TERRA RESEARCH

Application of the chlorine-36 method for the characterization of the groundwater circulation in tectonically active areas: examples from northwestern Anatolia/Turkey

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ABSTRACT

For groundwaters of tectonic active regions the problem of determining the residence time above the range of the tritium method arises. The usually applied isotope techniques are often not appropriate because of (i) the high amount of water–rock interaction, (ii) the underground production of nuclides in crystalline fissured rocks under geothermal conditions, (iii) the occurrence of highly saline waters at boiling temperature affected by waterrock interaction processes, as also the high fluxes of CO_2. However, the ^{36}Cl evolution will be affected by these processes, too. Nevertheless it gives an independent tool to investigate the groundwater evolution. Therefore the application of the ^{36}Cl method looks very promising. Within this publication the interpretation of ^{36}Cl measurements of three study areas along the North Anatolian Fault zone (from East to West) of Kuzuluk/Adapazari, Bursa and of Canakkale (Tuzla/Kestanbol) are discussed. By considering for each area the sources of ^{36}Cl and the water–rock interaction with respect to the chloride cycle, information on the ongoing processes of groundwater circulation and evolution have been derived. In addition, ranges of residence times of these waters were gained which are compatible with the results of geological, hydrogeological and hydrochemical investigations (Balderer *et al.*, 1991; Greber, 1992, 1994; Imbach, 1992, 1994; Imbach and Balderer, 1990; Mützenberg, 1989) as well as with already developed conceptual groundwater flow models.

Terra Nova, **8**, 324–333, 1996.

1 INTRODUCTION

Within the joint interdisciplinary project 'Marmara' of ETH Zürich and the Istanbul Technical University (ITÜ) the effects of active tectonics as evidenced by geology, geodesy and seismology on groundwater circulation and on the heat flow pattern are studied.

The selected areas (Fig. 1) along the North Anatolian Fault Zone have active crustal movements and very high seismicity (Schindler *et al.*, 1993; Straub *et al.*, 1994). They show the following hydrogeological features:

1.1 Bursa area

In this area thermal springs arise within two locations at the northern slope of the Uludag massif (peak altitude of about 2500 m) near Kükürtlü/Bursa and Cekirge just above the valley plain (elevation 150 m–200 m). Cold groundwaters with Tritium contents between 10 and 23 tritium units, sampled at altitudes between 100 m and 2300 m represent local systems of shallow circulation (Balderer *et al.*, 1991; Imbach and Balderer, 1990; Imbach, 1992). The outflowing hot waters in the Bursa/Kükürtlü area are of Na–Ca–HCO_3-type with a total mineralization of 1220 mg L^{-1}. They have temperatures of up to 82°C. The tritium concentration of the thermal water from the Kükürtlü thermal spa is very low (1.1 ± 0.7 TU), quite close to the detection limit of the tritium measurements. Based on this result a residence time of greater than 30 years has to be admitted.

1.2 Kuzuluk area

About 40 thermal and mineral waters arise in springs within the subsidence basin of the Kuzuluk area (Greber, 1992, 1994). All these waters are of Na–(Ca)–(Mg)–HCO_3–Cl-type having a total mineralization up to 7 g L^{-1}. They are dominated by CO_2-outgasing and very high CO_2 contents of up to 1 litre per kg of water at surface conditions are found. This is primarily caused due to the tectonic activity in the vicinity of the North Anatolian Fault zone. At the naturally occurring hot springs water temperatures up to about 56°C, resp. of 82°C were observed within the two bore holes of about 160 m and 240 m depth. The observed mineralised waters contain generally no anthropogenic tritium in measurable amounts except if some mixing with shallow ground waters occur. With respect to the δ^2H and $\delta^{18}O$ values a distinct deviation of the cold mineral and thermal waters from the meteoric water line of the local shallow groundwaters can be observed. This deviation can be attributed to water/rock interaction and/or isotopic exchange with the uprising CO_2. (Balderer

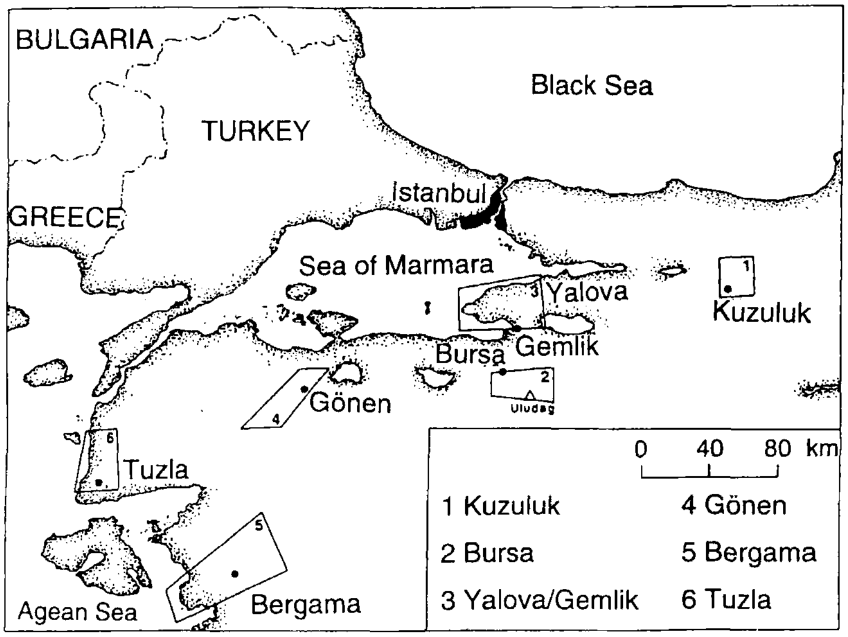

Fig. 1. *Geological and hydrogeological study areas of the Marmara Project.*

et al., 1991; Greber, 1992, 1994). Additionally, the very low δ^2H values of these waters indicate a distinct origin which is not connected with the shallow groundwaters of recent recharge.

