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Variations in the Cl, SO_4, δD and $\delta^{18}O$ in Water from Thermal Springs near Acapulco, Guerrero, Mexico, Related to Seismic Activity

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ABSTRACT

Chemical and isotopic analyses of waters from 4 thermal springs of the Guerrero Pacific coast, the most seismically active area in Mexico, were weekly performed during a period of 1.5 years (October 2002 - March 2004). Within the same time interval more than 150 earthquakes with $3.5 < M < 5.3$ occurred in the area. The data display several anomalies in Cl, SO_4, δD and $\delta^{18}O$, always immediately after an event, with a relaxation time of 3 - 4 weeks. The responses occurred only with earthquakes having an estimated epicentral site very close or almost coincident with the location of a spring. These results indicate that: 1) at least for earthquakes with $M < 5.3$ within the Guerrero "seismic gap" there were no precursors in the chemical (ionic) and isotopic composition of thermal waters (on the weekly basis); 2) two groups of springs near Acapulco, Dos Arroyos and Paso Real, are sensitive to seismic activity and therefore further monitoring of these springs may help to unravel the mechanisms of the "hydro-seismo-interaction" in the area.

(Key words: Thermal springs, Geochemistry, Seismic activity, Mexico)

1. INTRODUCTION

The search of short-term precursors of earthquakes has been mostly concerned with gases (e.g., King 1986; Thomas 1988; Igarashi and Wakita 1990; Toutain and Baubron 1999; Chyi et al. 2005; Walia et al. 2005; Yang et al. 2005). Among unambiguous precursory changes in

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the chemistry (ionic composition) of mineral springs there were only few convincing examples. In two studies the authors used commercial bottled drinking and mineral waters and covered a period before and after the major 1995 Kobe earthquake (Tsunogai and Wakita 1995), and a M = 5.2 Pyrenean earthquake (Toutain et al. 1997; Poitrasson et al. 1999). The source of water analyzed after the Kobe earthquake was a 100 m-deep well located about 20 km east of the epicenter. Toutain et al. (1997) analyzed the bottled water from a mineral spring located 29 km from the epicenter. In both cases an increase in Cl concentration before the earthquake was observed. The anomalies started about 5 months before the M = 7.2 Kobe event and about 5 days before the M = 5.2 Pyrenean earthquake. Both effects were caused by the stress-strain induced mixing of waters from adjacent aquifers. Biagi et al. (2000) have demonstrated a strong negative (dilution) anomaly in the ionic composition of water from a deep, drainless well, 4 month before the M = 6.9, shallow Karymsky earthquake that occurred in Kamchatka, Russia, in January 1996, 100 km from the well.

The Pacific coast of the Guerrero state, Mexico, is characterized by very high seismic activity related mainly to the subduction of the Cocos oceanic plate under the North America continent. The Mid American Trench here is close to the shoreline and therefore most of the epicenters of the subduction induced earthquakes cluster on the continent close to the Pacific coast. The coast of Guerrero includes the Guerrero "seismic gap" (Singh and Mortera 1993) to the NW of Acapulco (Costa Grande), where the most recent large (M = 7.6) earthquake occurred in 1911. After that only a few M~6 events have occurred in this area, therefore, the next major interplate earthquake in this part of Guerrero could have moment magnitude > 8 (Suarez et al. 1990). To the SE of Acapulco (Costa Chica) the last strong event occurred in 1957 (M = 7.6), and in 1962 two strong earthquakes (M = 7.0, each one) had epicenters near the city of Acapulco. In other words, the probability of a large earthquake in the vicinity of Acapulco in the near future is quite high. It can be suggested that the preparation to a large event may cause changes in the ground water chemistry similar to those observed before Kobe, Pyrenean or Karymsky earthquakes.

Geologically, this part of Guerrero state belongs to the so-called Xolapa block or terrain (De Cserna 1965) [YANG1] and composed of Cretaceous granites and older (up to Jurassic) metamorphic rocks (Herrman et al. 1994). Several groups of thermal springs (39 - 43°C) are located within an area of about 100×30 km^2 close to Acapulco (Fig. 1).

