

Determination of Elements in Thermal Springs for Monitoring Pre-Earthquake Activities by ICP-MS

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INTRODUCTION

Because earthquakes occur frequently and are often destructive, the detection of short-term precursors for signs of possible earthquakes has generated much interest and is of great importance. Prediction of timing, location, and magnitude must be reliable because of the economic and social impact of preemptive action and because false alarms can quickly undermine societal confidence in scientific advice. In other words, predictions must be timely such that preemptive action remains feasible, but not too long before an earthquake, so as to risk public complacency (1).

It is considered that deep geodynamic processes in the Earth's crust can simultaneously produce anomalies in gas composition, changes in water temperature, electrical conductivity, etc. (2). Earthquake-related changes were reportedly observed before and after many destructive earthquakes, especially at certain relatively "sensitive" sites (3-4). These sensitive sites are usually situated along active faults, especially at intersections of faults, and for large events may be at unexpectedly large epicenter distances hundreds of kilometers (km) away (5).

Seismically active faults are characterized by relatively high values of permeability. Since earthquakes are physical phenomena, most of the techniques currently used for prediction purposes are based on geophysical approaches, including

ABSTRACT

This study presents the results of hydrogeochemical studies carried out at the Kos thermal springs in Bingol, located in East Anatolia, Turkey. More than 250 thermal water samples were collected on a regular basis from November 2006 to January 2009 to measure element concentrations as a monitor of earthquake precursors. Water samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS). The B, Ba, Br, and Ge concentrations were monitored for three years and ranged from 6822-7666, 64-101, 271-406, and 4.1-6.0 $\mu\text{g L}^{-1}$, respectively. The chloride concentrations for this period were in the 89-127 mg L^{-1} range. The data identify some element anomalies at least two hours prior to a major earthquake and for some time afterwards. These anomalies are characterized by decreases up to 20% in B, Ba, Cl, and Ge concentrations and can be attributed to stress/strain-induced pressure changes in the subsurface water systems. From this study, it can be suggested that thermal springs in a fault line area are ideal sites for monitoring precursors to earthquakes.

seismology, magnetism, electricity, and geodesy. Since the 1960s, various geochemical effects have been examined as possible earthquake forerunners mainly as a result of instrumental developments. Therefore, hydrologic and geochemical changes, like other geophysical parameters, have been studied extensively during the past decades, mainly in search of possible premonitory changes useful for

earthquake prediction (6-13). It was reported that many terrestrially generated gases (such as CO_2 , He, H_2 , Rn, CH_4 , N_2 , and various alkanes) and highly volatile metals (such as Hg, As, and Sb) (5, 14-15) can be expelled from active faults. Furthermore, most of the studies concerning geochemical precursors have been carried out in seismically active countries at hydrothermal systems mainly by gas monitoring and noting the concentration variations of dissolved ions such as HCO_3^- , Cl^- , SO_4^{2-} , Na^+ , and Ca^{2+} (3, 16-18). Anomalous changes in gases and ions dissolved in groundwater associated with seismic and volcanic events, which support the view that groundwater responds sensitively to the crustal strain changes and/or seismic waves, have been reported on numerous occasions (6, 19). These chemical and hydrological changes can be attributed to changes in groundwater circulating systems due to earthquake generation (20). Thus, it has been concluded that chemical changes in groundwater have provided useful information for earthquake prediction (6, 10). The enormous complexity of this challenge has not yet been met with adequate funding or manpower.

Graphite furnace atomic absorption spectrometry (GFAAS) together with preconcentration methods and inductively coupled plasma mass spectrometry (ICP-MS) are the most commonly used analytical methods to determine trace elements in various matrices including environmental, biological, and food samples (21-28). The advantages of ICP-MS over other methods

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are undoubtedly its sensitivity and multi-element capability, particularly when multi-element determinations are required (29-30).

In this study, the concentration of elements including B, Ba, Br, Cl, and Ge in groundwater were determined by ICP-MS. The changes in their concentration were evaluated when earthquakes occurred. The water samples were collected from the Kos thermal springs in Bingol, a city in the East Anatolia area of Turkey.

