

Effects of the Cinarcik - Ismiit August 17, 1999 earthquake on the composition of thermal and mineral waters as revealed by chemical and isotope investigations

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RESUMEN

Se presentan los efectos del sismo Ismiit ocurrido el 17 de agosto de 1999 sobre los cambios en la composición química de aguas termales y minerales en las zonas más afectadas de (1) Kuzuluk, (2) Bursa, y (3) Yalova/Gemlik en la zona de fallas "North Anatolian". Los muestreos se realizaron antes del evento, en julio de 1999 y después del evento, en octubre de 1999 y octubre de 2000. En estas tres áreas las aguas han mostrado cambios en su composición isotópica de ²H y ¹⁸O; de ³⁶Cl y ¹³C, así como en sus constituyentes químicos y parámetros físicos durante el período 1987-1996. Tales variaciones están relacionadas probablemente con la actividad tectónica del área y la circulación inducida del agua subterránea.

PALABRAS CLAVE: Actividad tectónica, precursores de sismos, hidrogeoquímica, composición isotópica, aguas termales y minerales, fluorescencia, ácidos fúlvicos/húmicos.

ABSTRACT

Effects of the August 17, 1999 Ismiit earthquake include to short-term changes in the composition of thermal and mineral waters in the areas of Kuzuluk, Bursa, and Yalova/Gemlik along the North Anatolian Fault Zone. We report the results of groundwater sampling campaigns before and after the earthquake. For these three areas changes of isotopic composition in ²H and ¹⁸O of the water, and in ¹³C of the dissolved species of inorganic carbon, as well as changes of some chemical constituents and physical parameters, were observed. These changes are most probably related to the active tectonics of the area and to induced groundwater circulation.

KEY WORDS: Active tectonics, earthquakes precursors, hydrochemistry, isotopic composition, thermal and mineral waters.

INTRODUCTION

The area which was affected by the Cinarcik - Ismiit August 17, 1999 earthquake (Figure 1) is situated within the North Anatolian Fault Zone (NAF), is subject to several investigations related to active tectonics and seismic survey (Schindler *et al.* 1997, Zschau and Ergünay, 1996). Schindler *et al.* (1997) reported the effects of active tectonics, as evidenced by geology, geodesy and seismology, on groundwater circulation and on the heat flow pattern in six selected areas along the North Anatolian Fault Zone in the years 1987 to 1996.

The mineral and thermal waters of these six areas (Figure 2) were investigated in the frame of an IAEA Co-ordinated Research Project, leading to new sampling activities in the time span of 6 to 11 July 1999. About one month later, on August 17, 1999 the M 7.4 Gölcük - Izmit earthquake occurred.

In order to observe possible effects of this catastrophic earthquake on the isotopic and chemical composition of thermal and mineral waters within the surrounding areas, another sampling campaign was undertaken between 2 to 6 October 1999 that included the thermal areas of Kuzuluk (Adapazari), Bursa/Cekirge and the three spas of Yalova, Armutlu and Gemlik on the Yalova peninsula.

Additional sampling campaigns were carried out from 3 to 8 October 2000 and from 8 to 14 July 2001. The time interval of about one year was selected in order to obtain observations in periods of reduced tectonic activity.

EXPERIMENTAL LABORATORY ANALYSES

Physical parameters such as temperature, electrical conductivity, and pH were directly measured at the sampling sites. The CO₂, HCO₃ and O₂ contents of the sampled waters were directly determined by titration in the field.

