

**FLOW CHANGES AND GEOCHEMICAL ANOMALIES IN WARM AND COLD  
SPRINGS ASSOCIATED WITH THE 1992-1994 SEISMIC SEQUENCE AT  
POLLINA, CENTRAL SICILY, ITALY.**

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*-Abstract-* During a three-years discontinuous geochemical monitoring of some warm springs and cold discharges located in central-northern Sicily, some hydro-geochemical changes were observed. Excluding a possible related to a moderate seismic activity were accidentally identified. The observed anomalies showed amplitudes that were modulated by the different geometries and volumes of the feeding aquifers. A poroelastic aquifer contraction, a shaking-induced dilatancy theory as well as seismogenetic-induced changes in the properties of the aquifers have been proposed as possible mechanisms for the water flow and hydro-geochemical changes.

These preliminary results could be used to design a monitoring network aimed at surveilling the seismic activity of the studied area from a geochemical standpoint.

*1. Introduction*

In the last decades, several researches in Japan, China, the USA and Europe, have been focused on the understanding of the seismogenetic processes for earthquake prediction purposes. In particular, researchers have directed their attention towards two main features of the seismogenetic process:

- 1) the role played by the fluids during seismogenesis (Dworkin, 1999; Sornette 1999 and literature therein);
- 2) theoretical modeling of the physical processes responsible for the hydrological, chemical and isotope changes in crustal fluids, such as gases and groundwaters, induced by increasing crustal strain. (Rikitake, 1976; Wakita 1977, 1982; Carapezza et al., 1980; Cai et al., 1984; Barsukov et al. 1985; Thomas 1988; Valenza and Nuccio, 1993; Favara et al., 2001a; Favara et al., 2001b and the references there cited).

In order to recognize the geochemical anomalies related to earthquake preparation and to use them as practical tools in earthquake prediction, each natural system needs to be investigated in detail. For each studied area, basic information regarding geological and structural setting, origin of the fluids and model of their circulation, as well as the definition of the geochemical background (including natural and non-natural variations) is crucial to the formulation of a valid geochemical model able to explain the recognized anomalies and their relationships to increasing crustal strain (Favara et al., 2001a).

A seismically active area located in the northern part of Sicily (Pollina area, in Figure 1) was affected by a long seismic sequence. It started in September 1992, during which more than 500 seismic shocks, at a depth ranging between 3 and 5 km, were recorded. The seismic swarm culminated with the strongest event that took place on June 26, 1993, and that had a magnitude of 4.4 (Figure 2)

Some significant geochemical variations in both the output and in the chemical composition of He, CO<sub>2</sub>, Rn and Ne, were observed during the strongest event of the recorded seismic swarm. This was ascertained by comparing the data collected during three soil gas investigations (De Gregorio et al., 1996).

During the same period, groundwaters from 7 springs and 1 well (PC), representative of different aquifers present in this area and discontinuously monitored every three months

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for a more ample hydrogeological study, showed both hydrological and geochemical anomalies.

## *2. Geology and hydro-geology*

The studied area is located in the eastern part of the Madonie Mountains in north central Sicily (Italy). The Madonie Mountains extend for an area of about 220 km<sup>2</sup> (Fig. 1). Several cold springs, giving a total flow discharge of about 3500 l/s (Favara et al., 1984), lie in this region, and represent one of the most important hydrogeological domains in Sicily. The main springs are located both within the area of the Madonie Mountains and along the northern coast of Sicily, near the town of Cefalù.

The stratigraphic sequence of this area consists only of sedimentary terrains: no crystalline or metamorphic rocks outcrop, neither have any been found during drillings. This sequence includes Triassic-Miocene limestones, siliceous-limestones (Imerese Basin) and Triassic-Eocene limestones and dolostones (Panormide Platform). Shales and quartz-sandstones of the Upper Oligocene Numidian Flysch outcrop on the borders of the studied area. Clays and sandstones deriving from the erosion of the Sicilide Domain deposits, Upper Cretaceous in age, outcrop near the coast. Post-orogenic deposits including clays, sandstones and evaporite deposits of Upper Tortonian to Pleistocene age complete the stratigraphic succession. In particular, the evaporitic sequence is present only in the southern part of the Madonie Mountains, as it had already emerged during the deposition of the Messinian gypsum-dominant series. Fluvial and marine deposits of Quaternary age are also present on the coast and in fluvial valleys.

Tectonics resulted from several compressive and distensive episodes from Miocene to Upper Pliocene (Abate et al., 1982). The main fault systems are characterized by N-S and NE-SW directions. These different tectonic phases created a building with vertical recurrences of platform and basin limestones and dolostones, over-thrusted with their cover of alternating sandstones and clays (Numidian Flysch).

As stated in previous studies (Cusimano, 1989; Cusimano et al., 1992; Madonia, 1993; Grassa et al., 2002), the main aquifers are of mixed type, with a main contribution from the carbonate sequences and a minor component to be referred to underground circulation into the permeable portion of the Numidian Flysch. The carbonate aquifers are of two different sub-types: in the NE portion karst is predominant, related to the platform limestone sequences of the Panormide domain; in the SW portion fractured rocks related to the deep sea sequences of the Imerese basin domain prevail. The two hydro-structures are probably in lateral hydraulic continuity (Madonia, 1993) and, as the higher portion of the Panormide aquifer is located at higher altitudes than those of the Imerese hydro-structure, underground waters may flow from the previous to the latter.

From a hydro-geochemical point of view (Cusimano et al., 1992; Madonia, 1993), the prevailing carbonate species are modulated by its different mixings with waters circulating into the permeable portions of the Numidian Flysch. These latter are characterized by higher concentrations of ions derived from the interaction with sulphur minerals and H<sub>2</sub>S, as better specified in chapter 4.

Sandstone-hosted aquifers became dominant only in the south-east portion of the Madonie area, while marine, fluvial and alluvial deposits of the Northern Imera and Pollina rivers form lateral aquifers of minor importance. The total water storage capability was estimated at about 1.1 X 10<sup>8</sup> m<sup>3</sup> (Cusimano, 1989).

## *3. Analytical methods*

Electrical conductivity, pH and water temperature were measured directly in the field. Conductivity was measured using a Crison 524 conductimeter (accuracy ± 3%); pH by using an Orion 250pHmeter (accuracy ± 0.01 pH unit) and water temperatures by means of a mercury thermometer (accuracy ± 0.1°C). HCO<sub>3</sub> was determined by volumetric titration

with 0.1 N HCl Suprapur. Major and minor constituents were determined by a Dionex 2000i ion chromatograph (reproducibility within  $\pm 2\%$ ). A Dionex AS4A-SC column was used for anion determinations (F, Cl,  $\text{NO}_3$ , Br,  $\text{SO}_4$ ), whereas a Dionex CS-12 column was used for the cations (Li, Na, K, Mg, Ca).

#### 4. Water geochemistry

Water temperature, electrical conductivity and pH range between 13.2 °C and 28.6°C, 342 and 2869  $\mu\text{S}/\text{cm}$  and 6.74 and 7.87 respectively. A first classification of the sampled waters was obtained by using a Langelier-Ludwig diagram (Fig.3):

- The Scillato (SC) and Favara di Collesano (FC) springs fall within the bicarbonate alkaline-earth field (group A). They are characterized by low salinity (TDS < 400 mg/l) and their chemistry is dominated both by  $\text{HCO}_3$  and by alkaline-earth metals (Ca and Mg). The Scillato spring is located at an altitude of 380 m a.s.l., on the western flank of the Madonie Mountains and has a flow rate of several hundreds of l/s. Due to its location along the lateral contact between the Imerese and flysch series and to the fact that the amount of discharged water represents more than 50% of the whole calculated recharge of the Imerese structure, it can be considered as being the main basal discharge of the Imerese domain (Madonia, 1993). The Favara di Collesano spring is located at a slightly higher altitude (i.e. 450 m a.s.l.), and has a flow rate of only a few tenths of a l/s. It is a secondary discharge of the Imerese aquifer and is linked to the contact between two different carbonate thrusts with an interposed Numidian Flysch layer. These springs reach full chemical equilibrium with the carbonate rocks, as suggested by the saturation indexes of calcite and dolomite that close to zero.

- The Marcatagliastro springs (M2 and M3) fall within the chloride-sulphate alkaline-earth field (group B). They belong to groundwaters circulating within the Numidian Flysch formation. There, the observed sulphate-enrichment could probably be related to two different mechanisms: the weathering of sulphides and sulfate-rich minerals and the oxidation of  $\text{H}_2\text{S}$  minerals, such as Pyrite ( $\text{Fe}_2\text{S}$ ), Natrojarosite ( $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ ) and Thenardite ( $\text{Na}_2\text{SO}_4$ ), which were found in the clay interlayers of the Numidian Flysch (Alaimo and Ferla, 1975). Moreover, the potentially high redox values measured in the aquifers allow for the oxidation of S-rich fluids, both of deep origin and derived from the alteration, in anoxic conditions, of the organic content of the Numidian Flysch clays.