EXPERIMENTAL

Sampling Area

The site was selected based on previous observations and historical seismic crises. The Kos thermal springs are located in the highlands of East Anatolia, in Bingol, Turkey, at 39° 00' N, 40° 38' E (Figure 1). The temperature of these springs ranges from 36–47 °C. The city of Bingol is located in one of the most seismically active parts of Eastern Anatolia, and more than 10 destructive earthquakes ($M > 5$) have been recorded in this vicinity during the 20th century. One of the biggest earthquakes occurred on May 1, 2003, with a moment magnitude of $M = 6.4$, which caused about 200 deaths (31). On May 22, 1971, another large earthquake occurred ($M = 6.8$) and caused about 1000 deaths.

Sampling

Thermal water samples from the Kos thermal springs were collected in plastic containers on a regular basis from November 2006 to January 2009. The waters were sampled daily between 07:00-10:00 a.m. Prior to sampling, the plastic containers were cleaned with 0.1 mol L⁻¹ HNO₃, followed by rinsing with distilled water. The water samples were acidified with nitric acid (1.0 mL of concentrated HNO₃ was added to 1.0 L of water sample) to avoid precipitation and then trans-

ported to the lab for analysis. Each sample was analyzed three times; the mean values are given in the results section.

The data were analyzed using Minitab® 10 software (Minitab Inc., USA) for the Windows® program. One-way analyses of variance (ANOVA) were conducted to test the equality of the mean values for each element of interest. One of the pair-wise comparison tests, Tukey HSD, was carried out to establish the difference in element concentrations from one day to the next. A statistical analysis program (Statistical Packages for the Social Sciences, SPSS-version 13, SPSS Inc. Chicago, IL, USA) was used for all

statistical computations. Statistical significance was considered when P was equal to/or higher than 0.05.

Instrumentation

All measurements were performed using a PerkinElmer ELAN® 9000 ICP-MS spectrometer (PerkinElmer, Inc., Shelton, CT, USA), equipped with a Ryton® double-pass spray chamber and cross-flow nebulizer. The ICP-MS operating conditions were used as provided by the manufacturer (Table I). A surface water reference material (SPS-SW2 Surface Water, Spectrapure, Oslo, Norway) was employed to evaluate the accuracy of the measurements.

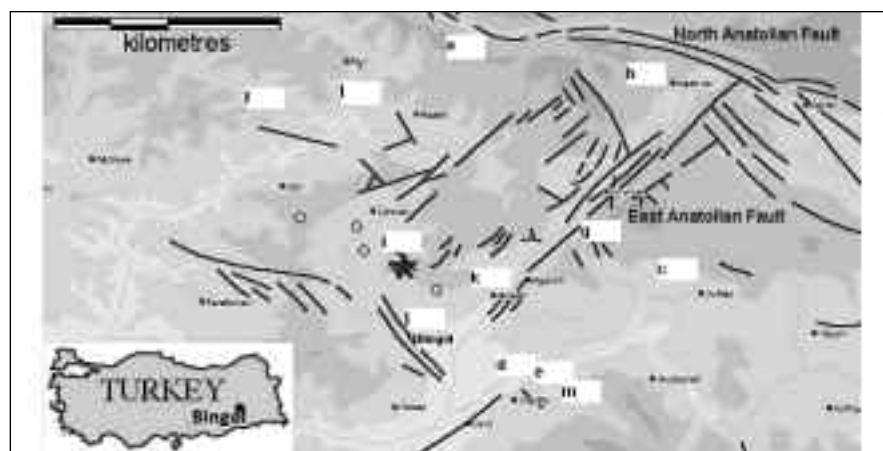


Fig. 1. Map of studied area (Eastern Anatolia, Turkey). The letters show where the earthquakes occurred in the period studied.

Water samples collected from points: a=Yedisu site, b=Karliova, c=Solban, d=Servi, e=Genc, f=Yayladere, g=Goynuk, i=Sancak, j=Bingol city center, k=Illica. Water samples collected from point k: l=Kigi, m=Sogutlu.