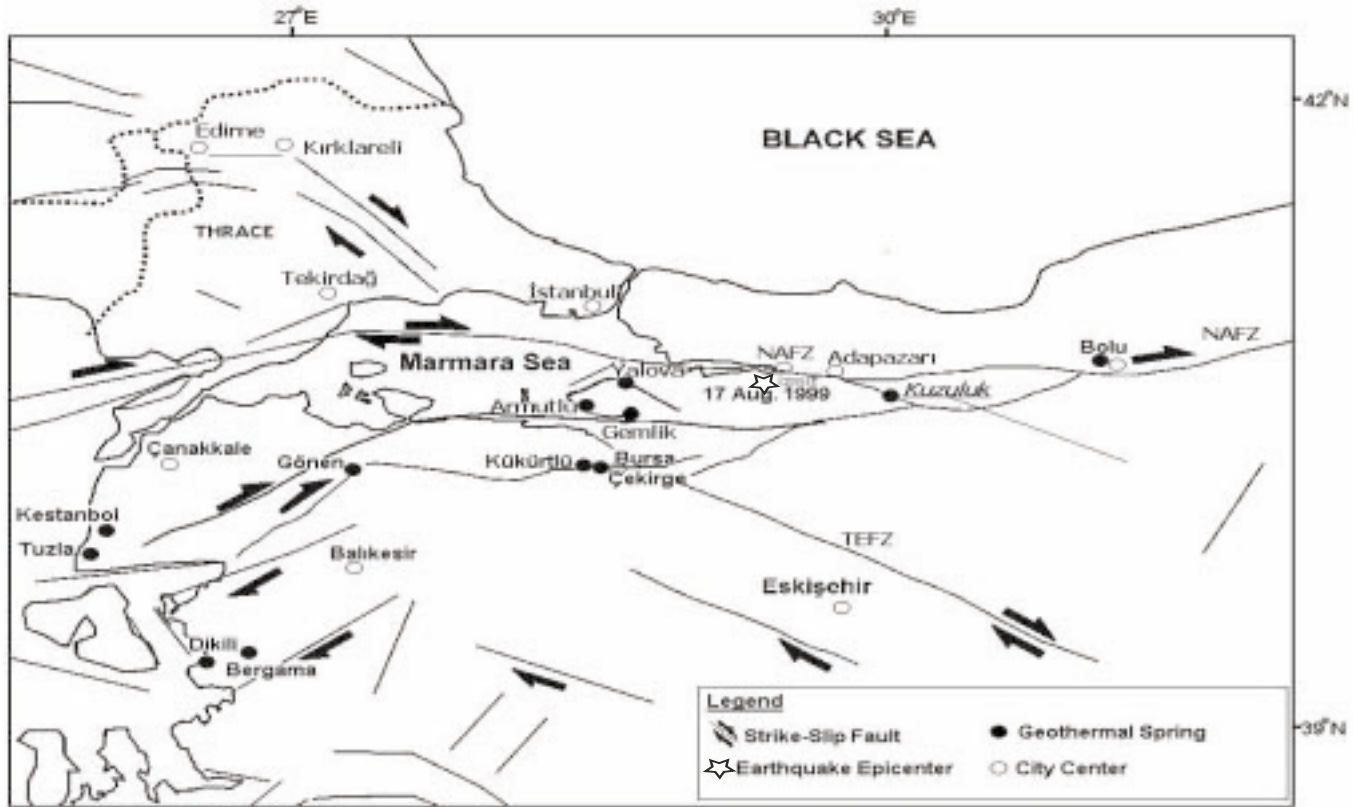


Fig. 1. Active fault lines and hot spring distribution in the Eastern Marmara region, North-Western Turkey (according to Simsek and Yildirim, 2000)

The water samples were then analysed for its main chemical composition by Ion Chromatography (IC) at the hydrochemical laboratory of Engineering Geology, Geological Institute of ETH (Eidgenössische Technische Hochschule, equivalent to Federal Institute of Technology) in Zurich. The isotopic composition of the investigated waters in ^2H , ^{18}O , and tritium were determined at the Gesellschaft für Strahlen- und Umweltforschung (GSF) Hydrology Laboratory in Neuherberg, Germany. BaCO_3 precipitation made directly at the sampling sites by adding $\text{Ba}(\text{OH})_2$ to the volume of about 20 l of the sampled water was processed for ^{13}C and ^{14}C at HYDROISOTOP, Germany.

From the analyses of water samples for the three major sampling campaigns, variations with respect to sampling prior and after the August 17, 1999 earthquake (Figure 1 and 2) were observed as follows

(a) **Variations in the concentration of some cations e.g. calcium, potassium, sodium, and anions such as nitrate, sulphate and chloride.**

- The variation of chemical constituents of the samples from the Kuzuluk mineral spring (KuzMin), the Bursa Kükürtlü and Yalova Thermal springs, and the Armutlu thermal

borehole (Figure 3), may be interpreted as related to the mixing of waters of superficial origin, which may contain some anthropogenic pollutants such as nitrates, and the mobilisation of deep-seated brines by seismic-tectonic activity as revealed by changes in the chemical composition of the thermal and mineral waters.