1.3 Kestanbol/Tuzla Area

This area is located in the northwestern part of Anatolia along the western coast of the Biga Peninsula. Here two main centres with thermal water discharges named Kestanbol Kaplica (Kaplica meaning spa) and Tuzla occur. The thermal springs appear within an intrusive body of quartz-monzonite type in the Kestanbol Kaplica, or within a 600 m thick volcanic sequence of calcaline volcanic and ignimbrites in the Tuzla area. In Kestanbol Kaplica the thermal water is used today for the spa. It is originating from a 290 m deep artesian bore hole. Around Tuzla the surface thermal activities cover an area of about 1 km^2. The outflow zones of the thermal brines are situated about 30 m up to 80 m above sea level (Mützenberg *et al.*, 1992). In both areas the outflowing thermal waters are of Na-Cl type with temperature in the range of 76°C and total mineralization of 21 g L^{-1}. The outflowing thermal waters of the Kestanbol bore hole have temperatures close to the boiling point and a maximum value of 65 g L^{-1} of total dissolved solids for the highest mineralised spring in the Tuzla area. In both areas springs of low mineralized fresh water at lower temperatures exist at the same or at slightly higher altitudes.

2 PRINCIPLES OF THE APPLICATION OF THE ^{36}CL METHOD

With its half life of about 301,000 years ^{36}Cl is one of the very promising isotopes for environmental studies. Since its detection became possible by the development of the accelerator mass spectrometry (AMS) it has been used as a dating tool in various hydrological systems. The principles of the ^{36}Cl method are well described by several authors such as Andrews *et al.* (1986, 1989), Airey *et al.* (1983), Bentley (1978), Bentley *et al.* (1982, 1986), Elmore (1982), Calf and Habermehl (1983), Fontes (1985), Fontes and Michelot (1983), Fontes *et al.* (1984), Kubik (1983), Kubik *et al.* (1984), Michelot (1988) and Pearson *et al.* (1991).

The ^{36}Cl contents are usually expressed as concentration with respect to the volume of water as number N of ^{36}Cl atoms per litre of H_2O or as atomic ratio R of ^{36}Cl with respect to the total chloride. The conversion factors are: $N = (1.7\times10^{19})RC$, or $RC = N(5.89\times10^{-20})$, where C is the chloride content of the water in mg L^{-1}.

However, despite the fact that it presents a very promising tool for the evaluation of the residence time of deep groundwater it is not used up to the present days as a standard technique in isotope hydrology. The main reason is that the application of the ^{36}Cl method in groundwater studies is difficult. It needs, in principle, a detailed knowledge of all the different processes within the water cycle. All the sources and sinks of ^{36}Cl which influence the ^{36}Cl concentration have to be evaluated.

2.1 Sources of ^{36}Cl within the water cycle

The following sources of ^{36}Cl production can be considered with respect to groundwater evolution.

2.1.1 Atmospheric input

Natural ^{36}Cl is produced primarily in the stratosphere in spallation reactions of secondary cosmic protons and neutrons on ^{40}Ar. Its atmospheric residence time is about 1–2 years. From the atmosphere it is removed and subsequently stored in terrestrial deposits. Due to atmospheric mixing processes the ^{36}Cl input to these deposits is expected to show a latitude dependence (Lal, 1967). A peak fallout rate of 28 atoms m^{-2}s^{-1} is quoted by Bentley (1986) for the latitude of Western Turkey at about 40°N. New ^{36}Cl measurements on ice cores from Greenland at latitudes between 60° and 70°N result in ^{36}Cl fallout rates of about 20 atoms m^{-2}s^{-1} (Synal, 1994). This is approximately a factor of 2 higher than the expected fallout rates according to Bentley. Taking these new experimental data into account the fallout distribution given by Bentley was normalized to the experimental data from Greenland. The resulting fallout rate for Western Turkey will then be 56 atoms m^{-2}s^{-1} With known precipitation rates P and known evapotranspiration rates E the ^{36}Cl concentration for the infiltration water is given by the following equation:

$$N_o = F/P\ (3.156\times10^7)\ 100/(100-E), \quad (0)$$

The mean annual precipitation rate for the three areas under investigation are

847 mm (Bursa 782 mm, Akyazi/Kuzuluk 872 mm, Kestanbol/Tuzla 888 mm). The evapotranspiration rate is estimated to be about 80%. With these assumptions the ^{36}Cl content of infiltration water in Western Turkey would be 1×10^7 atom L^{-1}. The direct evaluation of the corresponding ^{36}Cl/Cl ratio is dependent on the chloride content of the local precipitation water or of the shallow groundwater of local recharge. A direct determination of the initial ratio R_0 could therefore be strongly influenced by the evaporation effect. Another approach to avoiding these difficulties is presented in Bentley and Davies (1981) where the ^{36}Cl ratio R_0 is determined directly by combining the fallout rate F and the total chloride input of precipitations (Eriksson, 1960). However, this chloride input is quite variable depending on the distance to the sea and on the directions of winds. This approach can only be used if the chloride contents of precipitations and the amount of annual precipitations are known and if the measured ratios of shallow groundwaters are representative for direct recharge.