TABLE I
ICP-MS Operating Conditions

Instrumentation	PerkinElmer ELAN® 9000 ICP-MS
Nebulizer	Crossflow
Spray chamber	Ryton, double-pass
RF power	1000 W
Plasma gas flow rate	15 L min ⁻¹
Auxiliary gas flow rate	1.0 L min ⁻¹
Carrier gas flow rate	0.9 L min ⁻¹
Sample uptake rate	1.0 mL min ⁻¹
Detector mode	Auto
Integration time	Element-dependent
Internal standard	Ir

Standard Solutions and Reagents

The standard solutions of the elements (B, Ba, Br, Cl, and Ge) were prepared from their stock solutions (E. Merck, Darmstadt, Germany). A solution of 10 mg L⁻¹ Ir (E. Merck, Darmstadt, Germany) was employed as the internal standard because the mass of Ir covers the mass of each of the elements studied. Concentrated HNO₃ (Merck) was used for preparation of the water samples.

RESULTS AND DISCUSSION

In this study, we determined the concentration of over 30 elements in the thermal spring waters by ICP-MS. Among all of the elements studied, only the B, Ba, Br, Cl, and Ge concentrations were considered because increases or decreases in the concentrations of these elements were found near the earthquake areas. Accuracy of the results was checked by examining the Standard Reference Material SPS-SW2 Batch 113, Surface Waters. The barium concentration in this sample is 250 µg L⁻¹. It was observed that the recovery values were more than 95%.

Table II lists the mean element concentrations of more than 250 samples at the Kos thermal springs. As can be seen, the B, Ba, Br, and Ge concentrations in the groundwater samples during the sampling times in 2006, 2007, and 2008 ranged from 6822–7666, 64–101, 271–406, and 4.1–6.0 µg L⁻¹, respectively. Toutain et al. (3) also observed that chloride concentrations in spring water increased about 36% five days prior to an earthquake (3). Various models have been suggested to account for the chemical variations in spring water. Mixing of previously isolated groundwater systems is generally proposed to explain the ion changes. This procedure shows the variations in both cation and anion

concentrations, as well as temperature changes in the aquifers. The other hypothesis suggests that stress-induced variations in relative pressure among aquifers may generate reversible changes in hydraulic levels. Chloride concentrations in groundwaters are at ppm levels due to the high solubility of many chloride compounds. As a result, we also measured the chloride concentrations which ranged from 89 to 127 mg L⁻¹. A limited mixing of chemically different groundwaters is the most likely phenomenon that can generate such a drastic ion concentration change. Chloride-pure waters can therefore be expected to have been introduced within the chloride-rich waters.

The distribution of elements found in thermal water samples on days when earthquakes occurred are depicted in Figures 2–6. As observed, the change in concentration of B, Ba, Cl, and Ge are characteristic before and after the earthquake. The decrease or increase in concentration of these elements is summarized in Table III. It can be seen that the concentration of B, Ba, Cl, and Ge decreased by 12–20%. Considering all of the earthquakes observed, the largest variations occurred on February 3, 2007 (see Figures 2–6). On the other hand, an increase of about 10% in all studied elements was observed after the earthquake (M=5.4) occurred on the August 26, 2007. This is the only earthquake which occurred during this study with a magnitude of more than 5.0. This implies that water samples should be collected and analyzed within shorter periods, such as at 10-minute intervals.

The data show the studied element anomalies, at least one day prior to a minor earthquake occurring on February 3, 2007. There was a decrease in Cl⁻ concentration up to 19% and in B concentration of about 20% (Table III). Yalcin et

al. (2003) also observed variations in trace element concentrations in thermal water after an earthquake, particularly an increase in Cu and Ni and a decrease in Fe, Mn, and Zn (12). These anomalies can probably be attributed to the stress-/strain-induced pressure changes in the subsurface water systems which then generate precursory limited geochemical discharges at the subsurface reservoirs.

As can be expected, the variations in the concentration of dissolved ions in the groundwaters collected in this study are often very large. The variations of B, Ba, Cl, Ge, and Br concentrations are shown in Figures 2–6. It can be seen that the increase or decrease in element concentration varies depending on element species and time, and can also be attributed to the depth of the water sample taken. Therefore, it is suggested that more studies should be done and groundwater samples collected within 5- or 10-minute intervals.

Possible Mechanism

The earth's crust contains numerous pores and fractures filled with water, gas, and other fluids that have different chemical compositions at different places. When the crust is deformed in the tectonic process of earthquake generation, certain transient movements (fissure opening, fault creep, etc.) may be induced in the earth's crust (32). Fluids in the fault and other weak zones may be forced to migrate to different locations and thus cause the observed hydrologic and geochemical changes at these locations. Because of this difficulty (as well as the poor quality of some studies which sometimes failed to take proper account of background noise caused by such environmental variables as rainfall, barometric pressure, temperature, and earth tide), many geophysicists dismissed the earthquake-relatedness of such changes.