(b) **Variations of ^2H and ^{18}O contents of waters (Figure 4).**

The ^{18}O isotopic composition of the water of Kuzuluk thermal well, Kuzuluk mineral spring, and Bursa Kükürtlü thermal spring (Figure 4) show variations in oxygen content which may be caused by isotopic exchange with the CO_2 gas phase (Greber, 1994). Additionally, observed changes in ^2H contents of the Kuzuluk samples are most probably due to an exchange with H_2S gas, which is observed at both sites (Balderer, 2001, Greber, 1994).

For all other water samples the observed variations of the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values are attributed to mixing processes as the variations are occurring along the local meteoric water line (Balderer, 1997, in Schindler et al., 1997), with groundwater of shallow or deep origin of different infiltration conditions.



Fig. 2. Investigation areas of the Marmara Project in Western Turkey.

(c) *Variations in ^{13}C - content of the total dissolved inorganic carbon (TDIC) together with varying HCO_3 , CO_2 contents.*

These observed variations (Figure 5) are attributed to an additional process of enhanced upwelling of CO_2 in tectonically induced fractures, which affects the content and isotopic composition of dissolved carbonate species and of CO_2 , and to the ^{18}O isotopic composition of water by isotopic exchange with the CO_2 gas phase (Balderer *et al.*, 1991, Greber, 1994, Tschudi, 1997, Balderer, 2001)

MECHANISMS RESPONSIBLE FOR THE OBSERVED VARIATIONS IN CHEMICAL AND ISOTOPIC COMPOSITION OF THERMAL AND MINERAL WATERS

In order to find the most probable links to a seismotectonic incidence, a further interpretation of some observed isotopic and chemical parameters is attempted by applying

combined interpretation methods of isotope hydrology and hydrochemistry.

Within the system of dissolved inorganic carbon (TDIC) in groundwater three different types of interaction should be considered between the dissolved species of inorganic carbon and the carbonate minerals, mainly calcites within crystalline rock environments, or calcite and dolomite in sedimentary rock environments (Balderer *et al.* 1987): (i) the open system reaction controlled by a large independent CO_2 reservoir, (ii) the opposite case of a closed system reaction, where the TDIC is formed by mixing CO_2 and solid carbonate subsequent in partial equilibrium with the gas phase or with the solid carbonate phase, and (iii) a step-by-step case, where reactions occur first under open-system and then under closed-system conditions.

Observed changes in ^{13}C and HCO_3 and CO_2 concentrations suggest consideration of an "open system approach",