2.1.2 Anthropogenic thermonuclear production of ^{36}Cl

An increased atmospheric ^{36}Cl fallout was predicted by Bentley (1981) originating from the period of atmospheric nuclear weapon tests (1952–58) In shallow groundwaters also containing anthropogenically produced tritium (IAEA, 1983) an increased ^{36}Cl concentration was measured (Bentley, 1986). ^{36}Cl contents which are about three orders of magnitude above the normal level in precipitation waters were observed for the period 1952–56 in ice cores from Dye-3 in Greenland (Elmore *et al.*, 1982; Synal *et al.*, 1990). Due to the common origin of anthropogenic tritium and ^{36}Cl, the tritium level of a groundwater is a good indication if some amount of anthropogenic ^{36}Cl could potentially be present in the analysed groundwaters. However, the fallout patterns and atmospheric removal mechanisms of ^{36}Cl and tritium are quite different. Therefore, predictions of anthropogenic contributions in a groundwater system based on measurements of one radio isotope are generally insufficient.

2.1.3 Near surface production of ^{36}Cl

Secondary cosmic ray particles interact with nuclei of lithospheric matter (rock/soil surfaces) producing long-lived radio nuclides such as ^{36}Cl (Lal, 1990). In case of calcium carbonate formations, ^{36}Cl production from cosmic muons is of importance down to depths of 100 m below surface. According to Kubik (1983) and Kubik *et al.* (1984) measured ^{36}Cl/Cl ratios of subsurface production R_s of 200×10^{-15} up to 700×10^{-15} for depths of 75 m, respectively, between 30 m and 60 m below surface are reported for limestones samples originating from a quarry near Regensburg/Germany. In Synal *et al.* (1994) a ^{36}Cl depth profile is described on samples from a limestone drill core of Vue des Alpes (Swiss Jura Mountains). Measurements and model calculations are in agreement and show ^{36}Cl/Cl isotopic ratios up to 480×10^{-15}. If by weathering reactions parts of such limestones are dissolved, some chloride with an increased ^{36}Cl/Cl ratio can be acquired by the infiltrating water. Investigations of dipping waters in karstic caves representative for the unsaturated zone (12 samples) by Miserez (1971) reveal that already in shallow depth, the infiltrating waters are almost saturated with respect to a calcite content of about 100 mg L^{-1} of HCO_3. If most of this HCO_3 originates from dissolution of limestones within the uppermost 22 m the also dissolved chloride would be in equilibrium of in-situ production. Assuming conditions similar to limestone formation at Vue des Alpes (Switzerland, Synal, 1994) a ratio R of the dissolved chloride of about 240×10^{-15} is possible. In shallow groundwaters of carbonate rocks (marbles) in the recharge area of the Bursa thermal springs on Mount Uludag the chloride contents range from 2.4 to 4.1 mg L^{-1} with HCO_3 contents of 106–254 mg L^{-1}. The resulting ^{36}Cl concentrations N due to subsurface production would range between 9.8×10^6 and 1.7×10^7 atom L^{-1}. Additionally, ^{36}Cl production by neutron activation on ^{35}Cl of salt crusts at surface and within the unsaturated zone up to about 5 m depths is observed in arid to semi arid areas (Fontes *et al.*, 1984). In such climates this process contributes a non negligable amount to the actual ^{36}Cl input concentration.

2.1.4 Radiogenic production of ^{36}Cl in the deep subsurface

Within the geological environment ^{36}Cl is naturally produced by the radiogenic reaction ^{35}Cl $(n,\gamma)^{36}$Cl. The amount of ^{36}Cl produced by this reaction is directly related to the neutron flux depending on the radio element content of the rocks, mainly of uranium and thorium. Calculations of the neutron flux and the resulting ^{36}Cl ratio of underground production R_{eq} for various rock types according to the model of Feige *et al.* (1968) are presented in Bentley (1978), Andrews *et al.* (1986), Andrews (1989), Lehmann *et al.* (1989, 1991). If chlorine is dissolved in groundwater of long residence in such a rock environment its ^{36}Cl ratio is enhanced by this process of underground production according to the following equation:

$$R = R_{eq}\,(1 - e^{-\lambda t}). \qquad (1)$$

The radio element contents of selected rock samples have been measured in the investigated areas of Bursa and Kuzuluk (Rybach *et al.*, in press). Calculations of the resulting underground production for the investigated crystalline rock types result in the following ^{36}Cl- ratios R_{eq}:

Andesite Kuzuluk: 6.3×10^{-15} (mean of 4 samples),
Volcanite Bursa: 10×10^{-15}
Rhyodacite Kuzuluk: 19×10^{-15}

Unfortunately no rock sample of the Bursa and Kestanbol intrusion (granite resp. quartz monzonite) could be measured within this study for their radio element contents. Therefore, a range from literature for granitic rocks is used. A ratio R_{eq} of 30×10^{-15} for average granite is given by Bentley and Davies (1981). Experimental data exist for crystalline rock samples originating from the basement of Northern Switzerland (Lehmann *et al.*, 1991). They have isotopic ratios ranging from 30 to 97×10^{-15}. For interpretation of the groundwater evolution a mean ratio R_{eq} of $50 \pm 10 \times 10^{-15}$ has been admitted. For sedimentary rocks the measured two samples of Marble and Travertine of the Bursa area yield ratios of 5.6×10^{-15} and 0.9×10^{-15}, respectively.

2.1.5 Radioactive decay during residence in the aquifer along flow path

If no other processes occur during the transit of the groundwater along the flow path within the aquifer, the ^{36}Cl nuclides originating from recharge will decay according to its half life. In this case the equation of radioactive decay is applied:

$$R = R_o\, e^{-\lambda t}. \qquad (2)$$

As this equation is applied in terms of ratios (atoms of ^{36}Cl per atoms of stable chloride), no correction for effects of evaporation is needed. But it must be admitted that there has no input of dead chloride taken place, otherwise the use of the same equation in term of concentrations is necessary:

$N = N_o\, e^{-\lambda t}$, which is equal to:

$$RC = R_o\, C_o\, e^{-\lambda t}. \qquad (3)$$

2.2 Evolution of ^{36}Cl within the groundwater cycle

For the final aim to use the ^{36}Cl as a dating method for groundwaters the various processes which affect its ratio R and its concentration N have to be considered.