All the other water samples but PC sample are distributed within a triangle, the corners of which represent three end members, suggesting the existence of mixing processes between sea water (SW), groups A and B waters:

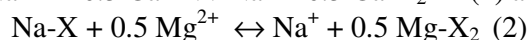
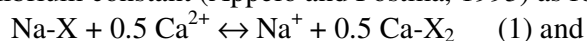
- The Presidiana (PR) spring lies in the chloride-sulphate-alkaline field. It is located at sea level, it has the greatest flow rate in the Madonie area (up to 1000 l/s), and is the main northern discharge point of the basal aquifer that is hosted within the Panormide domain (Cusimano et al, 1992). Its chemistry reflects sea water contamination (up to 3%).

- The waters of the S. Maria (SM) spring are chloride-sulphate alkaline-earth. Its flow rate is of the order of a few decimals of a l/s, and is fairly constant during the entire hydrological cycle. It is not affected by seawater mixing, as indicated by the chloride/sulphate ratio (Figure 4). Its related aquifer develops entirely within the Numidian Flysch deposits, where the carbonate ions may derive from the dissolution of the calcite cement of sandstones and/or from carbonate olistolithes present in the Numidian sequences.

The Sonno spring (SO) is a transitional term between bicarbonate-alkaline earth and chloride-sulphate-alkaline waters, and its maximum flow rates are 1-1.5 l/s. It lies along a very important tectonic discontinuity, marked by the deep Isnello valley, and its chemistry is the result of the mixing of Panormide and Numidian aquifers.

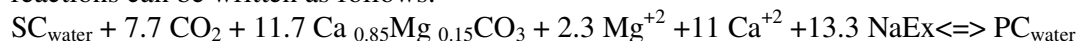
The Pozzo Casalo sample (PC) lies in the bicarbonate alkaline field and shows relatively high salinity (about 2500 mg/l). Na and HCO<sub>3</sub> are the dominant chemical constituents as the sum of the two is greater than 90% of the total dissolved ions (in meq/l).

These unusual chemical features suggest a two-step geochemical process. First, the dissolution of carbonate minerals (both calcite and dolomite) by CO<sub>2</sub> enriched waters accounts for most of the solute content. In a second time, the ion-exchange reactions between groundwater and clay minerals, probably modify pristine ion ratios, causing an increase in Na and a consequent removal of Ca and Mg from the solution. The latter can be described by an equilibrium constant (Appelo and Postma, 1993) as follows:



where X indicates the clay exchanger.

In order to verify the hydro-geochemical processes inferred above, the computer program NETPATH (Plummer et al., 1991) was used to calculate the mass balance of the chemical reactions. The geochemical evolution during flow path was simulated starting from groundwater similar to that of the SC spring (the most representative carbonate groundwater). Taking into account the local geological setting, one of the most plausible reactions can be written as follows:



Another process that could produce Na-HCO<sub>3</sub> waters is the alteration of albite-rich rocks to form Na-montmorillonite enhanced by the dissolution of carbon dioxide. However, this hypothesis can be ruled out because of the lack of crystalline rocks in this area. As can be noted, both these reactions imply the presence of a CO<sub>2</sub>-rich phase interacting with groundwaters.

This agrees with the soil gas measurements carried out during the three surveys effected in the studied area (De Gregorio et al., 1996). Field investigations have revealed the presence of high CO<sub>2</sub> flux, with the highest values being about 3 \* 10<sup>-4</sup> cm/sec. The results of carbon isotope measurements (δ<sup>13</sup>C<sub>CO2</sub>) performed at only two sites having high CO<sub>2</sub> concentration (1-2% vol) are close to -25 ‰, vs V-PDB, thus indicating that this gas derives from the oxidation of organic matter.

#### 5. Temporal variations

Although the sampling rate was neither high nor constant, some physico-chemical changes were observed in some of the studied springs.

During the period Jun 91-Jan 93, the flow rate values at SM spring remained almost constant, showing only a seasonal trend at SO spring that resulted in lower values during the dry season, that in Mediterranean areas corresponds to late spring - beginning of autumn. In proximity of the 26<sup>th</sup> June event, the flow rate at SO and SM springs increased up to 10 times (Fig. 5).

If we analyze the entire sampling period more in detail, we will ascertain that some geochemical changes were also observed at the SM, FC and SC springs. FC and SM springs showed anomalies in the TDS content and SC spring displayed a marked change in Mg concentration.

First of all, our attention will be focused on TDS (Fig. 6). Unfortunately, due to some sampling problems, we have no data either for the FC spring immediately after the strongest earthquake or for the SM spring immediately before it. In spite of this lack of data for both these springs a common trend is evident. This consists of a relative minimum in January 1993 with TDS values of 1400 and 400 mg/l at SM and FC springs respectively. Subsequently, the values rose up to 1600 mg/l (SM spring) and 450 mg/l (at FC spring), falling outside their respective average values for the previous period.

The increases in TDS values are explained by a general increase in the salinity of water rather than to the increase of only one chemical component. However, both at SM and FC springs and also at SC and PR springs where TDS values remain within their respective background values, sulphate concentration changes with time (Fig. 7).

In these four springs, it is possible to observe a homogeneous style of variation although the amplitude of the anomalies in the  $\text{SO}_4$  content is quite different. All the discharges showed a decreasing trend before the earthquake of 26<sup>th</sup> June 1993 and subsequently an increase. This behavior is particularly marked at SM spring where the largest anomalies were recorded, while it is slightly evident at SC spring where the changes in sulphate concentration are less than 3 ppm.

In this discharge, during a non-seismic period between June 1991 and August 1992, the average sulphate was 386 ( $1\sigma = 12$  ppm). Before the earthquake of June 26<sup>th</sup>, 1993, the  $\text{SO}_4$  content decreased to below the background, while a few days after it, the  $\text{SO}_4$  concentration reached 475 ppm, thus increasing by 25% with respect to the mean values previously recorded.

At FC spring, during the same non-seismic period, the average  $\text{SO}_4$  content generally showed almost constant values ranging within  $28.1 \pm 0.8$  ppm ( $1\sigma$ ). An increase by about 13% with respect to the mean sulphate concentration was recorded just before the 26<sup>th</sup> June event.

Finally, SC spring showed also a decreasing trend in the Magnesium content (Fig. 8). At the beginning of this survey (July 1991) Mg concentration was 19.5 ppm and it reached its minimum in January 1993 with only 14 ppm showing a decreasing of about 30% with respect to the initial value.

## 6. Discussion

In order to identify the possible causes responsible for the observed temporal variations the hydrogeological and geochemical data have been compared both to the local rainfall data and to earthquake distribution during the Pollina seismic sequence (Figures 9-12). Precipitation values were collected during the 1991-1994 period at the rain-gauges of Isnello, Castelbuono, Scillato and Collesano, the nearest stations to SO, SM, SC and FC springs respectively. Seismic data were recorded from the ING network during the period from July 1992 to November 1993 (Azzara et al., unpublished data). It clearly appears that the observed anomalies in flow rate at SO and SM springs are not linked to a larger meteoric recharge because they were not preceded by any anomalous rain events. Moreover, if the increase in flow rate is due to anomalous meteoric recharge events, the expected modifications in the geochemical parameters are not compatible with the geochemical variations really observed. In fact, the marked increase of a meteoric component should have produced an evident dilution in the total amount of dissolved salts (TDS values) while a strong increase and almost constant values were observed at SM and SO spring respectively.

On the contrary, the anomalies in the flow rate seem to occur as a consequence of releasing of the major energy (June 1993) and for this reason, we think that the increasing in flow rate at SO and SM could be related to the local seismic activity.

An increase in the transmissivity of the aquifer, probably as a consequence of a shaking-induced dilatancy (Bower and Heaton, 1978) could be responsible for the increase of flow rate in both these springs. Unfortunately, due to the small amount of data available, it was not possible to constrain the temporal relationships to the observed increases and the strongest earthquake.

Because the increase in TDS results from a global increase of many dissolved chemical constituents, in our opinion, one of the possible mechanisms could be the progressive rock-

fracturing provoked by the release of accumulated crustal stress. This process exposes fresh surfaces to water-rock interaction and hence enhances the dissolution of minerals. Confirmation of this is given by similar anomalies in the TDS trend that were observed at the FC spring (Grassa et al., 2002) in coincidence with an M 4.0 earthquake that occurred on November 25, 2001. This was located by the Italian national seismic network in the area between the small towns of Scillato and Collesano (Fig.1), which are very near to this spring. Also at that time the TDS values progressively increased with respect to a minimum value, which however remains “*unknown*” due to the absence of pre-event samples.

A different explanation can be invoked for the temporal variation in the Mg content at SC spring. As already argued, magnesium can be considered a geochemical tracer of groundwater flowing within the dolomitic portion of the feeding aquifer mainly belonging to the Imerese basin domain. This part of the aquifer is characterized by lower permeability values and very reduced volumes than the limestones that constitute the prevailing lithology of the hydro-geologic structure feeding the SC spring. The lowering of the magnesium content before the strongest earthquake might be due to relative variations of the permeability between the limestones and dolostones, caused by a modification of the local crustal stress. However, the circulation of groundwater in the dolostones is to be referred to fracture-related permeability, which in the case of limestone karst phenomena assumes great importance. This results in a different degree of water-bearing discontinuities: they are greater in limestones and smaller in dolostones, and this is the reason why crustal stress accumulation is reflected more in the latter than in the former. However, seismic-induced permeability variations do not represent the only possible model capable of explaining the observed anomalies.