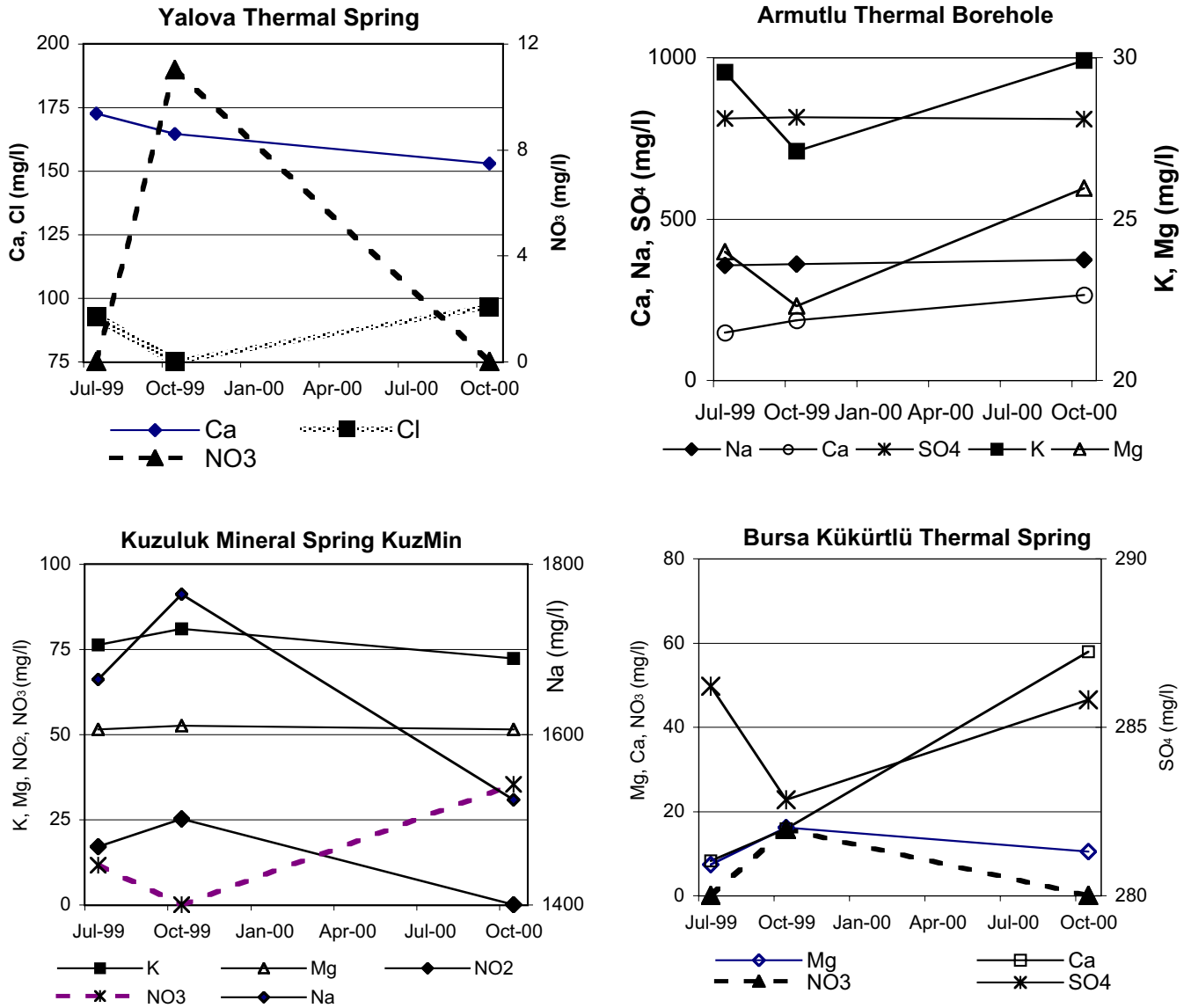


Fig. 3. Variations in the concentration of some cations for e.g. calcium the potassium, sodium, and of some anions such as nitrate, sulphate and chloride for selected samples of investigated thermal and mineral waters originating from 3 sampling periods (time intervals: July 1999, October 1999, July 2000)

which is also adequate for systems with additional CO₂ influx caused by tectonic processes as observed in the areas of Kuzuluk, Gemlik and Bursa (Greber, 1992, Eisenlohr, 1995, Balderer, 1997) from soil gas measurements.

For the **open system case** the following equations were used (Deines et al., 1974, Wigley, 1975, Wigley et al. 1978, Fontes, 1983, IAEA, 1983):

$$\delta_{\text{TDIC}} = \frac{[\delta_{\text{CO}_2(\text{g})} * m_{\text{CO}_2} + \delta_{\text{H}_2\text{CO}_3} * m_{\text{H}_2\text{CO}_3} + \delta_{\text{HCO}_3} * m_{\text{HCO}_3} + \delta_{\text{CO}_3} * m_{\text{CO}_3}]}{\sum m_i} \quad (1)$$

where $\sum m_i$ stands for the sum of concentrations of inorganic carbon species in solution equal to the total dissolved inorganic carbon = m_{TDIC} .

As in the case of open-system conditions with gaseous CO₂ an isotopic equilibrium exists between these dissolved carbon species, their ¹³C contents are related by

$$\epsilon_{\text{CO}_2(\text{g})-i} \approx \delta_{\text{CO}_2(\text{g})} - \delta_i, \quad (2)$$

where δ_i corresponds to the ¹³C values of the considered dissolved carbon species.