TABLE II
Mean Element Concentrations in Month-Year in Thermal Spring Waters
 (Values are mean concentrations $\pm$ standard deviation.)

Month-Year	Sample No.	B ($\mu\text{g L}^{-1}$)	Ba ($\mu\text{g L}^{-1}$)	Br ($\mu\text{g L}^{-1}$)	Cl (mg L^{-1})	Ge ($\mu\text{g L}^{-1}$)
November-06	2	7163 $\pm$ 206	64 $\pm$ 14	306 $\pm$ 50	93 $\pm$ 11	4.3 $\pm$ 0.4
December-06	5	6822 $\pm$ 224	65 $\pm$ 4	271 $\pm$ 18	89 $\pm$ 5	4.1 $\pm$ 0.2
January-07	23	6975 $\pm$ 136	74 $\pm$ 6	369 $\pm$ 53	112 $\pm$ 9	4.7 $\pm$ 0.2
February-07	24	7195 $\pm$ 342	79 $\pm$ 5	377 $\pm$ 24	110 $\pm$ 6	5.0 $\pm$ 0.3
March-07	22	7327 $\pm$ 89	70 $\pm$ 3	370 $\pm$ 10	113 $\pm$ 4	4.6 $\pm$ 0.1
April-07	11	7318 $\pm$ 158	70 $\pm$ 3	344 $\pm$ 33	110 $\pm$ 5	4.6 $\pm$ 0.3
May-07	11	7011 $\pm$ 426	69 $\pm$ 5	323 $\pm$ 18	107 $\pm$ 3	4.3 $\pm$ 0.2
June-07	3	6854 $\pm$ 30	68 $\pm$ 1	344 $\pm$ 2	108 $\pm$ 1	4.1 $\pm$ 0.1
July-07	10	7207 $\pm$ 271	80 $\pm$ 6	387 $\pm$ 16	101 $\pm$ 4	5.1 $\pm$ 0.3
August-07	13	7454 $\pm$ 248	83 $\pm$ 6	400 $\pm$ 18	108 $\pm$ 7	5.0 $\pm$ 0.4
September-07	4	7130 $\pm$ 188	74 $\pm$ 3	397 $\pm$ 23	118 $\pm$ 4	4.6 $\pm$ 0.2
October-07	11	7111 $\pm$ 113	78 $\pm$ 3	419 $\pm$ 13	127 $\pm$ 4	4.8 $\pm$ 0.2
November-07	3	7185 $\pm$ 145	77 $\pm$ 3	406 $\pm$ 14	124 $\pm$ 5	4.7 $\pm$ 0.3
December-07	25	7251 $\pm$ 129	75 $\pm$ 3	397 $\pm$ 28	122 $\pm$ 5	4.7 $\pm$ 0.2
January-08	15	7318 $\pm$ 142	74 $\pm$ 2	366 $\pm$ 24	124 $\pm$ 3	4.7 $\pm$ 0.1
February-08	13	7386 $\pm$ 129	75 $\pm$ 3	392 $\pm$ 7	125 $\pm$ 3	4.7 $\pm$ 0.1
March-08	17	7139 $\pm$ 85	71 $\pm$ 3	375 $\pm$ 10	118 $\pm$ 4	4.6 $\pm$ 0.2
April-08	12	6869 $\pm$ 180	68 $\pm$ 3	359 $\pm$ 11	110 $\pm$ 4	4.2 $\pm$ 0.1
May-08	11	6872 $\pm$ 102	69 $\pm$ 2	370 $\pm$ 8	105 $\pm$ 9	4.4 $\pm$ 0.2
June-08	19	6873 $\pm$ 65	73 $\pm$ 2	385 $\pm$ 30	110 $\pm$ 8	4.6 $\pm$ 0.2
July-08	19	7015 $\pm$ 131	74 $\pm$ 2	355 $\pm$ 35	105 $\pm$ 7	4.6 $\pm$ 0.2
August-08	1	7104 $\pm$ 34	74 $\pm$ 1	382 $\pm$ 10	96 $\pm$ 2	4.9 $\pm$ 0.1
September-08	1					
October-08	1					
November-08	7	7120 $\pm$ 96	75 $\pm$ 1	380 $\pm$ 14	95 $\pm$ 2	4.8 $\pm$ 0.1
December-08	8	7556 $\pm$ 103	99 $\pm$ 6	380 $\pm$ 17	100 $\pm$ 3	5.0 $\pm$ 0.2
January-09	5	7666 $\pm$ 68	101 $\pm$ 3	406 $\pm$ 9	104 $\pm$ 3	6.0 $\pm$ 0.1
Mean	296	7155 $\pm$ 267	74 $\pm$ 6	373 $\pm$ 35	111 $\pm$ 10	4.7 $\pm$ 0.3

