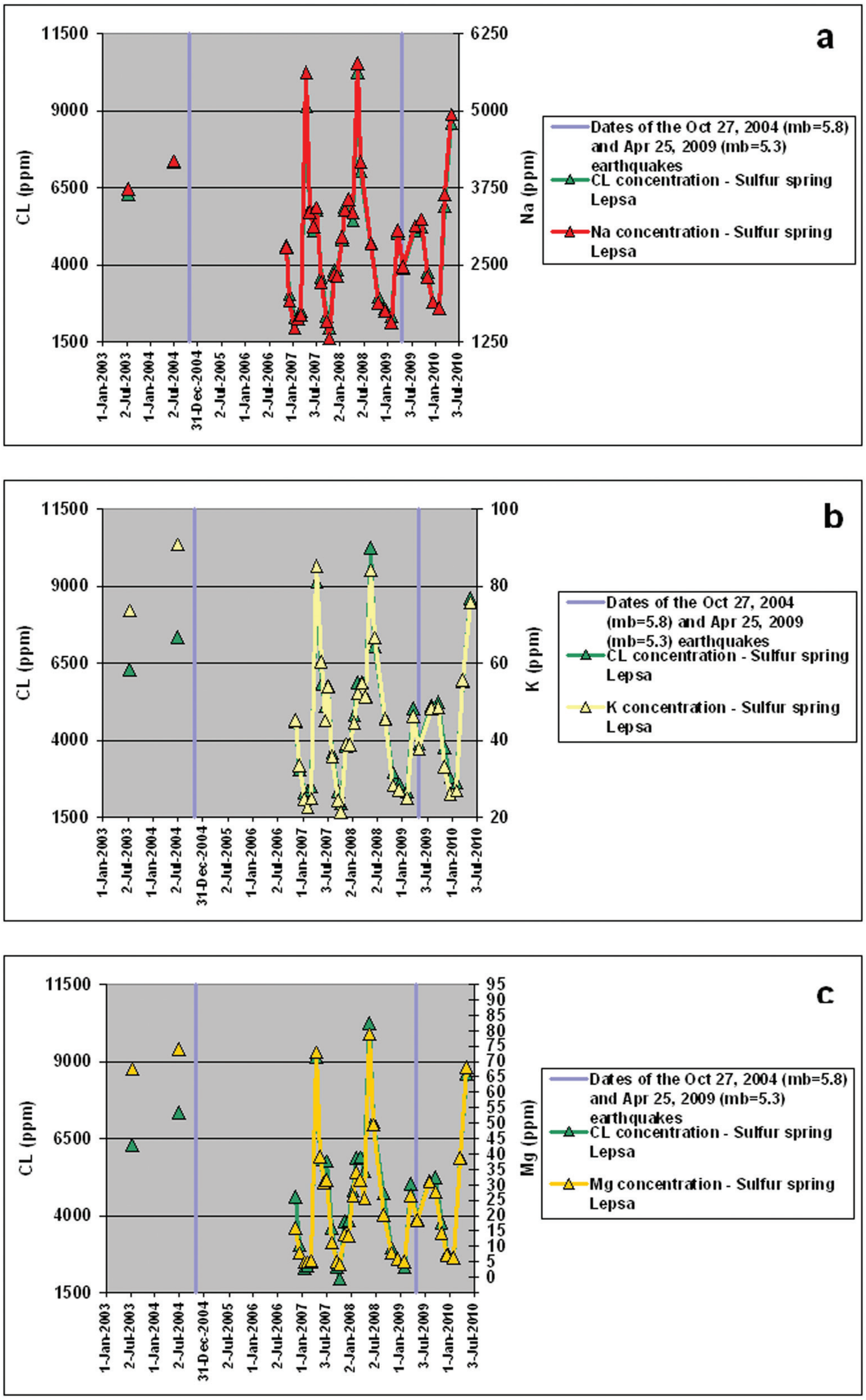


Fig. 3 The Sulfur spring of Lepşa. Time-series of the actually recorded concentrations of the main anion (Cl^-), appropriately plotted in correlation with the time-series of the actually recorded concentrations of the main cations: Na^+ (**a**); K^+ (**b**); Mg^{2+} (**c**). The blue vertical bars indicate the strongest Vrancea earthquakes having occurred during the monitoring operation.