As regards the change in sulphate concentrations at SO, SM, FC and SC springs it can be explained by a modification of the relative proportions of a simple two-component mixing process or by a mobilization of fluids from depth towards a shallower part to be referred to elastic compression actions. Both these processes can be the result of the stress-state modifications in the studied area

During the initial perturbation phase of a steady state due to changes in the stress field, a decrease in the near-surface permeability could have happened. On the contrary, when rupture limit conditions have been reached, at the time of the 26<sup>th</sup> June event, there could be an opposite effect (increasing of permeability) probably generated by micro-fracturing of hosting rocks.

The positive transient of the SO<sub>4</sub> content could also be explained by the release of a greater amount of deep component, such as S-rich fluids, that are mobilized by increasing compression actions. It is also possible that both the proposed mechanisms (i.e. change in crustal permeability and elastic compression) acted at the same time, thus producing a combined effect.

As already discussed, the widest anomalies were recorded at SM spring while very small changes were observed at PR and SC springs. A relationship between the width of the observed hydrogeological and geochemical changes and the volumes and geometry of the aquifers as well as their relative proximity to the tectonic structures involved in the seismogenetic process can be recognized.

The width of the geochemical anomalies is inversely proportional to the size of the aquifer. At the same way, the less distance between the spring and the epicentral area, the wider geochemical variations.

SM spring is the nearest spring to the seismogenetic structure of the 26<sup>th</sup> June 1993 event, and moreover it is fed by a very small aquifer. Its low flow rate ( $Q_{\text{mean}} = 0.05$  l/s) and the moderate capacity of its aquifer, seems to make SM spring one of the most sensitive sites

to modifications in the local crustal stress. On the contrary, because of their huge volume of the feeding aquifers, PR and SC springs showed the same style of variation but narrower than those observed at SM spring.

#### *7. Concluding remarks*

The present study has highlighted the main geochemical processes that affect the chemistry of the groundwater in the Polling area (i.e. Moonie Mountains). In particular, water-rock interaction involving carbonate dissolution and ion-exchange processes are the main sources of major dissolved ions (Ca, Mg, Na, HCO<sub>3</sub>). Dissolution of S-bearing minerals (sulphides and/or sulphates) and oxidation of H<sub>2</sub>S-rich fluids represent possible sources of SO<sub>4</sub><sup>-</sup> in the studied groundwaters. Only the Presidiana spring (PR) receives a minor contribution of seawater (up to 3%).

During the 1992-1994 period, an intense crustal stress field, generated by compressive actions, seems to have been responsible for the perturbation of the steady-state of the aquifers. This modification has probably caused changes in the water chemistry and in the flow rate in some of the studied springs. The recorded geochemical anomalies are quite similar to many hydrologic and physico-chemical changes reported in previous scientific papers worldwide in other active seismic regions.

On the basis of the observations we have proposed at least three possible physical mechanisms to explain the hydrogeochemical and geochemical changes in some local groundwater. They are briefly reported here below:

- Shaking-induced dilatancy;
- Poroelastic aquifer contraction;
- Seismogenetic-induced permanent or temporary changes in the mechanical properties of the aquifers.

In the studied area flow rate, magnesium, sulphate and TDS contents seem to be the most sensitive physico-chemical parameters to seismogenetic process. Geochemical surveillance of these parameters, by means of continuous measurements, could be used to reveal local anomalous crustal stress.

#### *Acknowledgements*

We wish to thank Dr. J.P. Toutain and Dr. R. Azzara, reviewers of this manuscript which helped us to improve and clarify the manuscript.

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### Figure captions

Figure 1: Location map of the study area. Main geological features, location of the sampling sites and the epicenters of the recent local seismic activity (1992-1994 and 2001) are also reported.

Figure 2: Plot of earthquake distribution during the Pollina seismic sequence from July 1992 to November 1993. Histogram (left scale), cumulative frequency (right scale) and shocks with  $M > 3.0$  are reported (from Azzara et al., Unpublished data).

Figure 3: Langelier-Ludwig classification diagram. Three main groups have been distinguished: bicarbonate alkaline-earth waters (group A), chloride-sulphate alkaline-earth waters (group B) and bicarbonate alkaline waters (PC well). SW = sea water

Figure 4: Triangular plot for anions. The  $SO_4/Cl$  ratio at the SM spring is constant with time and closer to that of the chloride-sulphate alkaline-earth end-member (M2 and M3 springs) rather than to that of seawater.

Figure 5: Temporal variation of flow rate at the SM (diamonds) and SO (circles) springs. Dashed line indicates the occurrence of the strongest earthquake (June, 26 1993,  $M=4.4$ ).

Figure 6: Changes in TDS values at the SM (triangles), FC (circles) and SC (squares) springs. The 26<sup>th</sup> June event ( $M=4.4$ ) is also highlighted (dashed line). The amplitude of the observed anomalies is inversely proportional to the extent of the aquifer, as such modifications are more evident at the SM spring that has a smaller reservoir.

Figure 7: Changes in  $SO_4$  contents at the SM (triangles), PR (diamonds), FC (circles) and SC (squares) springs. All these springs show a decrease before the main earthquake (June, 26 1993,  $M=4.4$ , dashed line) and subsequently an increase. Although the amplitude of the anomalies is quite different, a homogeneous style of variation can be identified. This behaviour is particularly enhanced at the SM spring which is fed by a small aquifer, while the SC, PR and SC springs showed lower variations because of the huge volume of their respective feeding aquifers.

Figure 8: Plot of temporal variations of magnesium content at SC spring. Dashed line indicates the earthquake of June, 26<sup>th</sup> 1993,  $M=4.4$ . The lowering of the magnesium content before this event may be due to relative variations of the permeability between limestones and dolostones caused by a modification of local crustal stress.

Figure 9: Plots of temporal variations of earthquake distribution, rainfall, geochemical parameter and flow rate at SM spring. Dashed line indicates the earthquake of June, 26<sup>th</sup> 1993,  $M=4.4$ . Earthquakes distribution from the ING network (Azzara et al., unpublished data). Rainfall are relative to the Castelbuono station.

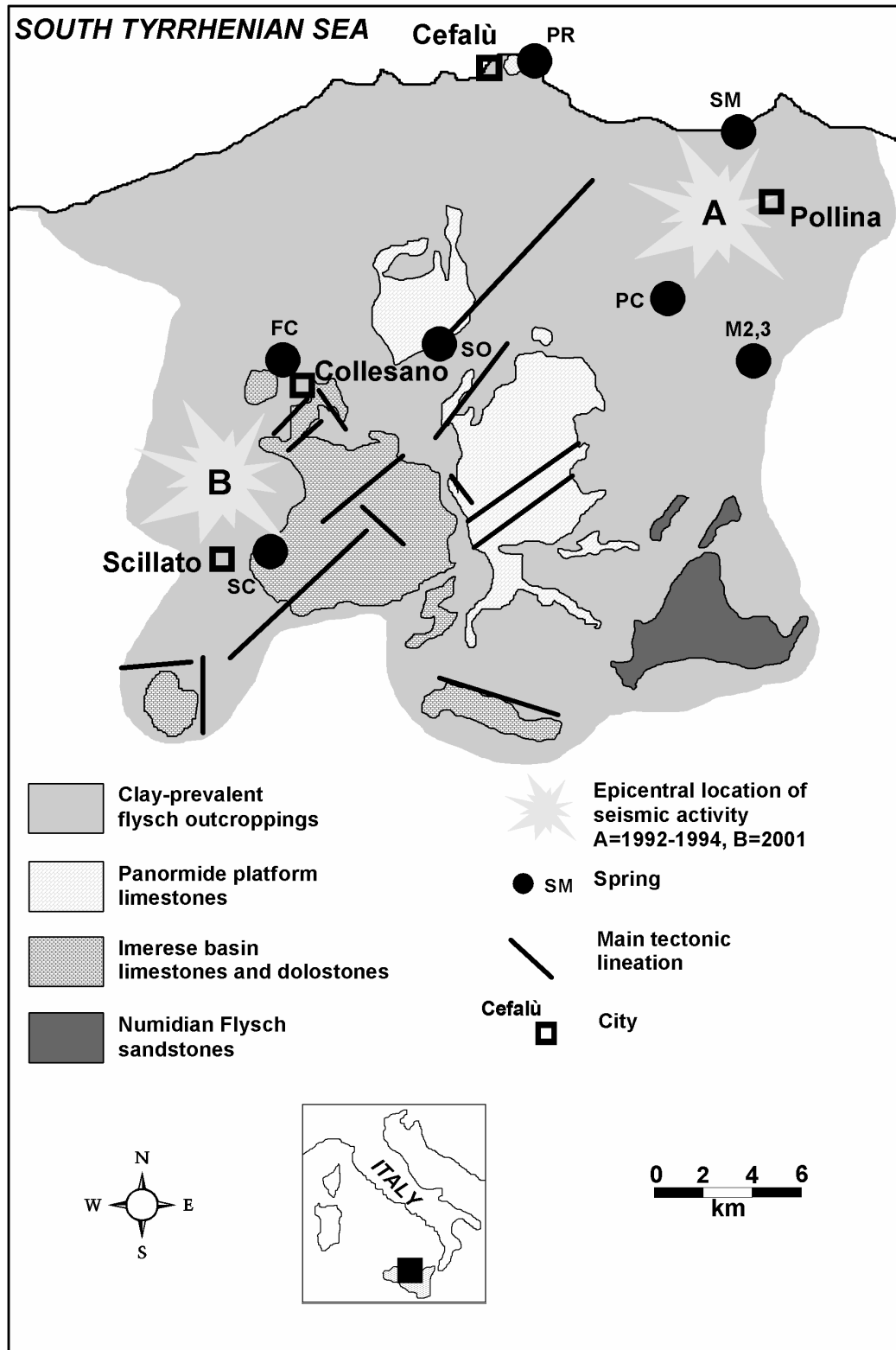
Figure 10: Plots of temporal variations of earthquake distribution, rainfall, geochemical parameter and flow rate at SO spring. Dashed line indicates the earthquake of June, 26<sup>th</sup> 1993,  $M=4.4$ . Earthquakes distribution from the ING network (Azzara et al., unpublished data). Rainfall are relative to the Isnello station.