We performed a weekly sampling from 4 groups of springs from October 2002 until March 2004. The main goals of the study were to recognize the background level of hydrochemical variations of these springs and to find variations in the chemical (Cl, SO_4) and isotopic (δD, $\delta^{18}O$) composition of thermal waters related to the seismic activity of the region.

2. GEOCHEMISTRY AND ORIGIN OF THERMAL WATERS

Origin of springs near Acapulco and processes of the water-rock interaction responsible for their composition have been discussed by Ramirez-Guzman and Taran (2004). All springs discharge water of low salinity (~0.5 g kg^{-1}), with high negative Eh (-400 mV) and high to very high pH (up to 10). The bubbling gas in all springs is H_2-rich, with very low CO_2 content

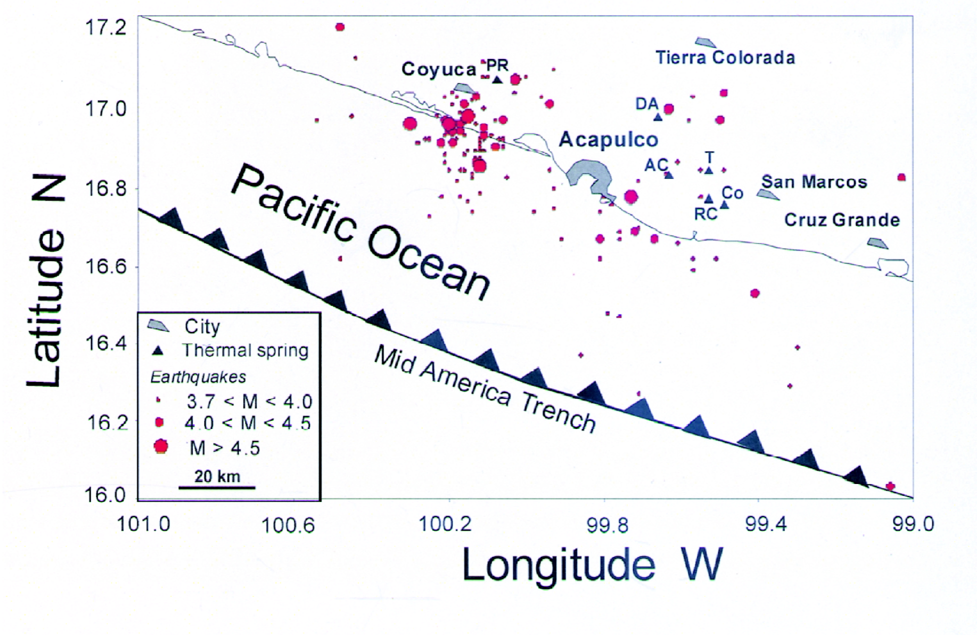

Fig. 1. Location map of thermal springs near Acapulco, Guerrero, Mexico and epicenters of earthquake occurring between October 2002 and March 2004. Names of springs: PR - Paso Real, DA - Dos Arroyos, AC - Agua Caliente, T - Tamarindo, Co - Coacoyul, RC - Rio Cortes.

(< 0.05 vol.%) and relatively high in He (300 - 1000 ppm). Gas from one of the springs (Coacoyul) is enriched in methane (9 - 11 vol.%). Helium isotopic composition of spring gases corresponds to the ages of the host crystalline rocks, being low (^{3}He/^{4}He = 0.15 Ra, where Ra is the atmospheric value 1.4×10^{-6}) in springs discharging from the Jurassic gneisses, and relatively high (0.95Ra) in the Paso Real spring issuing from fractures of Cretaceous granites. Main chemical features of springs and their coordinates are shown in Table 1. The recharge area for all springs as it follows from the water isotopic composition is the southern heights (1000 - 1500 m) of Sierra Madre del Sur. There is no deep drilling in this region, and local tectonic maps do not exist. Therefore it is difficult to make a detailed hydrogeological description of the area. The springs should be connected with deep-seated (3 - 5 km) fractured aquifers in crystalline rocks through a system of deep faults. The area is characterized by a well defined two-season precipitation rate with a dry season between November and May and the total annual precipitations of about 1400 mm (Atlas de Agua 1976). The aquifers feeding springs to the southeast of Acapulco are characterized by a different Cl and SO_4 content and this is the main factor permitting to expect that the crustal stress-strain interplay before a strong seismic event can cause a mixing of waters from adjacent aquifers and thus, precursory changes in the chemical composition.