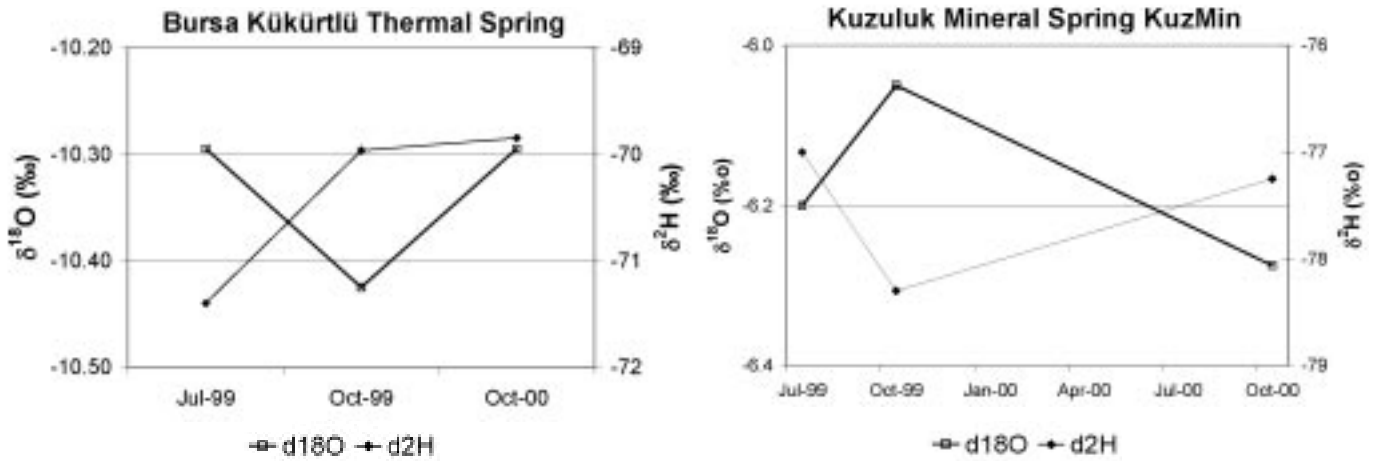


Fig. 4. Variations of the ²H and ¹⁸O contents of the investigated waters of the Kuzuluk Mineral Spring and the Bursa Kükürtlü thermal spring from 3 sampling periods.

The next steps are oriented to the determination of the ¹³C content of the TDIC by applying the above relationships with the simplifications:

$$m_{CO_2} \approx m_{CO_2(g)} + m_{H_2CO_3}$$

$$\text{and } \delta^{13}C_{CO_2} \approx [\delta_{CO_2(g)} * m_{CO_2} + \delta_{H_2CO_3} * m_{H_2CO_3}] / m_{CO_2} \quad (3)$$

where $m_{CO_3} \approx 0$

as in the measured pH range of 6.6 to 7.6 the amount of the carbonate species is negligible.

Finally this results in the following equations:

$$\delta^{13}C_{TDIC} = [\delta^{13}C_{CO_2} * m_{CO_2} + \delta_{HCO_3} * m_{HCO_3}] / [m_{CO_2} + m_{HCO_3}] \quad (4)$$

and with introduction of the corresponding fractionation factors:

$$\delta^{13}C_{TDIC} = [\delta^{13}C_{CO_2} * m_{CO_2} + (\delta^{13}C_{CO_2} - \epsilon_{HCO_3-CO_2}) * m_{HCO_3}] / [m_{CO_2} + m_{HCO_3}] \quad (5)$$

The $\delta^{13}C_{CO_2}$ may directly be determined by introducing the measured values of $\delta^{13}C_{TDIC}$ and the concentrations of the main carbonated species m_{CO_2} and m_{HCO_3} .

The resulting modelled $\delta^{13}C_{CO_2}$ are represented together with the measured values in Figure 6.

From the modelled $\delta^{13}C_{CO_2}$ values for three sampling periods (July 1999, October 1999, and October 2000) it is found that the addition of the following mixing components

of gaseous CO_2 are most probably responsible for the observed changes.