Figure 11: Plots of temporal variations of earthquake distribution, rainfall, geochemical parameter and flow rate at FCM spring. Dashed line indicates the earthquake of June, 26<sup>th</sup> 1993,  $M=4.4$ . Earthquakes distribution from the ING network (Azzara et al., unpublished data). Rainfall are relative to the Collesano station.

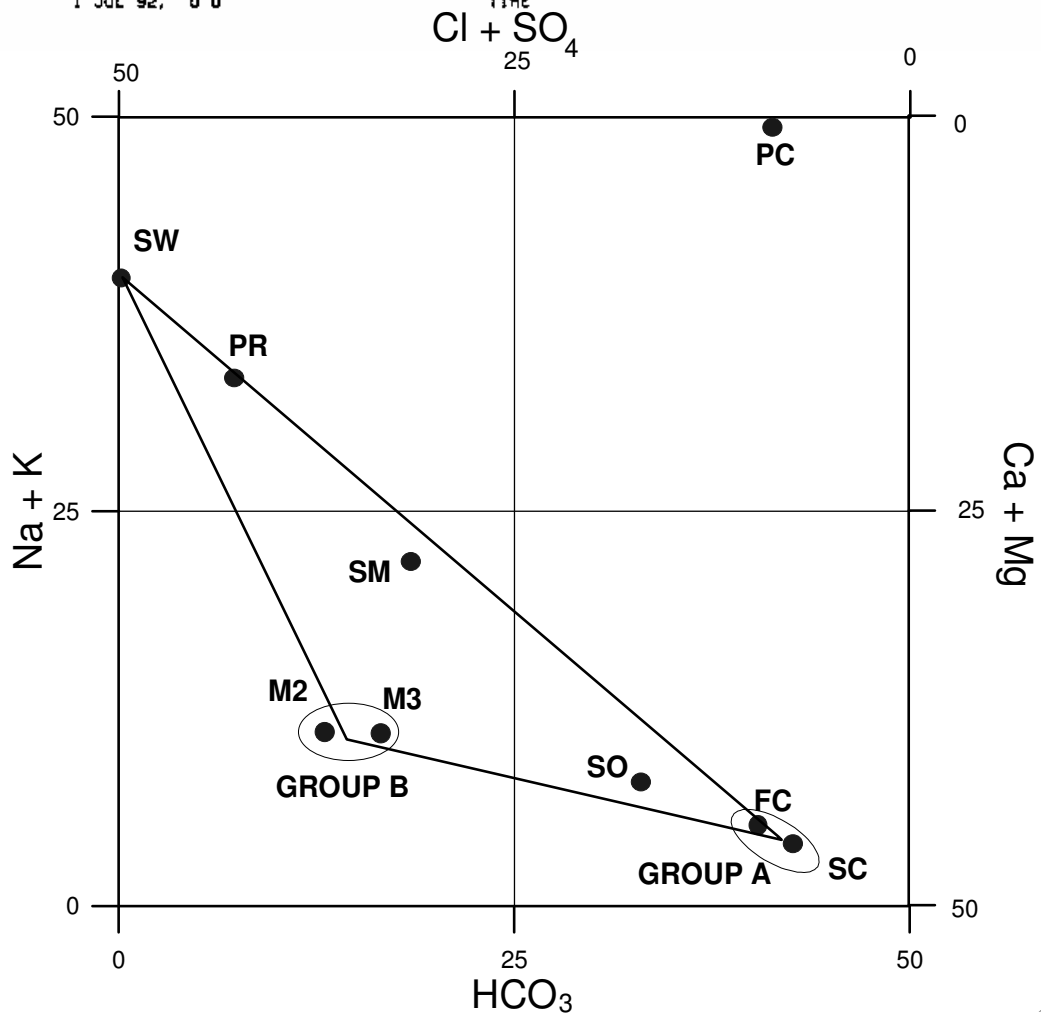
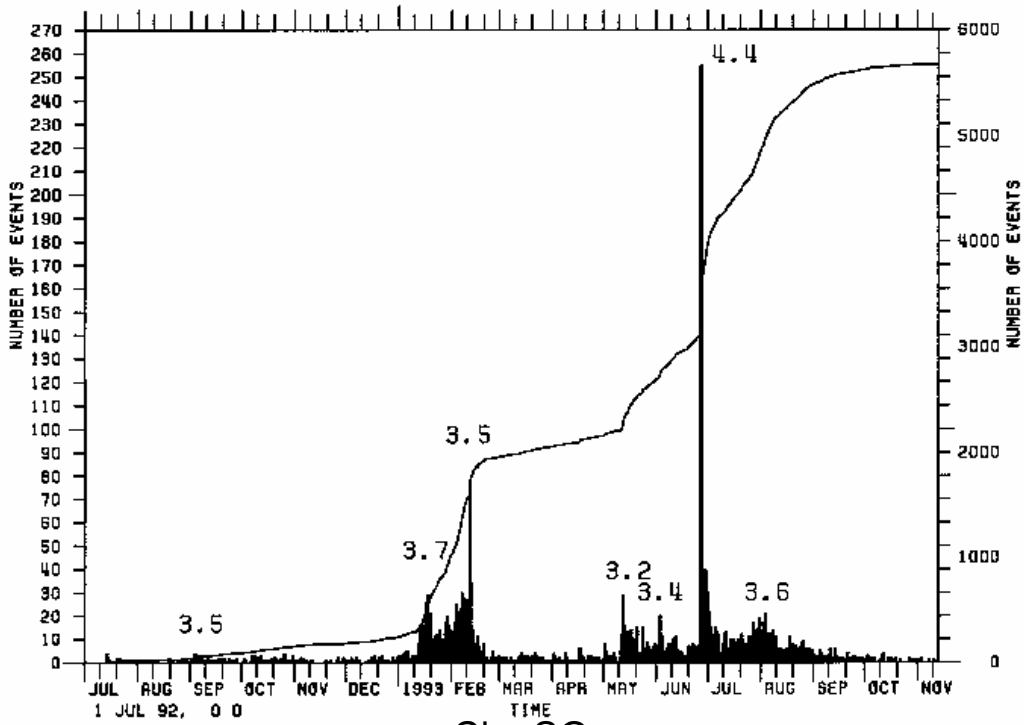
Figure 12: Plots of temporal variations of earthquake distribution, rainfall, geochemical parameter and flow rate at SC spring. Dashed line indicates the earthquake of June, 26<sup>th</sup> 1993,  $M=4.4$ . Earthquakes distribution from the ING network (Azzara et al., unpublished data). Rainfall are relative to the Scillato station.