1 Within the infiltration area the primary input concentration N_o of groundwater recharge has to be evaluated. This input concentration N_o is calculated according to eq (0). But the ^{36}Cl/Cl ratio representative for the atmospheric input depends on the chloride content of the precipitations (rain, snow). As for the investigated areas these values are not available, the only possibility is to compare with values of low mineralised, shallow groundwaters.

2 During the transit along flow path within the groundwater ^{36}Cl will be affected by the processes of radioactive decay but also of underground production. As a third source additional dissolved chloride originating from the aquifer rocks which is contained in minerals, fluid inclusions and as intergranular salt in pore spaces (Peters, 1987) has to be considered especially in geothermal and tectonic active areas with enhanced water/rock interaction processes. As this chloride is present in the rock for geological times it can be assumed that the ^{36}Cl has already achieved the secular equilibrium of production within the surrounding rock environment.

This evolution can be solved by a mass balance approach in terms of concentrations N [as $RC = N$ (5.89×10^{-20})], by a three-term expression (4) as proposed by Bentley *et al.* (1986) and Michelot *et al.* (1987):

$$R\,C = R_oC_o\, e^{-\lambda t} + R_{eq}C_o(1 - e^{-\lambda t}) + R_{eq}\,(C - C_o), \qquad (4)$$

where $R_oC_o\ e^{-\lambda t}$ is the decay of the atmospheric (input) contribution, $R_{eq}C_o(1-e^{-\lambda t})$ is the term of underground production, and R_{eq} $(C-C_o)$ is the additional chloride derived from the rock (water–rock interaction), other expressions as already mentioned.

3 DISCUSSION OF THE ^{36}CL DATA

3.1 Shallow groundwaters

All three analysed shallow groundwaters originate in the Bursa area and result in the following measured ^{36}Cl/Cl ratios R and concentrations N.

- Cifte Cesmeter spring (chloride content 9 mg L^{-1}): $R = 1097 \pm 45 \times 10^{-15}$, corresponding to a concentration N of $1.68 \pm 0.07 \times 10^8$;
- Groundwater of Sigorta Hospital well (originating from the shallow gravel aquifer, chloride content 17.6 mg L^{-1}): $R = 437 \pm 31 \times 10^{-15}$, corresponding to a concentration N of $1.31 \pm 0.09 \times 10^8$;
- Bakacak spring (chloride content 3.5 mg L^{-1}): $R = 266 \pm 8.8$ 10^{-15}, corresponding to a concentration N of $1.58 \pm 0.05 \times 10^7$.

The water of the Cifte Cesmeter spring presents the highest values of N and R. It has the highest Tritium content with 25.7 TU, too. Therefore, it could probably contain some residual anthropogenically produced ^{36}Cl.

Compared to the calculated atmospheric input concentrations as given in section 2.1, the measured concentration of the Bakacak spring is only slightly above the calculated input concentration N_o (1.0×10^7) atoms L^{-1}. The water has a low chloride concentration and moderately low tritium concentration of 15.4 ± 1.3 TU. This approximates to the value for modern precipitation. For these reasons the Bakacak spring water is most representative for 'modern' groundwaters of actual recharge. With respect to its ^{36}Cl ratio this water most probably presents the modern recharge conditions where no ^{36}Cl bomb peak remains. The higher ^{36}Cl concentration N in terms of atoms L^{-1} of the Sigorta Hospital may well be explained in part by an evaporation effect bearing in mind the higher chloride concentration. But the higher ratio together with the Tritium content of 18.1 ± 1.3 TU indicates that some anthropogenically produced ^{36}Cl is present also.

In Bentley and Davies (1981) and Bentley *et al.* (1986) the predicted values and measurements of ^{36}Cl ratios of groundwaters of pre-bomb recharge within the United States and of the Madrid Basin are mentioned. The area in Spain is at a similar latitude to the investigated areas of Western Turkey. At the Madrid Basin a mean ^{36}Cl ratio of $254 \pm 36 \times 10^{-15}$ is observed, that is similar to the ratio measured for the Bursa Bakacak sample.

From the measured ^{36}Cl ratio R_o of precipitation or of shallow groundwaters and the assumed fallout rate F (= 56 atoms m^{-2} s^{-1}) it is possible to calculate directly the total chloride input of precipitation. For the Bursa Bakacak sample, values of the total chloride in precipitation of 3.9 kg ha^{-1} yr^{-1} are obtained. Compared with the measured values presented in Eriksson (1960) the value is clearly within the range for middle Europe of 1.2–7.5 kg ha^{-1} yr^{-1}.

3.2 Deep groundwaters

For the investigated deep groundwaters the following values result: (see table)

The Tritium contents of all these samples are at about the detection limit, except for Kuzuluk KuzMin with 7.6 ± 0.8 TU.

A comparison with the already presented values of atmospheric recharge and of underground production reveals the following facts:

1 The ^{36}Cl/Cl ratios R of the Bursa Kükürtlü thermal water and the three thermal and mineral waters of the Kuzuluk area are within or even greater than the resulting range of ratios of underground production according to the measured radio element contents of selected rock samples.