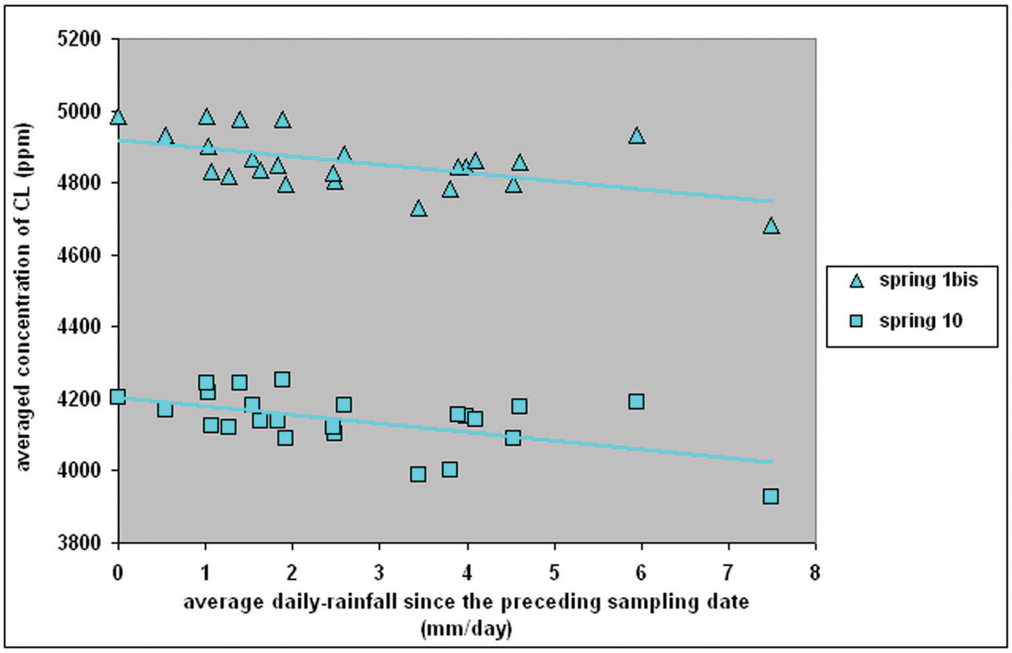


Fig. 4 Averaged concentrations of Cl^- in spring-water samples of Slănic Moldova, plotted against the average daily-amount of precipitation occurred between the current sampling date and the previous one. (Rainfall data are derived from local records which covered the time-interval between June 2005 and September 2007). The overall trend suggested by the regression lines is in agreement with the general correlation anticipated to exist between the amount of precipitation fallen during a certain period, and the subsequent spring-water dilution.

interval, to obtain the *"average daily-amount of precipitation occurred between two sampling dates"*. In Fig. 4, this *"average daily-amount of precipitation occurred since the preceding sampling date"* was used as a parameter against which the current *"averaged concentration of Cl^-"* (computed for each sample collected at Slănic Moldova) has been plotted. One would anticipate that periods subject to a heavier average daily-rainfall corresponded to smaller average concentrations of Cl^-, and vice-versa. However, while a rather general compliance with this kind of prediction is indeed noticeable in Fig. 4, it also appears that a detailed correlation with rainfall data is hard to invoke when ascribing a seasonal character to the Cl^- fluctuations. The explanation for this fact must derive from the previously mentioned complex relationships existing between rainfall and the ensuing dilution of a spring-water.