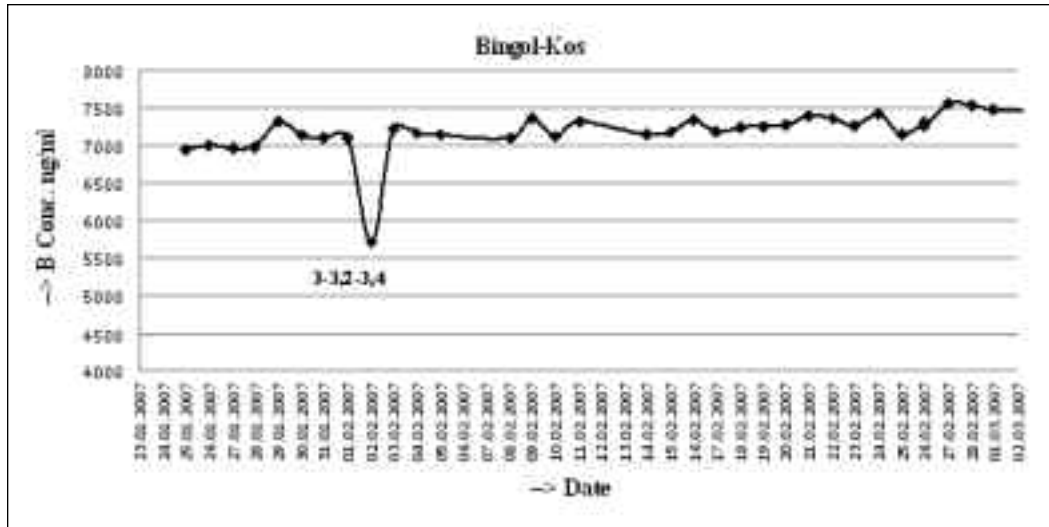


Fig. 2. Variations of B concentration in thermal water.

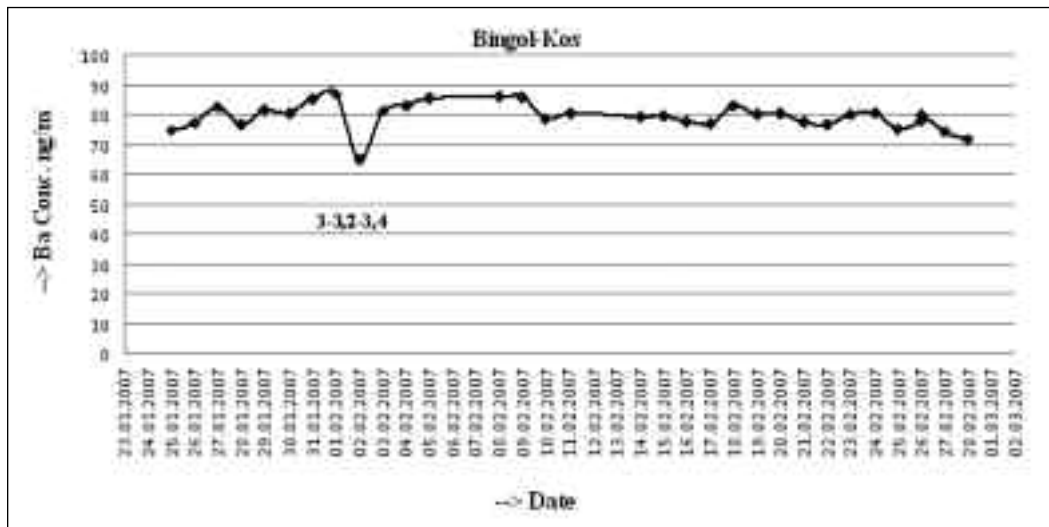


Fig. 3. Variations of Ba concentration in thermal water.