Table 1. Location, chemical (mg/kg) and isotopic (permil, V-SMOW) composition of thermal springs near Acapulco. Averaged data without the earthquake related anomalies (N- number of analyses).

	Dos Arroyos	Agua Caliente	Tamarindo	Coacoyul	Paso Real
N	70	4	70	85	70
t°C	41	38	42	41	38
pH	9.23	9.28	9.45	9.96	9.67
Eh, mv	-346	-156	-409	-472	-306
SiO_2	29	50	45	49	44
Na	38	107	59	69	90
K	0.65	1.1	1.0	1.1	1.1
Ca	0.6	5.0	1.6	0.9	0.4
Mg	0.1	0.3	0.15	0.1	0.21
Cl	6.5	109	20	56	34
HCO_3	37	53	40	37	89
SO_4	41	30	39	18	63
F	3.0	4.8	5.1	10.5	4.9
δD	-69	-56	-60	-56	-59
$\delta^{18}O$	-9.8	-8.3	-8.5	-8.3	-8.8
Lat. N	16.99	16.88	16.85	16.76	17.08
Long. W	99.66	99.66	99.53	99.49	100.07

3. METHODS

Samples of water were collected every week at the same day and hour (Wednesday, 10 -11 am) filtered through a 0.45 micron Millipore filter and stored in plastic bottles in a refrigerator until the date when we started the analysis, one year after October 15, 2002. This was done in order to avoid analytical errors associated with a storing and/or a re-preparation of the eluents and standard solutions, as well as with the re-conditioning chromatografic columns. Analyses of Cl and SO_4 were performed using a Metrohm-761 ionic chromatograph. Standard solutions were prepared with anionic composition close to that of each spring and analyzed after every 5 analyses of water samples. The reproducibility (1σ) was ~ 1% for Cl and ~3% for SO_4. Because of the very low salinity of the spring waters analyses were conducted without dilution. Water isotopic composition was determined on a DELTA plus XL mass-spectrometer. Analytical errors are ±0.2‰ (1σ) for δD and ±0.2‰ (1σ) for $\delta^{18}O$.

All data on magnitudes and depths of earthquakes in the area were taken from unpublished reports of the National Seismological Survey of Mexico (NSS) (htpp://www.ssn.unam.mx). According to the NSS catalogue, the errors in determination of epicenters vary depending on the location relative to seismo-stations. Three stations (Coyuca, Acapulco, San Marcos, see Fig.1) provide for events with M~4 the uncertainty of the epicentral locations within ±(2 - 5) km and more than 10 km for hypocenters.

4. RESULTS

Background temporal variations of chloride (Fig. 2) in all springs significantly exceed the analytical error level, and the two springs - Paso Real and Tamarindo have an unambiguous seasonal trend in the Cl content. It can be seen if to compare the chemical variations with a histogram of annual precipitations (Fig. 2) based on the averaged data set from the Acapulco meteorological station (Atlas del Agua 1976). The 1 STD level of the background scattering is about of 10% relative to the mean value. A stable base-line level in the Cl content demonstrates the most diluted Dos Arroyos spring. Several peaks can be seen; two anomalies, in Dos Arroyos spring (January, 2003) and Paso Real spring, (September, 2003) significantly exceed the 2σ range (Fig. 2). More than 150 events with magnitude from 3.7 to 5.3 occurred within the area (Fig. 1) during the period of monitoring (October 2002 - March 2004). Figure 3 shows histograms of the epicentral distances for each group of springs. It can be seen, comparing Fig. 1 and Fig. 3 that most of the events cluster close to the Paso Real springs. They are mainly replicas of the M = 5.9 Coyuca earthquake occurred in October 2001 (Pacheco et al. 2002). This earthquake was a shallow, < =10 km deep, normal-faulting event with the epicenter located ~18 km to the SW of the Paso Real springs and was followed by a long period of weak aftershocks. Despite many shallow earthquakes within the Paso Real area with epicentral distances less than 20 km (Fig. 1) and M > 4, the Paso Real spring has responded notably by changes in the Cl content only one time (Fig. 4), after a relatively deep, subduction-related earthquake with M = 4.1 (17.05N, 100.02W) occurred on September 18, 2003, ±5 km to the east of the springs (17.08N, 100.06W) with hypocenter at ~18 km depth. Two samples collected on September 22 and 24 had anomalous Cl and SO_4 content, and after several weeks the composition of water decreased to the base level (Fig. 4).