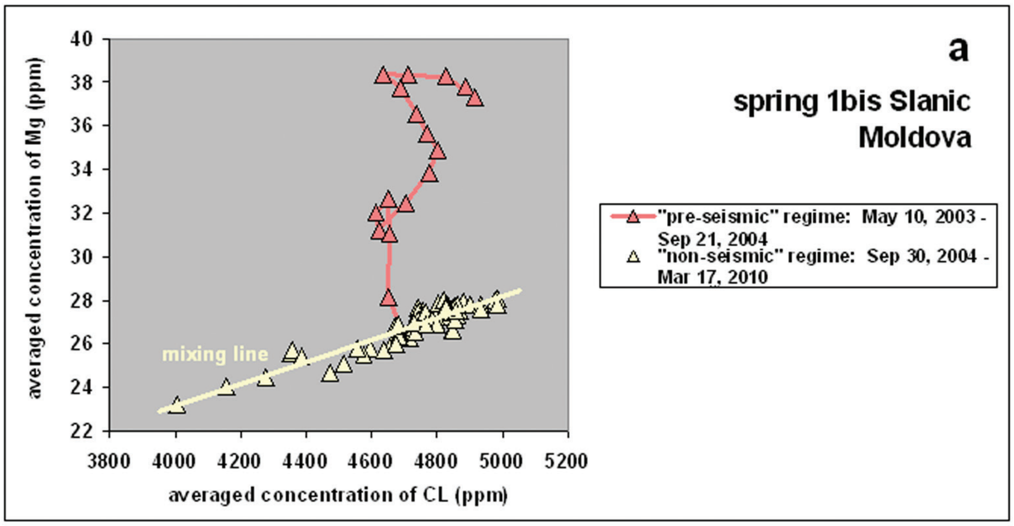
Consequently, no further attempt was made to extend the above-indicated rainfall data processing methodology also to the Sulfur spring of Lepşa - for which, anyway, no data provided by an analogous, closely operating rainfall-gauging station were available.

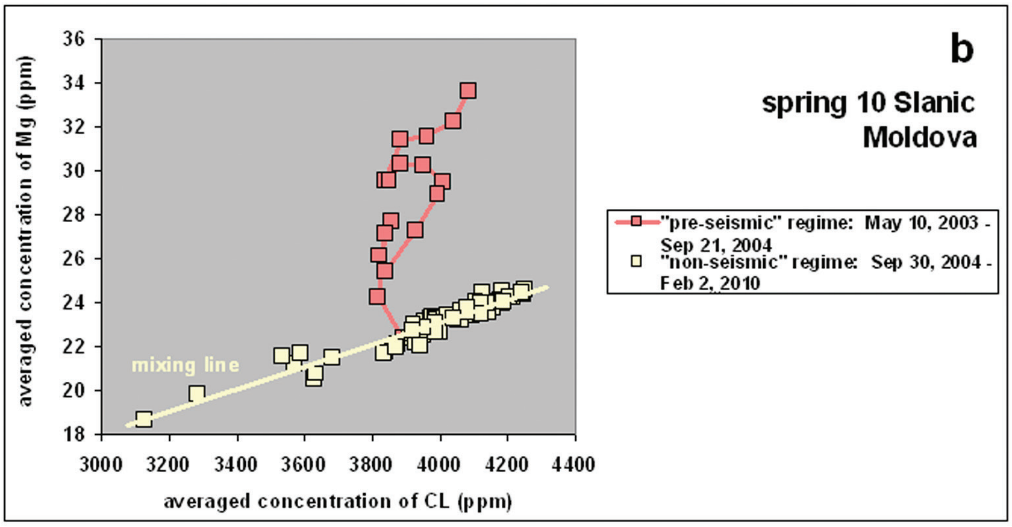
The seasonal variations of the various main ions are usually concordant in the non-seismic periods (Figs. 2 and 3). This shows that the deep-origin water usually keeps a stable composition in time and that, in such periods, the concentration fluctuations of the springs are induced, practically, only by the fluctuations of meteoric water influxes.

Yet occasionally, the Mg^{2+} and K^+ cations concentration of the Slănic Moldova springs No. 1 bis and No. 10 exhibited variations which severely deviated with respect to the "reference baseline" provided by the seasonal fluctuations of the Cl^- anion (Figs. 2b and 2c). The observed „abnormal" behavior extended during a quite long time-period, around 18 months. It is important to remark that this period preceded the October 27, 2004 Vrancea earthquake (*mb* = 5.8), ending shortly before the actual occurrence of that seismic event. In the case of the K^+ ion, a less ample perturbation seems to have occurred also in the interval July 2008 – April 2009, that is exactly before the second largest Vrancea earthquake (*mb* = 5.3, on April 25, 2009) of the monitoring period.