CO_2 of atmospheric origin: $\delta^{13}C$: -7 ‰ from thermal waters of Yalova and Bursa Vakif Bahce

CO_2 of biologic origin (root zone): $\delta^{13}C$: -25 to -23 ‰ from thermal waters of Gemlik and Bursa Havuzlupark

CO_2 of mantle origin: $\delta^{13}C$: -8 to -2 ‰ from waters of Bursa Kükürtlü and Kuzuluk (with a possible influence of Armutlu)

CO_2 of thermo metamorphic origin: $\delta^{13}C$: 0 to +2 ‰ from water of Armutlu

These results may further be used for the characterization of the involved processes.

The observed changes in water chemistry and the slight changes in stable isotope contents may be explained by mixing with some amount of water of different origin, as (i) with waters of superficial origin and (ii) by partial mobilisation of deep-seated brines by the increased seismo-tectonic activity. The observed changes of $\delta^{13}C$ values for dissolved inorganic carbon, and the concentration of dissolved species CO_2 and HCO_3 , may be related to the exchange in isotopic equilibrium with CO_2 for different sources of origin; (ii) enhanced upwelling of CO_2 in tectonically-induced fractures of thermo-metamorphic or mantle origin, and/or (iii) with CO_2 of atmospheric origin in contact with air by open fractures, or of biogenic origin from the normal infiltration evolution of groundwater.