2 In Fig. 2 the ^{36}Cl/Cl ratio R vs. chloride concentration are shown. Evaporation

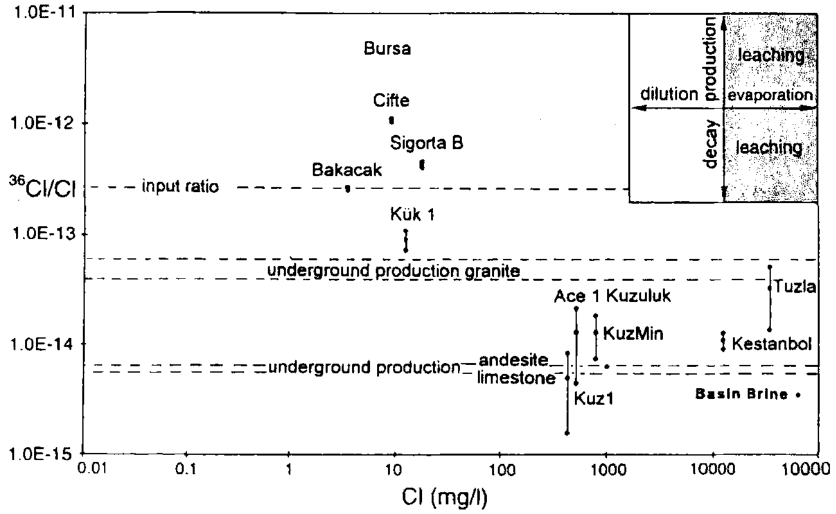

Fig. 2. *Diagram of ^{36}Cl/Cl ratio vs. chloride contents of investigated waters.*

Groundwater	R($\pm 1\sigma$)	N ($\pm 1\sigma$)	Cl (mg L^{-1})
Bursa Kük 1	92 ($\pm$14) $\times 10^{-15}$	1.92 ($\pm$0.40) $\times 10^{7}$	12.3
Kuzuluk Ace 1	13 ($\pm$8.5) $\times 10^{-15}$	1.12 ($\pm$0.74) $\times 10^{8}$	509
Kuzuluk KuzMin	13 ($\pm$5.5) $\times 10^{-15}$	1.71 ($\pm$0.73) $\times 10^{8}$	776
Kuzuluk Kuz 1	5 ($\pm$3.4) $\times 10^{-15}$	3.60 ($\pm$2.47) $\times 10^{7}$	423
Kestanbol	11 ($\pm$1.8) $\times 10^{-15}$	2.29 ($\pm$0.38) $\times 10^{9}$	12230
Tuzla	33 ($\pm$19.2) $\times 10^{-15}$	1.96 ($\pm$1.13) $\times 10^{10}$	918

and leaching of rock salt, that is in secular equilibrium of underground production, can be distinguished from the processes of evolution by decay. In addition, effects of underground production of an individual groundwater with its already acquired salt load can be identified. In this latter case only the ^{36}Cl/Cl ratio varies but not the chloride concentration. This diagram reveals a sharp clustering into the groups of low chloride waters of the Bursa area, to the medium chloride waters of the Kuzuluk area and to the high concentrated chloride waters of the Tuzla Kestanbol area.

4 INTERPRETATION OF THE RESULTING ^{36}CL DATA OF THE DEEP GROUNDWATERS

For the interpretation of ^{36}Cl results of deep groundwaters usually the evolution mass balance approach of (4) is applied. This equation can be solved to:

$$t = -1/\lambda \ln [C/C_o \, (R-R_{eq})/(R_o-R_{eq})], \tag{5}$$

This formula can be applied if the developed hydrogeological model is in agreement with the following evolutionary scheme:

(a) infiltration of water of atmospheric origin;

(b) subsequent decay of the atmospheric component;

(c) neutron activation of chlorine dissolved in the water phase; and

(d) water–rock interaction in the flow path of groundwater liberating chloride from the aquifer rock (contained in minerals, fluid inclusions and as intergranular salt in pore spaces), or by dissolution of limestones in contact with ascending CO_2.

4.1 Interpretation of the evolution of the thermal waters of the Bursa area

A geological cross-section of the Bursa area is shown in Fig. 3.

Recharge of the Bursa thermal groundwater Kükürtlü 1 is expected to take place in the area of the marble series at the top of the Mount Uludag. For the infiltration water a ^{36}Cl/Cl ratio similar to the ratio measured at Bakacak spring is assumed. For the chloride concentration a mean value of 4.33 mg L^{-1} is used. This value is representative for the chloride contents of analysed shallow groundwaters of the expected recharge area (Imbach, 1992). For the underground production in the crystalline rocks of the Uludag intrusion a ^{36}Cl/Cl equilibrium ratio of 30×10^{-15} and 50×10^{-15} is adopted. The mean resulting ^{36}Cl ranges of residence time of the Kükürtlü thermal groundwater are then 1.1×10^4 to 2.9×10^5 (mean value 1.3×10^5 yr), respectively, and 9.5×10^4 to 5.2×10^5 yr (mean value $2.6 \pm 1.7 \times 10^5$ yr). This model age takes into account the whole cycle of chloride in the groundwater cycle. It is valid under the assumption that the input value of infiltration water is in the range of the measured values of the Bakacak spring water. The large error of the model age is dominated by the uncertainty of the ^{36}Cl/Cl ratio measured at Kükürtlü. However, the resulting age range is independently confirmed by the results of the geothermal modelling which predict residence times of the order of 10^4–10^5 yr (Pfister, 1995).