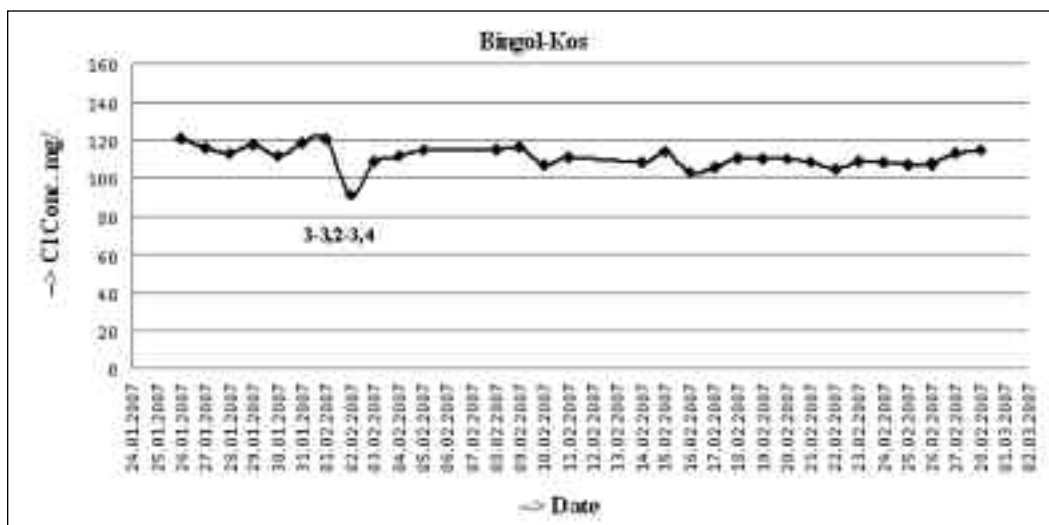


Fig. 4. Variations of Cl concentration in thermal water.

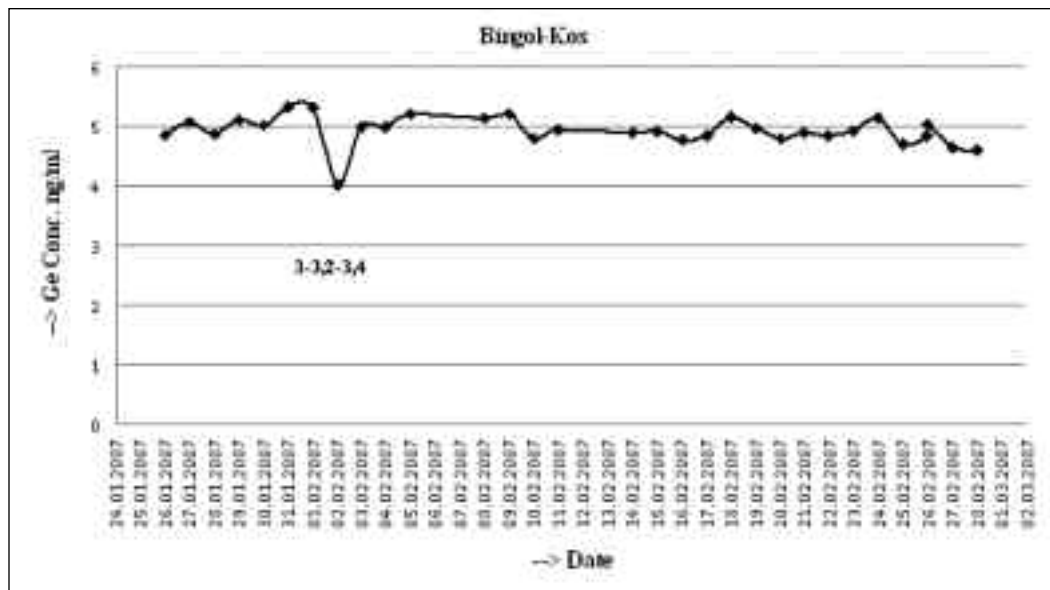


Fig. 5. Variations of Ge concentration in thermal water.