**Table Caption**

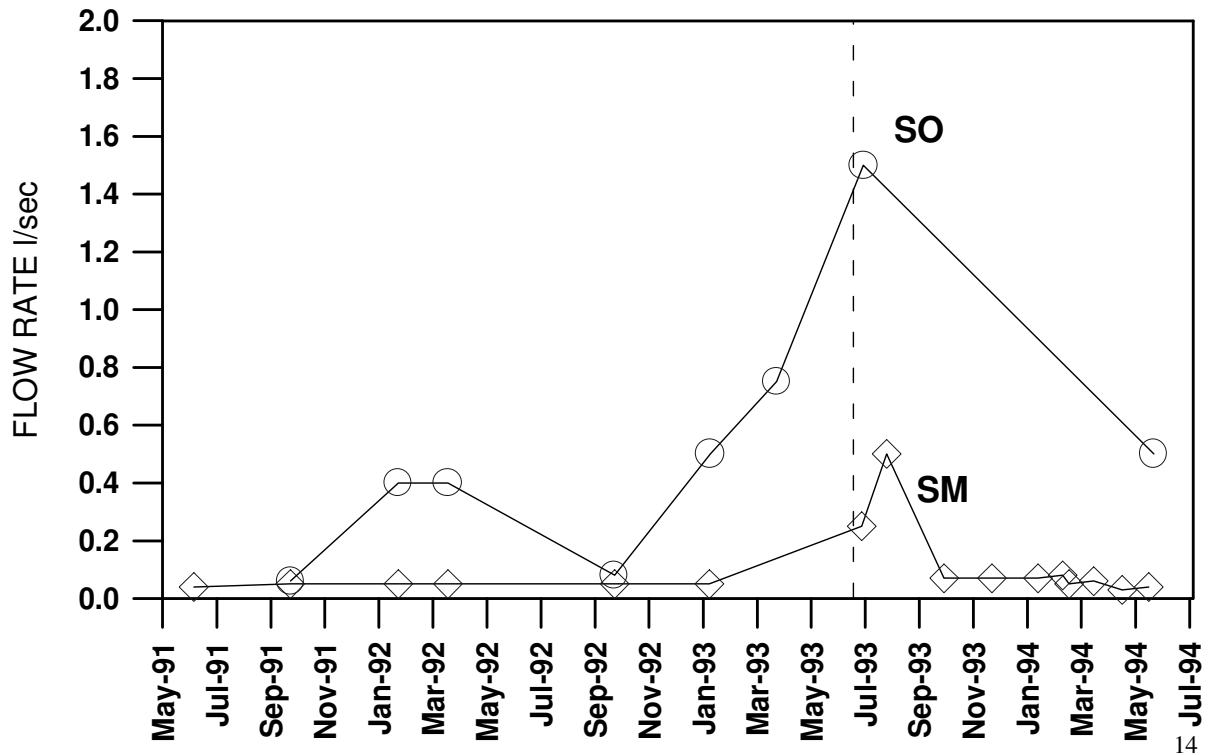
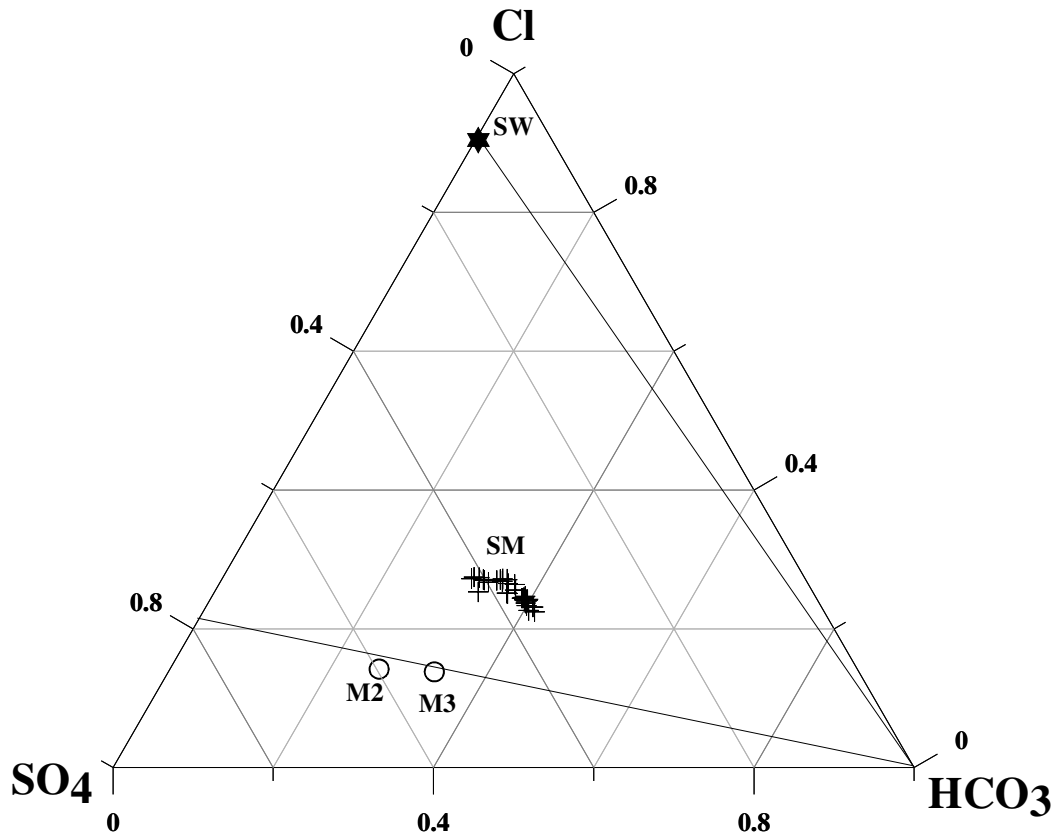
Table1: Chemical analyses of waters from the Madonie Mountains. Flow rates are expressed in l/s, pH in pH unit, EC = Electrical conductivity at 20°C is expressed in mS/cm, T= water temperature in °C. Concentrations and TDS are expressed in mg/l.; a = spring; b = well. n.m. not measured. Saturation indexes with respect to calcite ( $SI_{Calc}$ ) and dolomite ( $SI_{Dolom}$ ) are also reported.