The deviations exhibited by the Mg^{2+} and K^+ cations variations with respect to fluctuations undergone by the Cl^- anion clearly indicate that during the corresponding time periods, significant changes came up also in the composition of the highly concentrated, deep-origin water.

Similarly, during a "non-seismic" period (November 2006 – May 2010), the Sulfur spring of Lepşa (Fig. 3) shows fluctuations of the main cations (Na^+, K^+, Mg^{2+}) that are in agreement to the ones of the main anion (Cl^-). For this spring, the mentioned period has been appreciated as non-seismic (even if an earthquake with *mb* = 5.3 occurred in Vrancea on April 25, 2009) by comparison to the period that preceded the *mb* = 5.8 Vrancea earthquake of October 27, 2004.





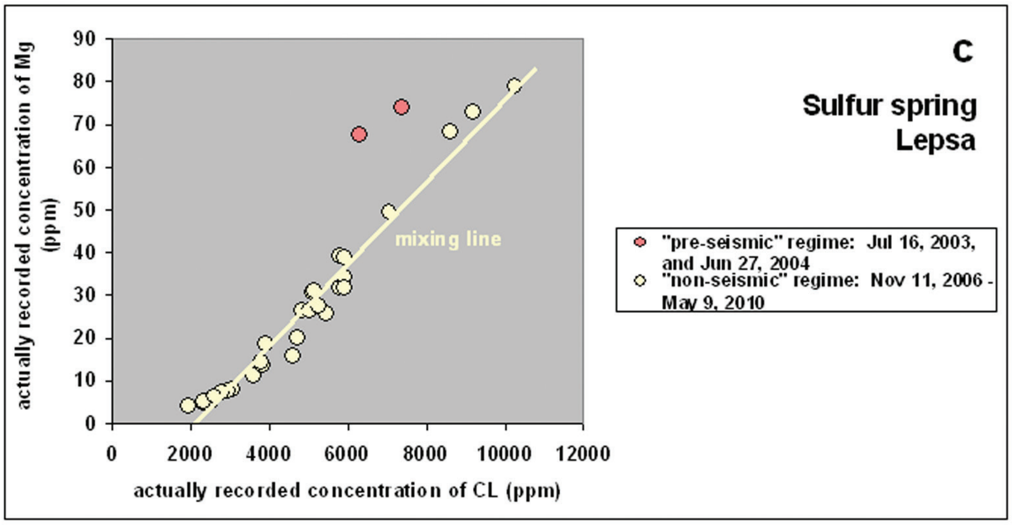


Fig. 5 Plots of Mg^{2+} versus Cl^{-} for the springs monitored at: **a**, **b** - Slănic Moldova; **c** - Lepşa.

Taking this into account, it can be noticed that the concentrations of the Mg^{2+} and K^+ ions in the two samples collected from the Sulfur spring of Lepşa before the indicated October 27, 2004, earthquake are much higher than they should have been if the compliance with the Cl^- ion variations had still been obeyed (Fig. 3b; 3c).

The contrasting behavior between non-seismic and pre-seismic periods becomes even more conspicuous when cation concentrations are directly plotted against the concentration of Cl^-. For instance, in the Mg^{2+} vs. Cl^- plots (Fig. 5), it can be noticed that the data-points corresponding to samples collected during a "non-seismic" period are rather tightly aligned. Such lineaments - which are a well-known signature of mixing between two distinct fluids of virtually constant composition - are noticeable both in the case of the Slănic Moldova springs (Figs. 5a and 5b), and in that of the Sulfur spring of Lepşa (Fig. 5c). Alternatively, most data-points belonging to the time-interval which preceded the October 27, 2004, earthquake plot far away from the indicated "mixing lines". The latter circumstance suggests that during the considered "pre-seismic" stage, processes other than mixing intervene to additionally control the Mg^{2+} concentration variations. In the case of the K^+ vs. Cl^- diagrams (not shown), a largely analogous behavior has been observed.