4.2 Interpretation of the evolution of the thermal and mineral waters of the Kuzuluk area

The thermal water sample from the well Kuzuluk 1 originates from an artesian bore hole with about 5 bars over pressure and a temperature of 82°C with Tritium content < 1.1 TU. The measured ratio is $R = 5 \pm 3.4 \times 10^{-15}$. It is within or even lower than the range of underground production calculated according to the radio element contents of the volcanic rocks (andesites) of this investigated area. Even the marble samples of the Bursa area have similar ratios. Therefore, it is assumed that this water has achieved a state of equilibrium with respect to the processes of water rock interaction. The ^{36}Cl/Cl ratio of this thermal water is also within this range of secular equilibrium ratio of limestones. This suggest that for this thermal water the original atmospheric component and also the small amount of build-up of underground production is masked by the much greater amount of chloride originating from dissolution of limestones caused by a thermo catalytic process that is also responsible for the high amounts of CO_2. This

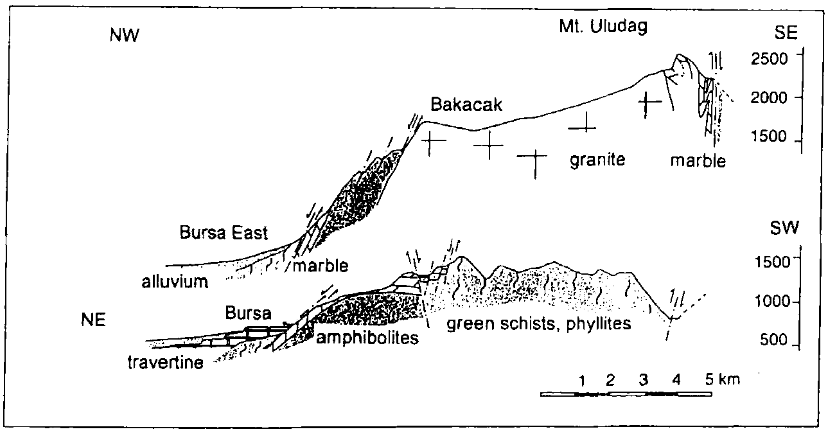

Fig. 3. *Schematic cross-sections of the Bursa Area (according to Imbach, 1992).*

estimation is in agreement (i) with the presence of limestones in deep situations within the admitted flow path of the thermal water and (ii) the high CO_2 emanation. The latter is caused by the occurrence of fault zones and the observed tectonic activity (Balderer *et al.*, 1991; Schindler *et al.*, 1993; Greber, 1992, 1994; Balderer, 1993, 1994). In this case, an evaluation of the residence time by the ^{36}Cl method is not possible.

For the two samples of surface springs the thermal water Ace 1 (temperature 19.5°C) and the mineral water KuzMin (temperature 13.0°C; Greber, 1994) the measured ratios are greater than the maximum value of possible underground production. As for the sample of the mineral spring Ace 1 a Tritium content at the detection limit < 1.3 TU resulting from an anthropogenic influence can be neglected. However, for the sample of the Kuzuluk mineral spring Kuz Min, according to the measured Tritium content of 7.6 ± 0.8 TU some admixture of a recent water component is probable. Nevertheless, the measured ^{36}Cl/Cl ratios of the two mineral waters are nearly identical which almost excludes any anthropogenic influence on the ^{36}Cl result.) Therefore, an atmospheric contribution is most probably still present and the mass balance approach (equation 4) is considered for the interpretation of ^{36}Cl results of these mineral waters (Fig. 4).

It is assumed that the liberated chlorine is in secular equilibrium of production with the corresponding rock environment. As limiting value of underground processes the ratio of Kuz1 $R = 5 \pm 3.4 \times 10^{-15}$ is adopted. For the recharge conditions again the ratio of the Bakacak spring is used. The initial chloride concentration is selected according to the shallow waters within the direct infiltration area of the Kuzuluk basin. A mean chloride content of 37.6 mg L^{-1} is adopted (range of the selected springs K11, K27, K29: 20.0–64.9 mg L^{-1}; Greber, 1992). Under these assumptions mean ^{36}Cl residence times for the mineral water at KuzMin of 2.0×10^5 years and for the thermal water at Ace1 of 3.8×10^5 years result.

But for these two naturally occurring spring waters sampled for chloride at surface (KuzMin 776 mg L^{-1}, Ace 1 509 mg L^{-1}) some additional chloride concentration due to evaporation effects in the near surface area is suspected in comparison with the sample from the artesian well Kuz 1 (423 mg L^{-1} Cl). If this enrichment in chloride is a last stage phenomena of evaporation at the surface it is not influencing the ^{36}Cl ratio resulting from the evolution along flow path. Therefore, it should be corrected before applying the mass balance equation (equation 4). By this additional assumption (using the chloride concentration of the Kuz 1 sample as representative for the two other mineral and thermal spring waters) the resulting mean residence time of the KuzMin and of the Ace 1 waters is 4.6×10^5 years. Taking into account the experimental errors and the uncertainties of the introduced assumptions the resulting error of the model residence time is of the same order of magnitude as the residence time itself. Therefore, the derived results can be taken only as indicative values for the residence of ^{36}Cl in the groundwater system.

The previous interpretation of the δ^2H and δ^{18}O-results of Kuzuluk thermal and mineral waters (Balderer *et al.*, 1991; Greber, 1992, 1994; Balderer, 1993, 1994) which pointed out that the infiltration took place during a time period of changed climatic conditions is supported by these results in a qualitative way. However, the identification of a distinct glaciation event is not possible.

4.3 Waters of the Tuzla Kestanbol Area

Following the conceptual model for the interpretation of a groundwater system resulting from geological mapping, hydrogeological and hydrochemical investigations, as well as from the results of isotopic studies (Mützenberg, 1990; Mützenberg *et al.*, 1992), the Tuzla and Kestanbol thermal brines present a mixing of two end-members. One corresponds to a highly saline brine which is mixed with low mineralized water subsequently, and the second type originates directly from the infiltration in the crystalline complex itself (Mützenberg, 1990; Mützenberg *et al.*, 1992). For the origin of the highly saline brine several possibilities are discussed in Mützenberg (1990) which are listed below.