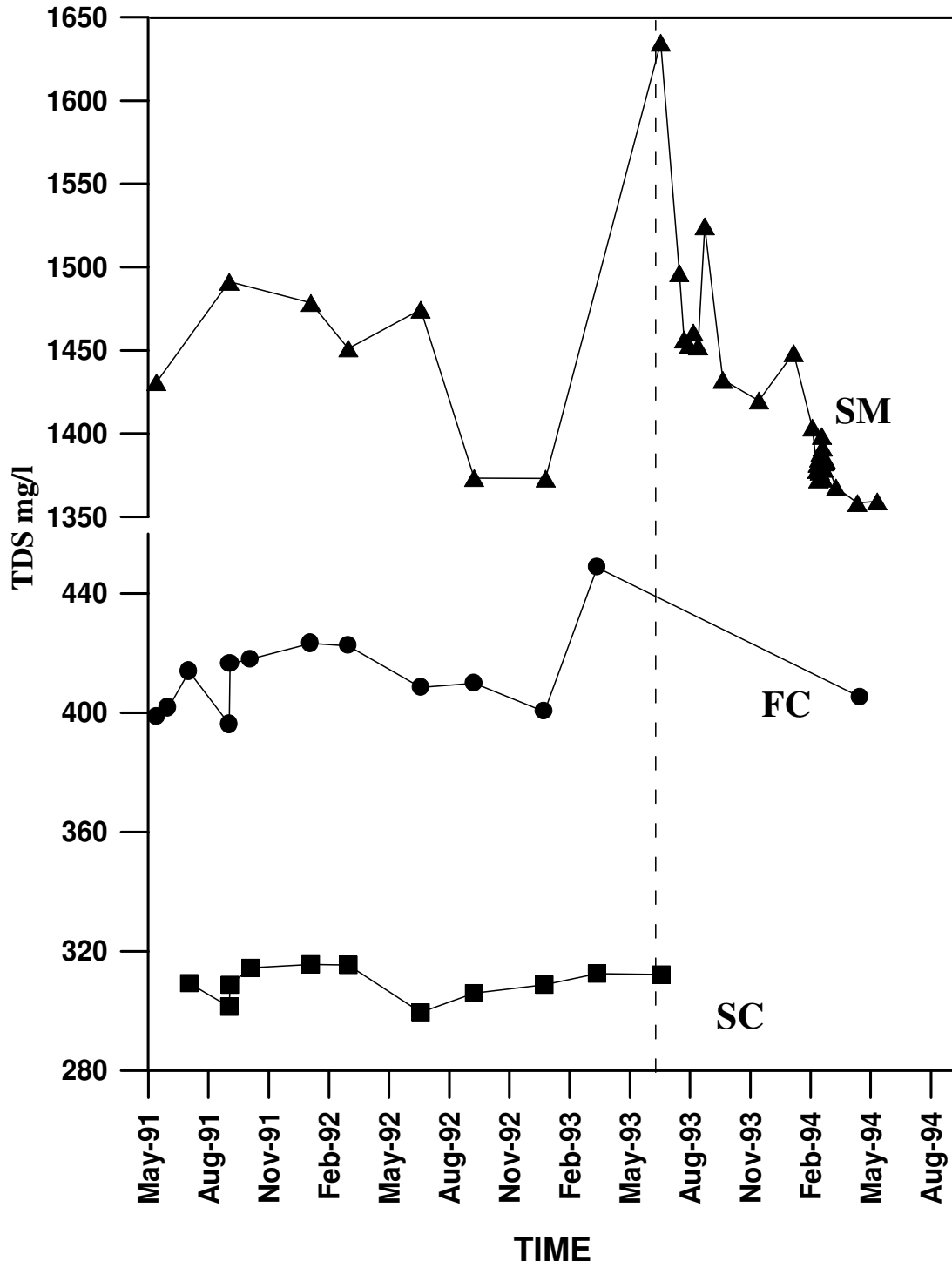


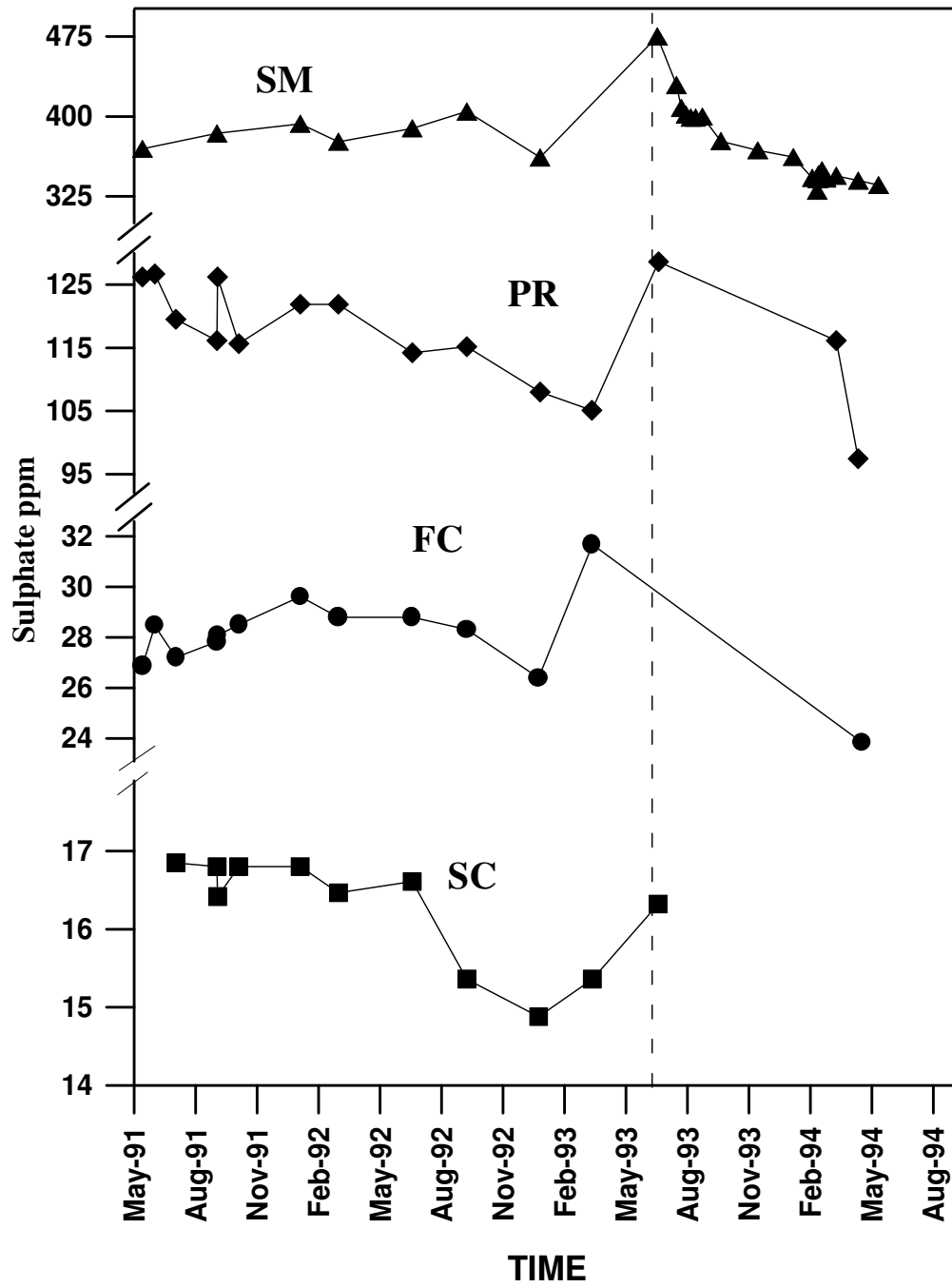
Flow changes and geochemical anomalies in warm...

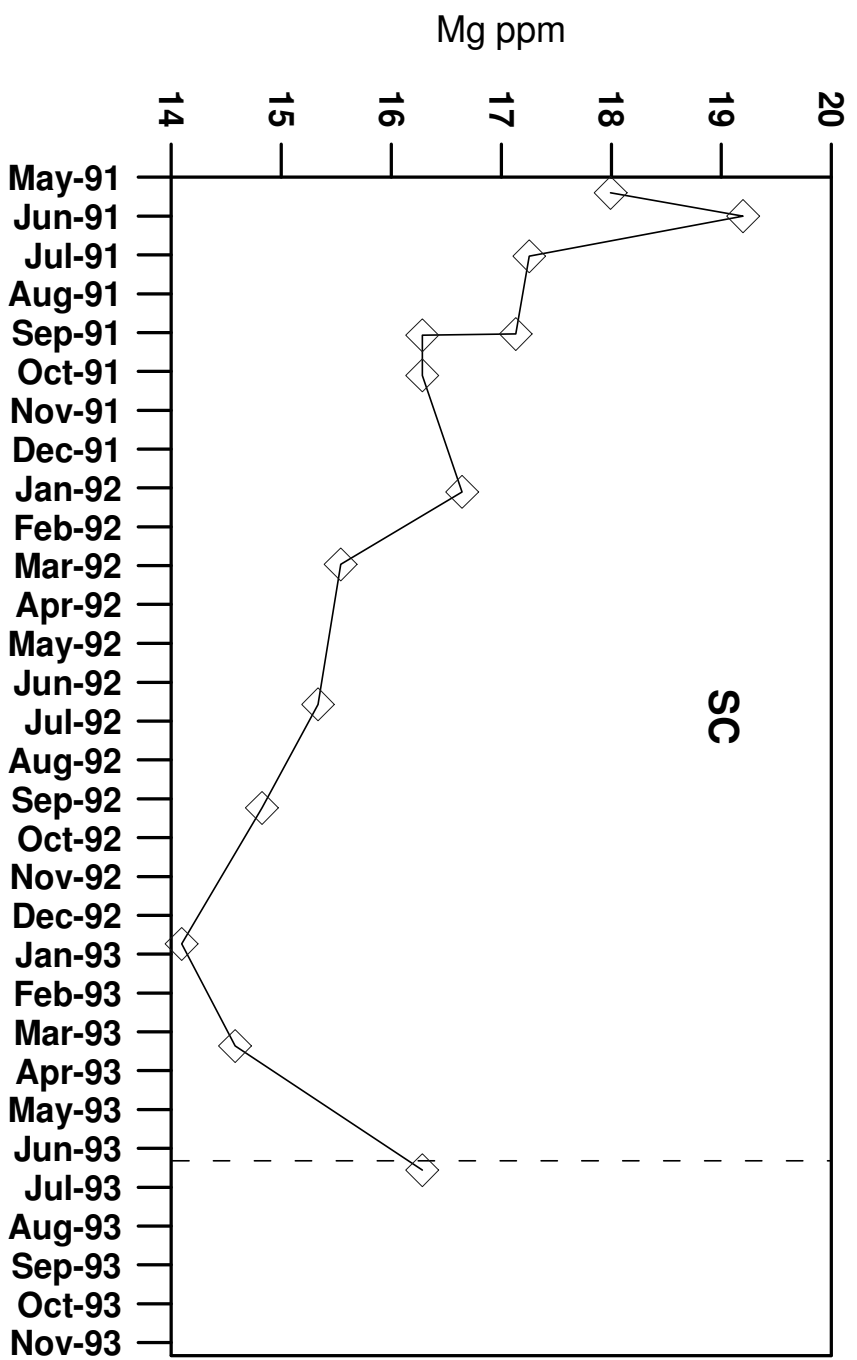


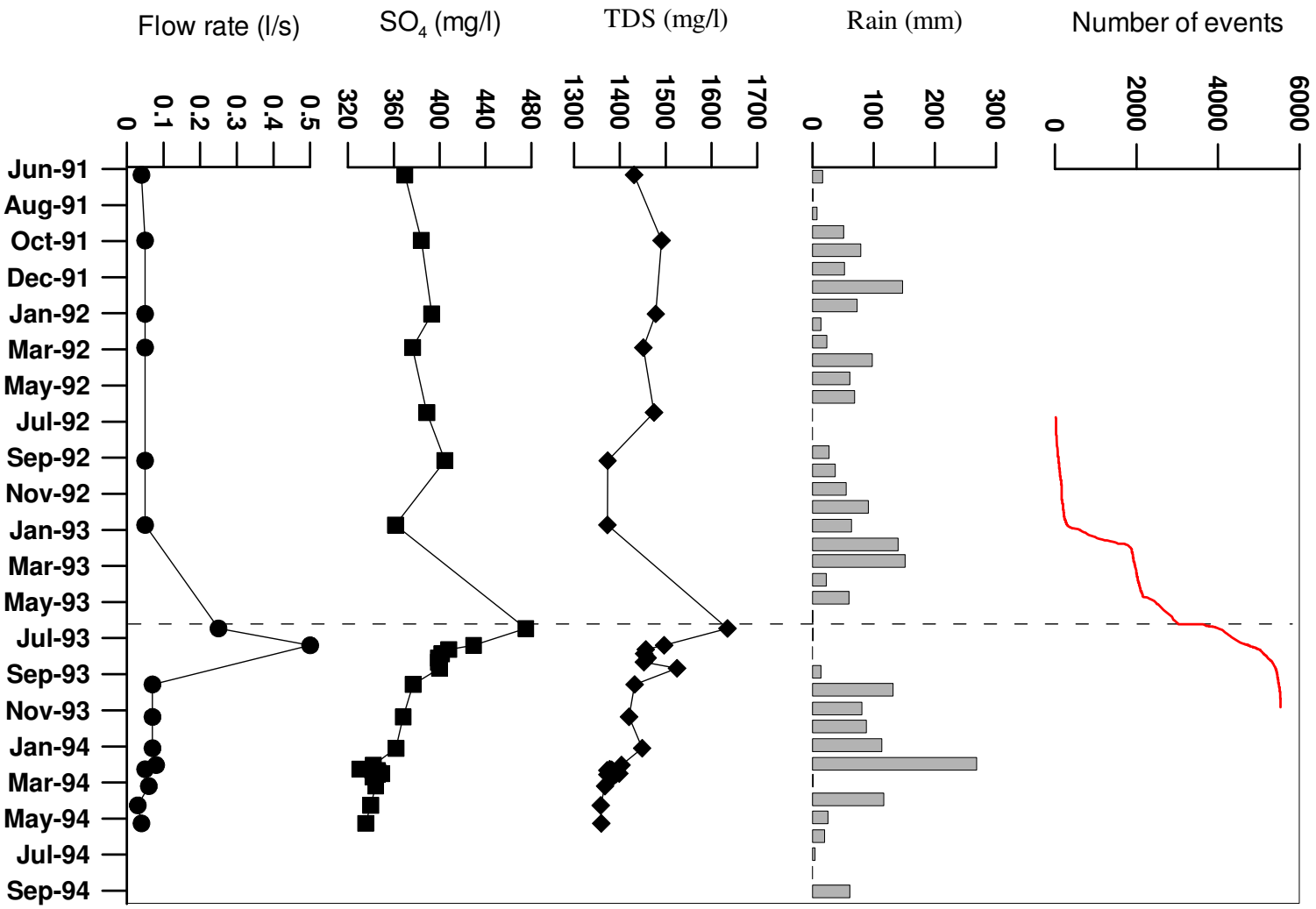
Flow changes and geochemical anomalies in warm...