It results that, also in terms of the K^+ and Mg^{2+} behavior exhibited during "pre-seismic" periods, a reasonable similarity is noticeable between the Sulfur spring of Lepşa on the one hand (Figs. 3b, 3c and 5c), and the Slănic Moldova springs No. 1 bis and No. 10 on the other (Figs. 2b, 2c and 5a, 5b). Consequently, it seems that comparable hydrochemical precursory phenomena associated to the October 27, 2004, Vrancea earthquake had been affecting a quite widespread territory, which included both the sampling site at Lepşa, and the one at Slănic Moldova (Fig. 1).

Although different, the behavior displayed by the Na^+ cation (Figs. 2a and 3a) is still noteworthy: Na^+ continues to follow, even during "pre-seismic" periods, the meteorologically-induced fluctuations of the Cl^- cation. It is thus suggested that the Na^+ concentration of the deep-origin fluid component remains virtually unchanged at all times. By taking into account, on the other hand, the large pre-seismic deviations undergone by the K^+ and Mg^{2+} cation concentrations, it results that the ratios of the three considered cations (Na^+, K^+ and Mg^{2+}) varied greatly during an earthquake-preparation stage. The latter circumstance suggests that, in terms of certain specific water-rock interactions, important contemporary modifications occurred. It is however beyond the scope of the present paper to consider in further detail the actual mechanisms which might possibly control the major cations distribution in the concerned spring-waters.

5.3. Inferences concerning the next occurrence of a strong Vrancea earthquake

Taking into account the anomalous behavior of the K^+ ion observed in the Slănic Moldova springs before the two indicated Vrancea earthquakes, which are the strongest of the hydrochemical monitoring period, one can notice obvious differences (Fig. 2b). Thus, the abnormal behavior duration was about 18 months for the earthquake of October 27, 2004 (*mb* = 5.8) and about 10 months for the earthquake of April 25, 2004 (*mb* = 5.3). By comparing the durations of anomalous behavior with the magnitudes, one can make a preliminary assumption that the stronger the Vrancea earthquake is, the longer is the duration of the hydrochemical abnormal behavior which precedes it. Relying on such an inference, and taking into account that in May 2010 no abnormal behavior was noticed for any of the monitored springs, it seems unlikely that a stronger earthquake, or at least similar to the one of October 27, 2004, may occur in Vrancea sooner than 18 months, that is before 2012.

6. CONCLUSIONS

Over the time-interval 2003-2010 a hydrochemical monitoring operation has been conducted on several saline springs in the Vrancea seismic area. As a result, it was ascertained that significant fluctuations in the Cl^- anion concentrations occurred only in response to dilution phenomena induced by meteoric water infiltration. The observed seasonal evolution of the Cl^- anion thus provided an appropriate "reference baseline", against which the evolutions of the main cations Na^+, K^+ and Mg^{2+} could be evaluated as well.

During non-seismic periods, the indicated cations fluctuations closely followed those of the Cl^- anion. This setting suggested a remarkably constant composition for the hypothetical, highly concentrated saline end-member which was presumably involved in the mixing with variable amounts of diluted meteoric water.

Alternatively, prior to the two strongest Vrancea earthquakes of the monitoring period (*mb* = 5.8 and 5.3 respectively), the K^+ and Mg^{2+} cations evolutions significantly departed from the Cl^- "reference baseline". Hence significant changes came up, under those particular circumstances, also in the composition of the highly concentrated, deep-origin end-member.

The approximate precursory durations of the two indicated "anomalous" periods, of 18 months and 10 months respectively, appear to be directly correlated to the corresponding earthquake magnitudes. Consequently, it was assumed that an earthquake of magnitude 5.8 or larger is expected to occur no earlier than 18 months after a last series of "un-perturbed" samples. In particular, since the concerned springs samples collected on May 2010 exhibited no abnormal signatures, it seems unlikely that a strong Vrancea earthquake would occur sooner than 2012.

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