The number of earthquakes to the east and southeast of Acapulco is much reduced (Figs. 1 - 3) and they were, as a rule, of interplate (subduction) origin. Nevertheless, during the period of monitoring several events with M > 4.0 occurred here, with some epicenters located close to spring sites. However, it can be seen on Fig. 2 that only Dos Arroyos spring showed a significant anomaly in the Cl content in January 2003. The anomaly coincides with a period of a relatively strong seismic activity (January 8 - 16, 2003) occurred within the area. This period included one interplate earthquake with M = 5.3, and 3 shallow events with M > 4, all close to the Paso Real spring without any statistically significant hydrochemical response in that spring. Two deep events (25 and 18 km), on January 11 and 16, with M = 3.8 and 4.0, respectively, had coordinates of epicenters (16.98N, 99.59W and 17.00N, 99.64W) very close to the Dos Arroyos spring location (16.99N, 99.66W). Most probably these events are responsible for the

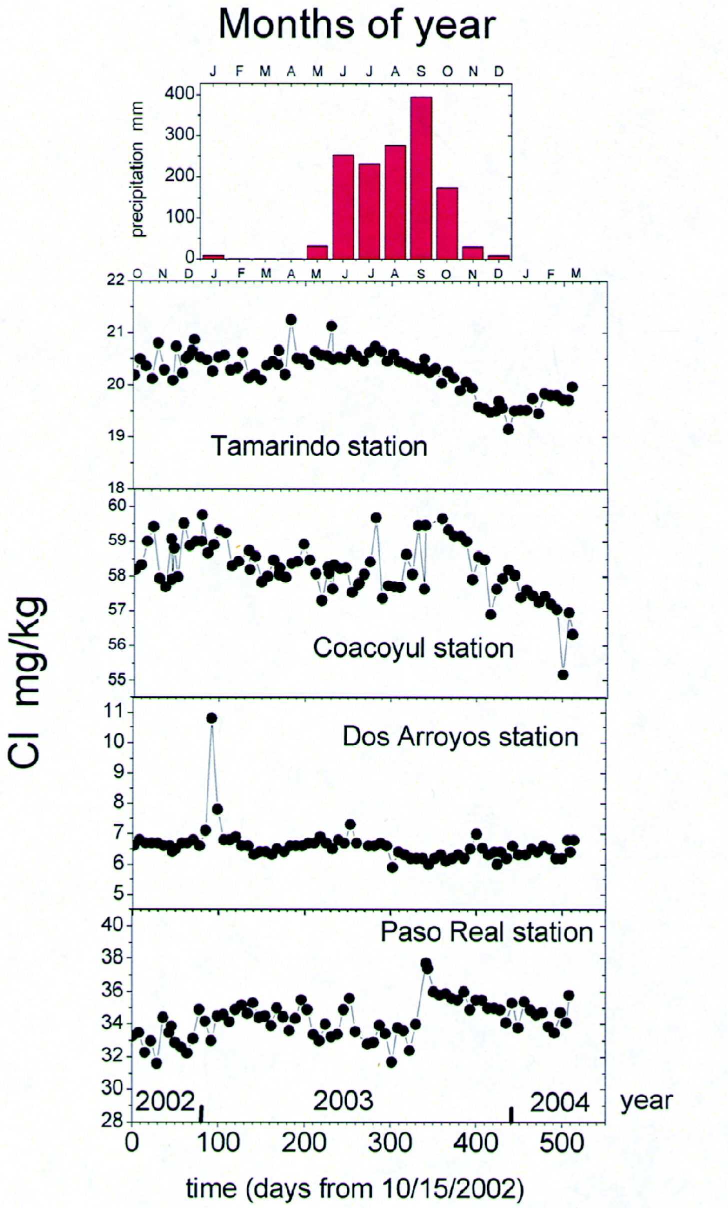

Fig. 2. Time series for the Cl content in all springs along with the average annual distribution of precipitations according to the Acapulco meteorological station (Atlas de Agua 1976). Tamarindo and Paso Real springs show seasonal trends in the Cl content, the Dos Arroyos spring shows a stable baseline in contrast to the Coacoyul spring, where very irregular and high fluctuations in the Cl content can be seen.