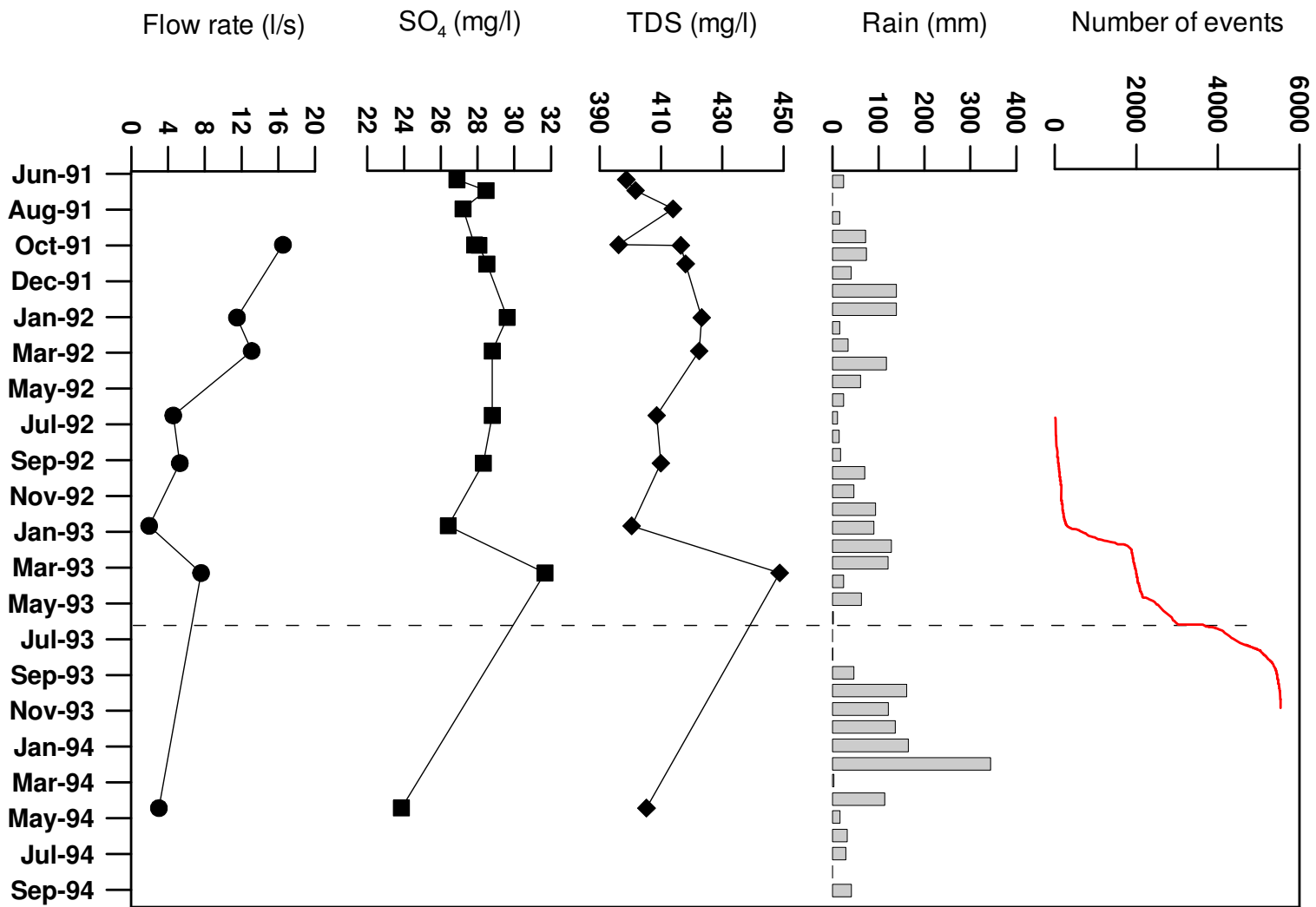


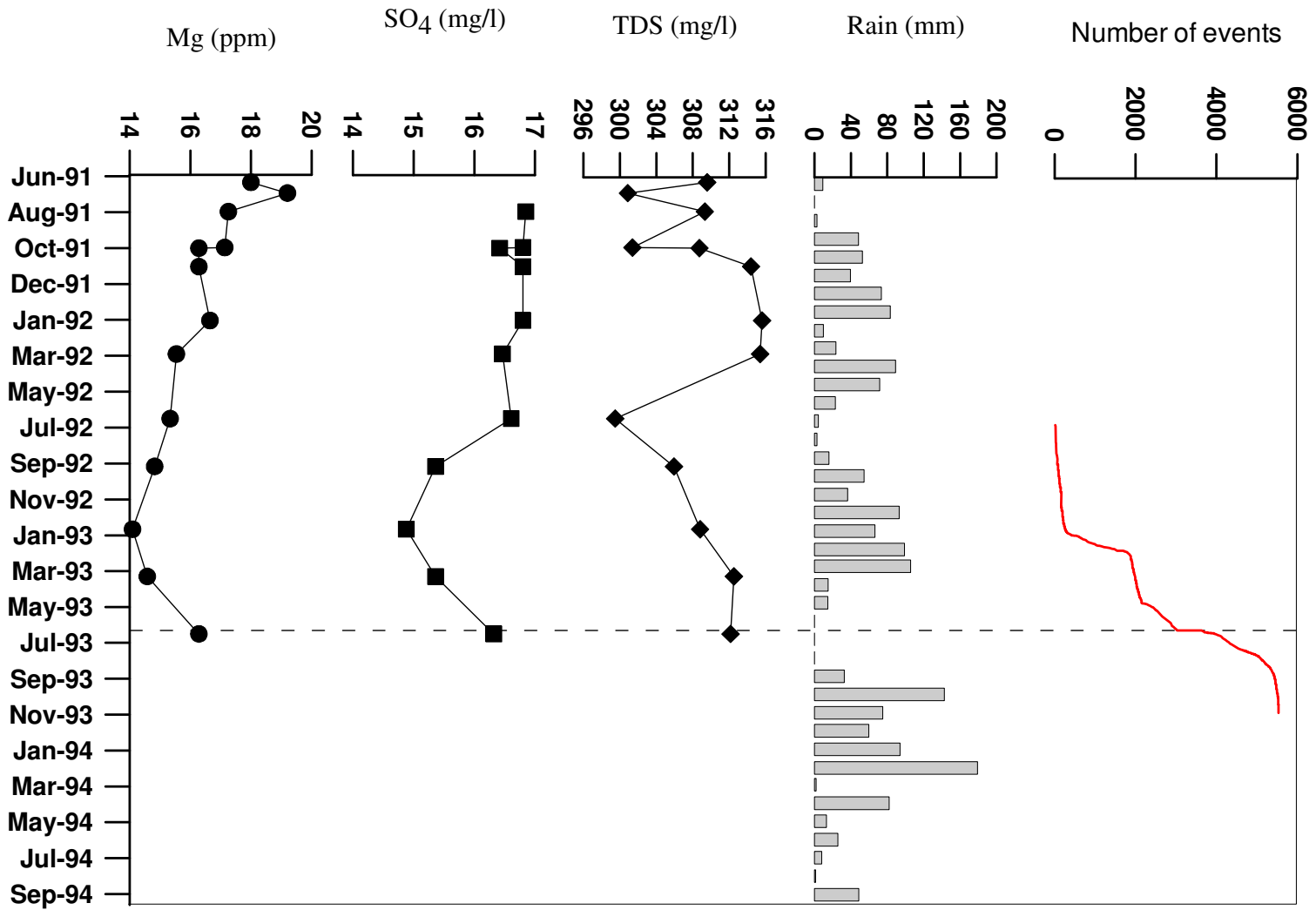






Flow changes and geochemical anomalies in warm...