1 Evolution within the crystalline basement itself. The acquired salt load originates only from water–rock interactions. This scenario is shown on the right side of the profile in Fig. 5.

2 Evolution from an altered formation water of marine origin (Permian, Triassic or Jurassic marine sequences). It has migrated into the crystalline rocks of the basement and remains there as a deep-seated stagnant water mass. This is also shown on the right side of the profile in Fig. 5.

3 Origin of a marine brine which is equivalent to the fossil pore water within the neogene sediments of the tertiary and early quaternary period. As a recent active process it is actually squeezed out of the neogene to quaternary sediments of the Agean Basin. In this case the brine of sedimentary origin is actively migrating into the rocks of the crystalline basement. It is heated up due to the high heat flow and is

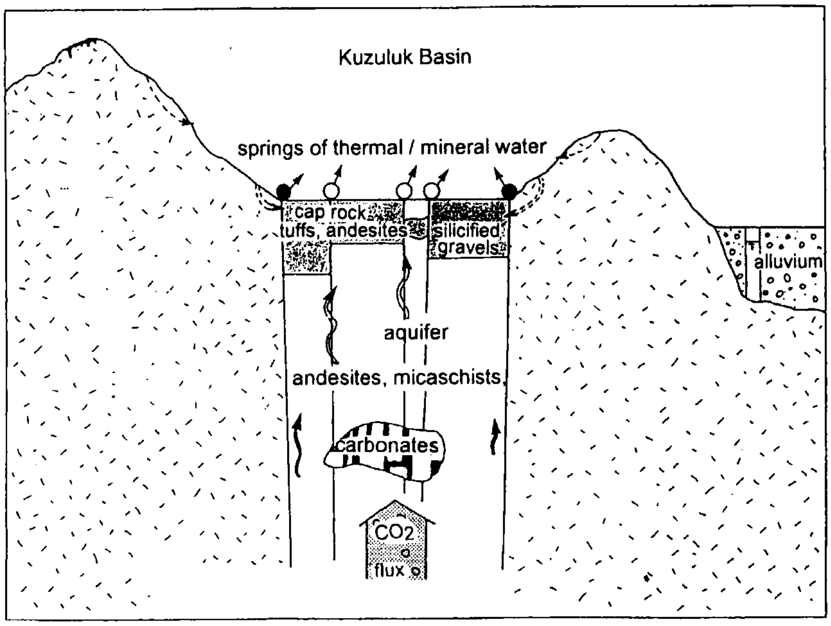

Fig. 4. *Schematic circulation model of the Kuzuluk waters (according to Greber, 1992, 1994).*

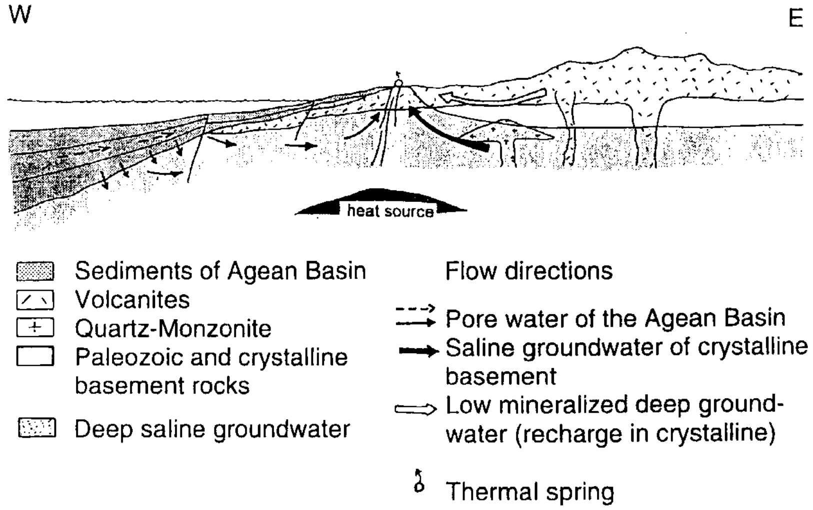

Fig. 5. *Schematic cross-section of the Tuzla geothermal area (On the right side of the thermal spring the assumptions of hypothesis 1 and 2, on the left side the assumption of hypothesis 3 of chapter 4.3 are represented, according to Mützenberg, 1990).*

upwelling in highly fractured fault zones by the buoyancy effect. In the near-surface areas mixing occurs with low mineralized waters of direct origin within the crystalline rocks itself. This scenario corresponds to the left side of the profile in Fig. 5.

According to the hydrochemical and isotopic results, it is most probable that the groundwater originates from a marine formation water or a deep basin sedimentary brine (Mützenberg, 1990; Mützenberg *et al.*, 1992). From the remaining possibilities II and III the existence of an old deep- seated formation brine which is almost immobile within the crystalline, seems to be very unlikely, if the geological evolution of this area is considered (extended plutonic activity in the Tertiary Period).

Most evidence points to an active process: *pressurized fluids as pore waters of Tertiary origin are migrating into the crystalline rocks of the basement.* This conclusion is in agreement with hypothesis **3** (above), since the Kestanbol thermal waters contain sulphates that are according to ^{34}S and ^{18}O isotope results of tertiary origin. From the ^{36}Cl results an independent check of these hypotheses is now possible:

For hypothesis **1** the application of the mass balance approach is inappropriate. Considering thermal waters of unique source or mixed water of two end members the application of equation (4) reveals no solution.