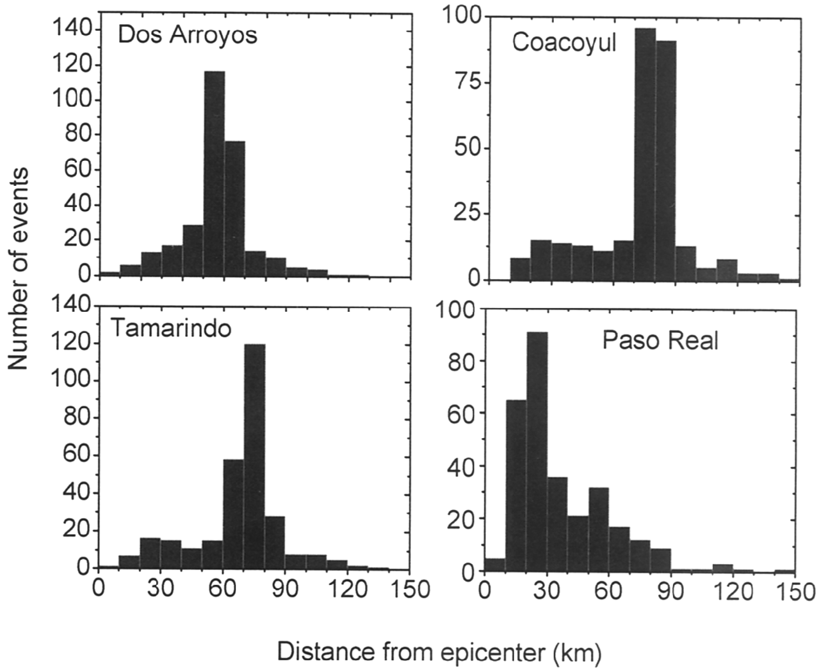

Fig. 3. Histograms showing distribution of earthquakes with M > 3.5 occurring in the area during the period of observations around each spring. Note, that for the Paso Real and Dos Arroyos springs there are a number of earthquake with epicenters very close (< 10 km) to the location of a spring. The nearest to the Coacoyul and Tamarindo springs earthquakes are all further than 10 km.

Cl anomaly at the Dos Arroyos spring water.

In order to have an independent source of geochemical data we performed also series of water isotopic analyses (D/H and $^{18}O/^{16}O$) for the Dos Arroyos and Paso Real springs. Figure 4 shows time series for Cl, SO_4, δD and $\delta^{18}O$ in Dos Arroyos (Fig. 4a) and Paso Real (Fig. 4b) springs. Isotopic anomalies, both in δD and $\delta^{18}O$ coincide with the Cl and SO_4 ones only for Dos Arroyos: in this case an increase in the Cl concentration accompanies the enrichment of waters with heavy isotopes. The Paso Real springs also showed the same enrichment, but the effect does not come out from the 2σ range.