Flow changes and geochemical anomalies in warm...

Sample	Date	Flow rate	pH	EC	T	Na	K	Ca	Mg	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	TDSS
SM <sup>a</sup>	13-6-91	0.04	7.36	1960	16.8	178	16	141	59	189	370	476	1431
	30-9-91	0.05	7.47	1970	18.6	211	18	143	63	201	384	470	1491
	30-1-92	0.05	7.72	1920	15.8	194	17	136	64	209	393	464	1479
	26-3-92	0.05	7.63	1930	15.4	209	15	140	49	202	376	458	1451
	12-7-92	n.m.	7.28	2000	17.8	211	13	136	60	203	389	458	1475
	30-9-92	0.05	7.26	1941	19.0	197	15	121	54	195	405	384	1373
	15-1-93	0.05	7.78	1860	15.9	184	13	140	58	175	361	439	1373
	6-7-93	0.25	7.18	1880	17.0	229	17	159	65	213	475	476	1635
	3-8-93	0.50	7.26	1860	17.4	210	18	146	65	211	430	415	1496
	10-8-93	n.m.	n.m.	n.m.	n.m.	210	18	144	61	203	408	409	1457
	17-8-93	n.m.	n.m.	n.m.	n.m.	212	18	143	61	200	402	415	1453
	24-8-93	n.m.	n.m.	n.m.	n.m.	209	18	146	61	198	399	427	1461
	31-8-93	n.m.	n.m.	n.m.	n.m.	213	19	144	61	198	399	415	1452
	10-9-93	n.m.	7.23	1991	17.8	211	17	152	60	194	400	488	1525
	7-10-93	0.07	7.10	1910	17.6	205	19	144	61	194	377	427	1432
	30-11-93	0.07	7.16	1375	16.1	206	19	143	60	193	368	427	1420
	21-1-94	0.07	7.25	1675	16.7	200	18	144	64	192	362	464	1448
	18-2-94	0.08	7.44	1816	16.5	197	17	137	61	168	342	476	1404
	25-2-94	0.05	7.37	1824	16.5	197	18	137	59	157	330	476	1378
	26-2-94	n.m.	n.m.	n.m.	n.m.	189	17	124	63	169	341	476	1382
	27-2-94	n.m.	n.m.	n.m.	n.m.	188	17	124	63	169	346	464	1373
	28-2-94	n.m.	n.m.	n.m.	n.m.	189	17	124	64	168	344	476	1385
	1-3-94	n.m.	n.m.	n.m.	n.m.	191	17	119	64	167	343	470	1377
	2-3-94	n.m.	n.m.	n.m.	n.m.	192	17	122	64	165	346	476	1389
	3-3-94	n.m.	n.m.	n.m.	n.m.	188	17	126	63	172	342	470	1386
	4-3-94	n.m.	n.m.	n.m.	n.m.	191	17	126	63	174	349	476	1399
	5-3-94	n.m.	n.m.	n.m.	n.m.	192	17	126	63	170	346	476	1392
	6-3-94	n.m.	n.m.	n.m.	n.m.	191	17	122	64	169	344	464	1373
	7-3-94	n.m.	7.20	1798	16.5	190	17	124	63	168	344	470	1379
	8-3-94	n.m.	n.m.	n.m.	n.m.	188	17	124	63	168	344	476	1383
9-3-94	n.m.	n.m.	n.m.	n.m.	188	17	124	63	169	343	476	1383	
10-3-94	n.m.	7.32	1760	16.5	192	17	124	63	168	342	476	1384	
25-3-94	0.06	7.12	1780	16.5	188	14	127	54	162	344	476	1368	
26-4-94	0.03	7.37	1805	16.6	187	14	130	55	155	340	476	1358	
26-5-94	0.04	7.41	1750	17.0	180	14	131	56	154	336	488	1359	
M2 <sup>a</sup>	30-11-93	0.13	7.28	1562	17.9	94	13	207	66	97	550	306	1335
M3 <sup>a</sup>	30-11-93	0.42	6.74	1635	20.6	92	12	203	66	95	492	392	1356
PC <sup>b</sup>	18-2-94	n.m.	7.40	2563	28.6	638	12	6	2	172	10	1484	2328
SO <sup>a</sup>	13-6-91	n.m.	6.95	696	13.1	31	1	122	21	21	129	403	729
	30-9-91	0.06	7.16	726	14.6	39	2	133	24	23	134	421	776
	30-1-92	0.40	7.28	728	13.1	36	1	136	24	25	164	403	792

Flow changes and geochemical anomalies in warm...

SC <sup>a</sup>	26-3-92	0.40	7.61	700	12.4	35	1	141	21	25	144	397	765	
	12-7-92	n.m.	n.m.	790	13.3	34	1	141	21	25	141	403	766	
	30-9-92	0.08	7.33	696	14.4	36	1	132	20	20	130	345	686	
	16-1-93	0.50	7.20	709	12.9	43	1	152	24	22	127	384	758	
	1-4-93	0.75	7.13	744	12.1	33	2	134	20	23	113	397	726	
	8-7-93	1.50	7.11	666	13.7	38	1	134	22	23	130	415	766	
	1-5-94	n.m.	7.04	802	12.7	31	1	125	20	18	109	397	707	
	1-6-94	0.50	6.93	800	12.7	32	1	130	21	19	112	409	729	
	13-6-91	432	7.69	342	14.2	8	1	50	18	9	16	207	310	
	1-7-91	n.m.	7.63	439	12.2	8	1	44	19	10	15	203	301	
	1-8-91	n.m.	7.74	425	14.1	7	1	50	17	9	17	207	309	
	30-9-91	410	7.20	314	14.6	6	1	49	17	9	17	201	301	
	1-10-91	n.m.	n.m.	382	13.8	7	1	51	16	9	16	207	309	
	1-11-91	n.m.	n.m.	405	13.7	7	1	50	16	9	17	214	314	
	30-1-92	452	7.77	315	13.4	7	1	50	17	9	17	214	316	
	26-3-92	447	7.61	306	13.8	7	1	51	16	10	16	214	315	
	12-7-92	419	7.42	312	14.3	7	1	48	15	10	17	201	299	
	30-9-92	380	7.64	303	14.5	7	1	49	15	8	15	210	306	
	13-1-93	380	7.87	296	12.3	7	1	51	14	7	15	214	309	
	PR <sup>a</sup>	2-4-93	550	7.77	293	13.1	7	1	52	15	8	15	214	313
7-7-93		500	7.63	315	14.5	7	1	50	16	10	16	210	312	
13-6-91		759	7.18	2745	15.4	507	21	134	63	910	126	275	2041	
1-7-91		n.m.	7.23	3891	15.5	548	20	125	62	892	127	276	2056	
1-8-91		n.m.	7.25	3720	15.3	534	19	127	60	863	120	275	2003	
30-9-91		651	7.17	2497	15.5	465	19	117	60	862	116	275	1916	
1-10-91		n.m.	n.m.	3292	15.5	471	16	121	56	809	126	275	1880	
1-11-91		n.m.	n.m.	3270	15.5	458	16	113	56	753	116	275	1794	
30-1-92		941	7.29	2431	15.5	436	13	106	51	807	122	275	1812	
26-3-92		588	7.36	2465	15.5	436	13	106	51	807	122	275	1812	
12-7-92		624	7.12	2662	15.4	482	13	123	56	887	114	281	1963	
30-9-92		619	7.42	2310	15.7	442	16	100	47	796	115	275	1796	
15-1-93		655	7.48	2594	15.4	465	20	118	63	808	108	275	1867	
1-4-93		403	7.41	2592	15.1	459	23	137	58	864	105	275	1942	
8-7-93		811	7.47	2610	15.5	520	20	129	58	917	129	275	2052	
25-3-94		n.m.	7.33	3080	15.6	535	11	126	56	938	116	275	2064	
26-4-94		n.m.	n.m.	n.m.	n.m.	425	14	106	51	740	97	275	1715	
FC <sup>a</sup>		13-Jun-91	26.40	7.39	442	16.5	13	1	59	26	15	27	253	399
		1-Jul-91	n.m.	7.47	546	16.5	12	1	55	28	16	28	258	402
		1-Aug-91	n.m.	7.46	546	16.5	12	2	58	27	29	27	256	414
	30-Sep-91	16.50	7.15	425	16.8	12	2	54	28	15	28	256	396	
	1-Oct-91	n.m.	7.44	524	16.5	13	1	56	27	15	28	275	416	
	1-Nov-91	n.m.	n.m.	527	16.2	13	1	57	28	14	29	275	418	
	30-Jan-92	11.50	7.47	430	16.2	13	1	58	29	15	30	275	423	

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26-Mar-92	13.10	7.32	432	16.2	12	2	58	28	17	29	275	422
12-Jul-92	4.56	7.26	416	16.7	11	2	54	27	15	29	268	409
30-Sep-92	5.28	7.20	428	17.1	11	1	56	26	13	28	271	410
13-Jan-93	1.94	7.83	398	14.9	10	2	51	27	13	26	268	400
2-Apr-93	7.59	7.57	477	15.9	14	2	62	28	18	32	287	449
1-May-94	3.00	7.44	450	17.0	12	1	58	25	14	24	268	405