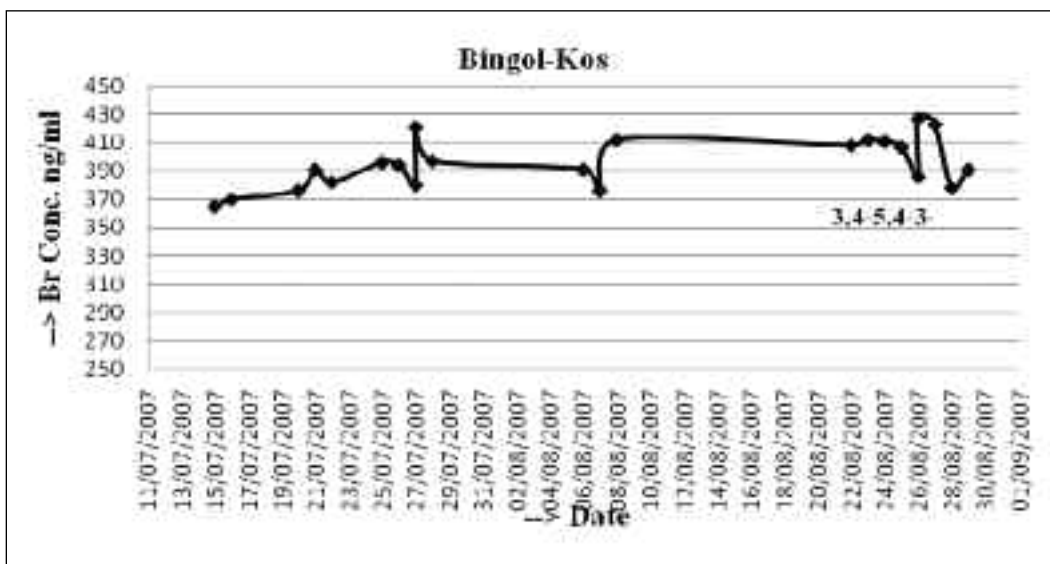


Fig. 6. Variations of Br concentration in thermal water.

TABLE III
Changes in (%) Element Concentrations of B, Ba, Cl, and Ge Based on the Results From Figures 2–5

Element	Figure Number	X _{av} ±s for			Change (%) in Element Concentrations		
		Total Data (ng/mL)	Data (ng/mL) in Figure	Except Data (ng/mL) for Day of Earthquake For Cl (μg/mL)	for Total Data	for Data in Figure	Except Data for Day of Earthquake
B	Fig. 2	7156±267	7060±275	7085±203	-20	-19	-20
Ba	Fig. 3	74±6	75±8	75±8	-12	-13	-13
Cl	Fig. 4	112±10	108±10	108±10	-19	-16	-16
Ge	Fig. 5	4.7±0.3	4.7±0.3	4.7±0.3	-14	-14	-14

X_{av} = X_{average}.

CONCLUSION

This study shows that short-term precursory geochemical anomalies were observed in the thermal spring groundwaters in Bingol, East Anatolia, Turkey, on a continuous basis over a three-year period. These precursory activities can help to predict a possible earthquake. An increase or decrease in element concentrations was observed depending on the time and place of the earthquake. Water samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS). The B, Ba, Br, and Ge concentrations were monitored for three years and were found to be in the range of 6822–7666, 64–101, 271–406 and 4.1–6.0 $\mu\text{g L}^{-1}$, respectively. Chloride concentrations for this period were in the 89–127 mg L^{-1} range. These results show that the data obtained can identify some element anomalies at least one day prior to a minor earthquake which even remain for some time after the event.

The anomalies in element concentrations can be attributed to the changes in the groundwater circulating system during the processes of earthquake generation. Variations in the cation or anion concentrations can also be measured. Depending on the water level in the wells, they can be either positive or negative, depending both on the site and the focal mechanism. However, further studies are required to assess these variations in element concentrations as possible precursors to an earthquake. It is also suggested that the groundwater samples be collected within shorter time periods, such as at 5- or 10-minute intervals.

The accuracy of the barium results, verified by using the recovery values for barium in the Standard Reference Material SRM SPS-SWS Batch 113 Surface Waters, were found to be at least 95%.

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