In order to estimate seismic activity at the spring site, at least semi-quantitatively, for each earthquake within the area (150 km radius of a circle around Acapulco) we calculated the strain step amplitudes using magnitude-distance relations of Windeman and Major (1967). These amplitudes for each event, also shown in Fig. 4 along with a threshold line of 10^{-8} derived by Igarashi and Wakita (1990) for the coseismic appearance of Rn anomalies in groundwaters.

(a) Dos Arroyos Station

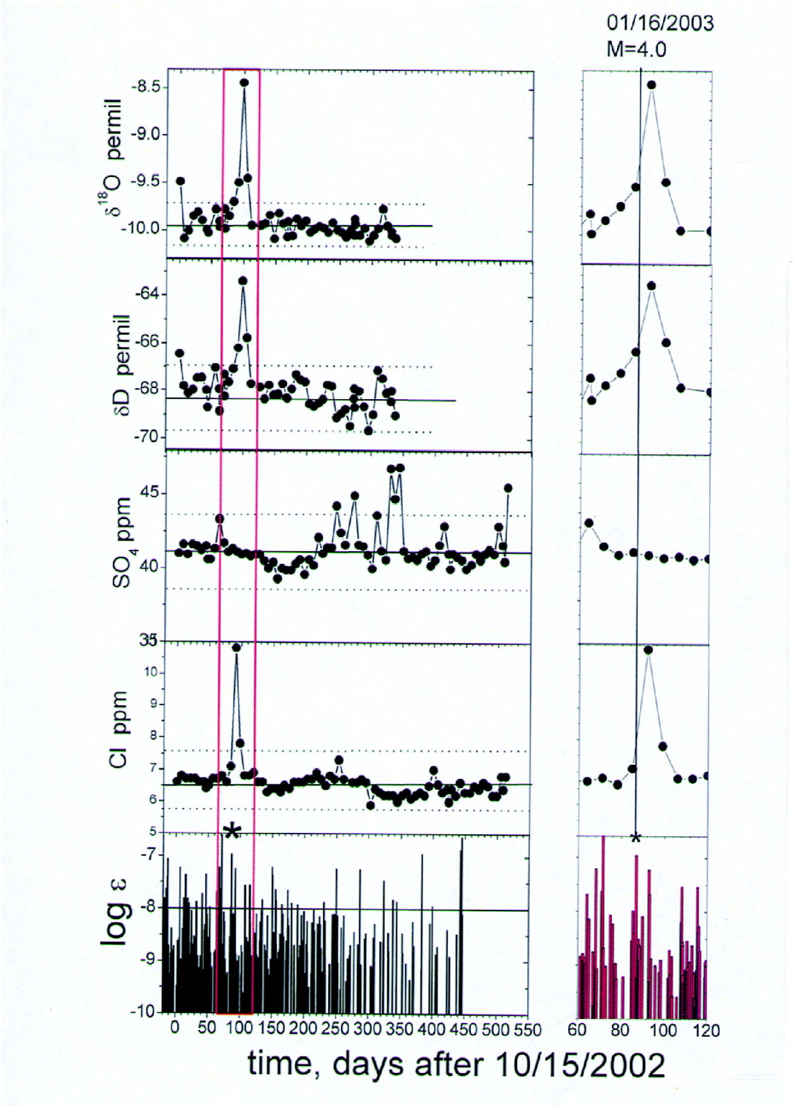

Fig. 4. Time series of Cl, SO_4, δD and δ^{18}O and the strain step amplitude (ε) for the spring location associated with each earthquake within the time interval. The same plots with the expanded scale around the time interval of anomalies are also shown. (a) - Dos Arroyos; (b) - Paso Real. The mean (solid line) and 2σ interval (dotted line) are shown for geochemical parameters and the 10^{-8} level of the strain step amplitudes (solid line). Stars on the strain-step plots indicate the closest earthquakes that occurred several days before anomalies (see text).