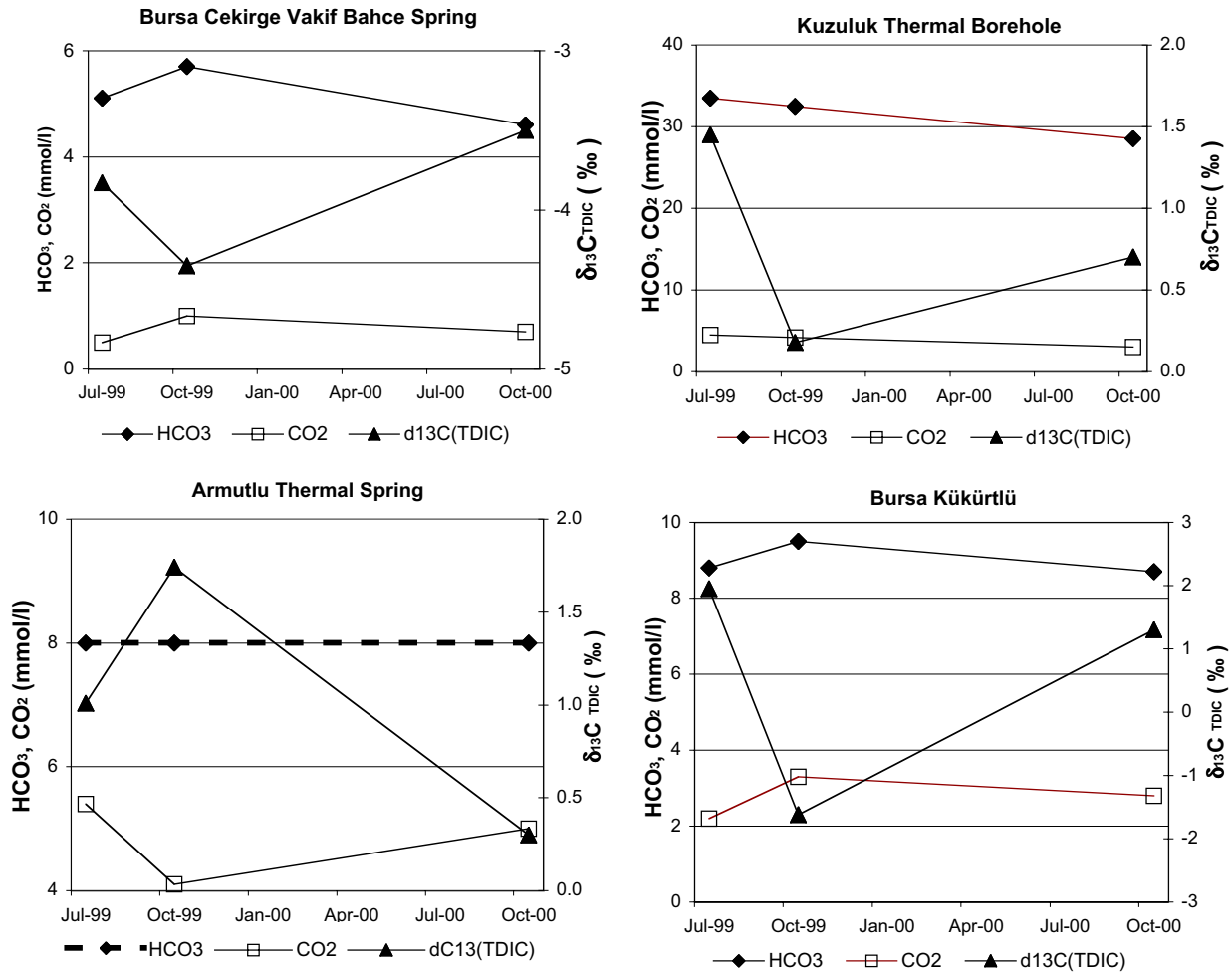


Fig. 5. Variations in the ¹³C- content of the total dissolved inorganic carbon (TDIC) which coincide with varying HCO₃, CO₂ contents for 4 investigated thermal and mineral waters originating from 3 sampling periods.

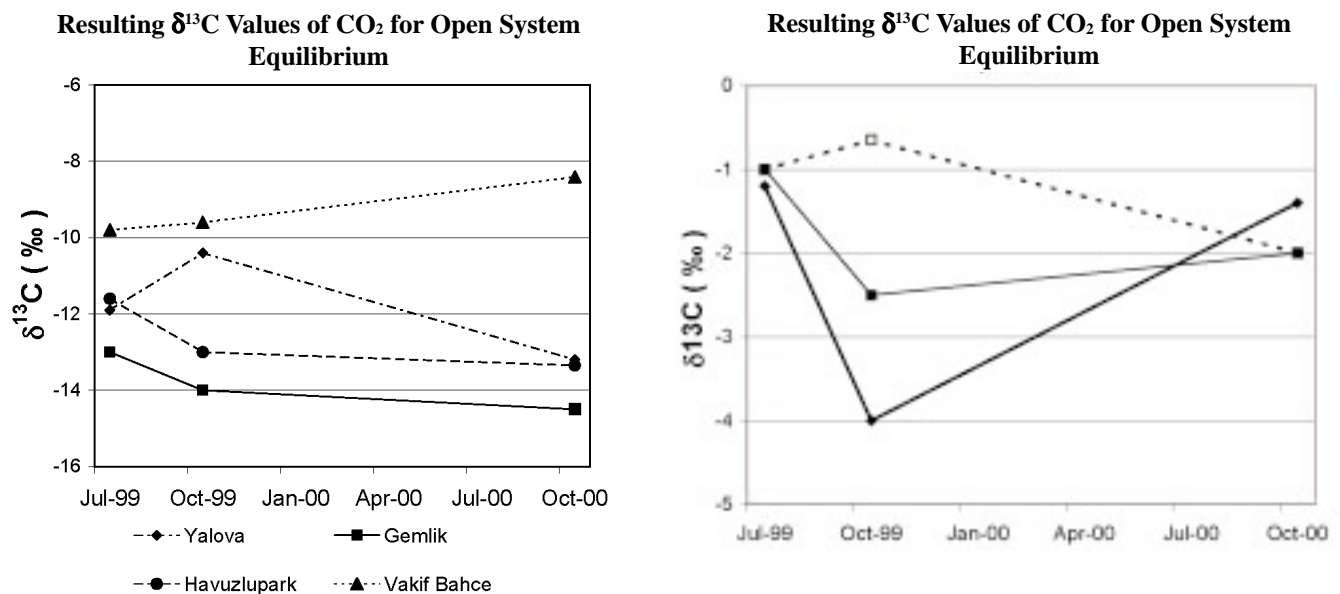


Fig. 6. Diagram of the resulting ¹³CO₂ values according to the application of the open system approach (isotopic equilibrium with the CO₂ gas phase) for the investigated thermal and mineral waters originating from 3 sampling periods.

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