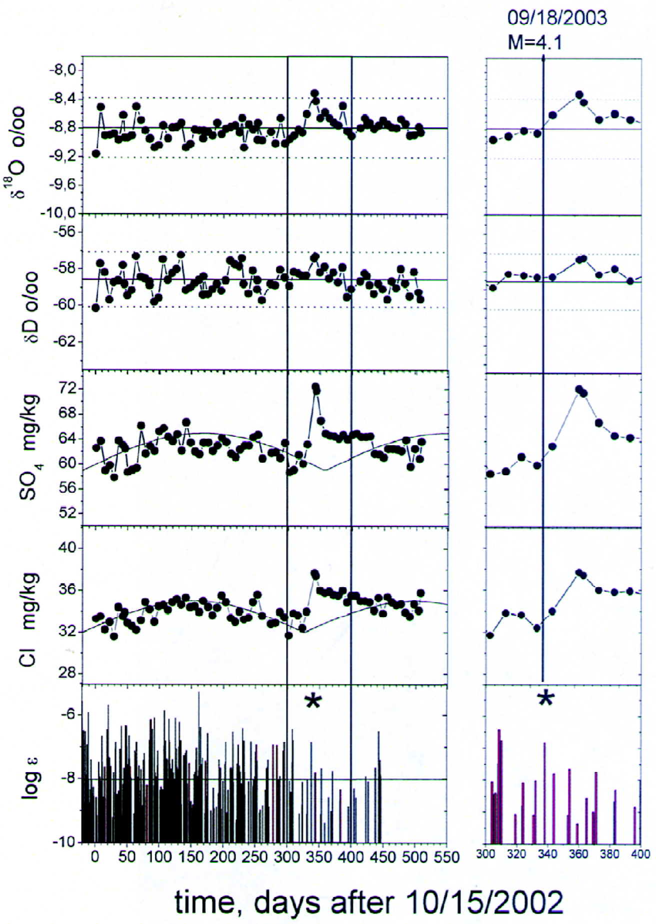
(b) Paso Real Station

Fig. 4. Continued.

5. DISCUSSIONS

The background level of variations in the Cl and SO_4 contents for the Coacoyul and Tamarindo springs is not as stable as that for the Dos Arroyos springs and does not show such a clear seasonal trend as the Paso Real spring. Therefore, we will discuss the data obtained for the Dos Arroyos and Paso Real springs which have clearly expressed anomalies in the Cl content and water isotopic composition (Figs. 2, 4). The main problem is to link the observed hydrochemical anomalies to specific seismic events. Another problem is to define an "anomaly" on a strict statistical basis, as it was discussed by Biagi et al. (2000). In our case, the observed anomalous variations in Dos Arroyos and Paso Real springs could be related to the case when anomalies occurred simultaneously for two or more components (Cl, δD and δ^{18}O for Dos Arroyos and Cl and SO_4 for the Paso Real).

Dobrovolsky et al. (1979) have suggested than any "precursory" geophysical and geochemical change can be observed if the elastic strain before an event at the site of observation is above a threshold level of 10^{-8}. Igarashi and Wakita (1990) determined the same level for the Rn coseismic anomalies (strain step amplitudes). Theoretically derived by Dobrovolsky et al. (1979) relationship between deformation ε, magnitude M and hypocentral distance H (km) is very close to that used by Igarashi and Wakita (1990) and Sato et al. (1992), taken from an earlier experimental work by Windeman and Major (1967). It can be seen from Fig. 4 that for springs in Guerrero there were many earthquakes with the estimated strain step amplitudes higher than 10^{-8}. Two doubtless strong anomalies in the chemical and isotopic composition of waters (Dos Arroyos and Paso Real) occurred after relatively weak (M~4) and deep events with the strain step amplitudes close to 10^{-7}. Some strong enough earthquakes with the strain step amplitudes at the spring location higher than 10^{-7} did not shift chemical characteristics of waters beyond the background level. The strain-step amplitude can be considered as an extremely averaged (isotropic) parameter designed for the estimations of a local strain field of the impending distanced earthquake, and it seems it cannot be applicable in the case of the pre- or co-seismic variations in the solute chemistry of ground waters.

Two statistically significant anomalies in the chemical and isotopic composition of waters (Dos Arroyos and Paso Real) have occurred immediately after relatively weak (M~4) events. The only important difference between these two events and more than 150 others in the area during that period of time was the location of their epicenters (Fig. 1). These two occurred very close, directly beneath, the springs. This is the main reason why we believe that the chemical anomalies were related to these particular earthquakes, and not to other seismic events occurring before or after the sampling. Among 11 earthquakes with M4 that occurred within a 20 km radius around the Paso Real spring, only one had an epicentral location coinciding with the location of the spring, and only immediately after this event the chemical anomalies were observed. Only one from 4 events with M4 that have been registered within a 20 km radius around Dos Arroyos springs occurred directly beneath the springs. And only after that earthquake we observed a significant chemical and isotopic anomaly. In both cases a peak in the Cl content lasting 3 - 4 weeks was accompanied with enrichment in heavierisotopes, clearly expressed only in the case of Dos Arroyos, indicating a mixing with a Cl-richer water. In the case of the Dos Arroyos spring, the mixing could be with water from the adjacent aquifer of the Agua Caliente spring (~100 mg kg^{-1} of Cl vs. 6.6 mg kg^{-1} in Dos Arroyos water and enriched in heavy isotopes as compared with Dos Arroyos water, see Table 1). In the Paso Real case Cl-enriched waters could be from a deeper part of the same aquifer. Our data confirm the earlier suggestions (Barsukov et al. 1985; Igarashi and Wakita 1990; Toutain et al. 1997; Italiano et al. 2005; Song et al. 2005) that the mechanism of the coseismic chemical (and isotopic) anomalies in most of the cases is related to a mixing of waters from adjacent aquifers with different water composition. The steady-state fluxes of water during a "quiet" period can be perturbed due to an earthquake by sudden changes in the pore and fracture pressure after releasing of elastic energy. It is not necessary to increase porosity or permeability on the interface between aquifers. Just a weak piston-like pulse from a proper direction can provoke changes in the chemistry of discharging water.

Therefore, the most "promising" site for the precursory hydrochemical changes is Dos Arroyos springs. They have a stable baseline and the geochemical anomalies there are well outside the background level. Prior to a strong event within the urban area of Acapulco we can expect that during the preparation time a chemical anomaly may appear in Dos Arroyos spring a few months before the quake as it did near Kobe in 1995 and in Kamchatka in 1995 - 1996.

If during the preparation of a strong seismic event the hydrochemical anomalies appear months before the event as it was observed for the M~7 Kobe and Karymsky earthquakes, it is not necessary to install a continuous monitoring system at a hydrochemical station. A weekly sampling is enough for the detection of an anomaly that lasts several months.

6. CONCLUDING REMARKS

This work represents a study of the background level of hydrochemical variations in the deep-seated groundwater within a seismically very active region near Acapulco, Mexico. We found that variations in the water chemistry for all groups of spring exceeded essentially the analytical error level and for two groups of springs showed a clear seasonal trend. Two peak-like anomalies in Cl, SO_4, δD and δ^{18}O were observed in two springs after earthquakes whose epicenters were close (< 10 km) to the spring location, indicating that these springs are sensitive to the mechanical changes in a block of the crust containing aquifers and thus might be a promising perspective for the search of hydrochemical precursors.

The Pacific coast of Mexico, from the boarder with Guatemala to the latitude of ~21°N, is an area of strong, destructive, seismic activity, where most hypocenters are located at relatively shallow levels of 15 - 20 km on the interface between the subducting Cocos and Rivera plates and the continental North America plate. This is also an area of low-temperature hydrothermal activity caused in most of cases by the so-called "geothermal gradient" meteoric thermal waters, heated deep (3 - 6 km) within the crust, and rising to the surface through deep faults (Taran et al. 2002). At least 9 groups of hot springs with temperature from 37 to 78°C are located within the epicentral zone of ~ 20 km parallel to the Pacific coast from Acapulco to Puerto Vallarta. It might be one of the most convenient natural laboratories in the world for the study of the relationship between seismicity and hydrochemistry.

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