For hypotheses **2** and **3** the two approaches were used as given below.

(a) First an approximate residence time is calculated for the chloride of sedimentary origin within the crystalline rock complex. Therefore, a one-step build up equation for the underground production is used:

$$RC = R_{eq}\,(1-e^{-\lambda t})\,C + C\,R_{brine}\,e^{-\lambda t}. \qquad (6)$$

For the sedimentary brine this one-step build-up results in the following residence time:

$$t = -1/(\ln\,[(R-R_{eq})/(R_{brine}-R_{eq})]. \qquad (7)$$

The ratio R_{eq} of volcanic rocks as the ignimbrites in Tuzla and the granodiorite in the Kestanbol area which are in secular production equilibrium, are evaluated according to section 2.1. For the initial ratio R_{brine} of the sedimentary brine a value of 3.5×10^{-15} is used. This ratio was measured at oil field brines adjacent to salt domes by Fabryika-Martin *et al.* (1983) as reported in Bentley *et al.* (1986). This value is taken as typical in the present contribution for the brines in the North Anatolian Fault Zone.

With a production ratio R_{eq} of 50×10^{-15}, the model age of the Kestanbol thermal brine is 7.6×10^4 yr and that of the Tuzla thermal brine is 4.4×10^5 yr. The uncertainties induced by the assumptions made and the experimental method result in errors which are within the range of the derived residence times. Consequently these residence times can be taken as indicative values for the evolution in the ground water system only. In the case of the Tuzla sample, the model age is very sensitive to the equilibrium ratio R_{eq} of *in situ* production. If a ratio R_{eq} of 30×10^{-15} is adopted the resulting residence time exceeds the 10^6 limit. Therefore, it cannot be excluded that the Tuzla groundwater system is in a state of equilibrium with the *in situ* production. (b) In the second approach the mixing of two groundwater components is discussed. The first component is a low mineralized groundwater of recharge within the crystalline outcrops. Its chlorine content is C_{re} and its ^{36}Cl/Cl ratio is R_{re}. The second component is a deep basin brine of sedimentary origin having a chlorine content C_m and an isotopic ratio R_m. For the resulting mixed water system the following equation is used:

$$R\,C = R_{re}C_{re}\,(1-x) + R_mC_m\,x, \qquad (8)$$

where $R_{re}C_{re}$ $(1-x)$ is the mixing component of low mineralized water, and $R_mC_m\,x$ is the mixing component of high mineralized brine as present within the outflowing spring water, where x is the mixing proportion. The mixing components can be determined according to the corresponding concentrations:

$$C = C_{re}\,(1-x) + C_m\,x. \qquad (9)$$

For the Kestanbol area a chlorine content C_{re} of 112.1 mg L^{-1} is assumed for freshwater of the direct recharge. This value is the average chlorine content of spring samples K20/1 and 20/2. For the Tuzla area $C_{re} = 39.5$ mg L^{-1} as mean value of the freshwater spring samples T22/1 and T22/2 is used.

For the sampled high mineralized thermal waters the measured chloride contents of C = 12, 230 mg L^{-1} for the Kestanbol sample, and 34, 918 mg L^{1} for the Tuzla sample are used. For the undiluted brine end- member of the *mixing within the crystalline rocks* a chloride content of C_m = 65,000 mg L^{-1} is accepted. This value has been determined from the chloride content and the stable isotope (δ^2H and δ^{18}O) relation according to Mützenberg (1990) and Mützenberg *et al.* (1992).

With these values the following mixing proportions for the saline end member result:

Kestanbol: x = 0. 19, Tuzla: x = 0. 54.

If, for R_{re}, a ratio equal to 266×10^{-15}, according to the ratio of the Bursa Bakacak spring, is admitted, the mass balance equation as presented above can be solved as:

$$R_m = (RC - R_{re}C_{re}\,(1-x))/(C_m\,x), \qquad (10)$$

This equation takes into account the chloride cycle and the mixing processes of the freshwater infiltrating the crystalline with the highly saline brine of (probably) sedimentary origin which is migrating into the crystalline basement rocks. The residence time of the mixing component can now be calculated using the same one-step build-up equation as applied for the brine of sedimentary origin within the crystalline. The resulting residence time t is given by:

$$t = -1/(\ln\,[(R_m - R_{eq})/(R_{brine} - R_{eq})]. \qquad (11)$$

From this approach a mean residence time of 5.6×10^4 yr results for the Kestanbol thermal brine. For the Tuzla thermal brine the mean value is 4.3×10^5 yr. These residence times do not differ much from the residence times obtained with the previous approach. Again the resulting errors are large and the residence times can be taken as indicative values only.

From this ^{36}Cl study, it can be stated that clearly no equilibrium of underground production is achieved for the brine of the Kestanbol hot water even if the small amount of freshwater mixing component is deduced. For the Tuzla sample the brine seems to have a distinct residence time. With respect to the overall uncertainties of the result, a residence time up to about 1 million years is in agreement with the experimental data. Therefore, it is also possible that the secular equilibrium of production is achieved in the Tuzla area.

Hypothesis 3 is in agreement with the ^{36}Cl interpretation given above. This hypothesis represents the most probable *evolution with respect to chemical and* isotopic constituents, as well with respect to the geological history of this region. It seems, therefore, that there is an ongoing process which is squeezing out the fossil pore water of the Agean Basin within the neogene sediments from the Tertiary and early Quaternary periods. This process is caused by the tectonic activity of this area (Straub and Kahle, 1994). The sedimentary brine is actively migrating into the rocks of the crystalline basement along fault zones where it is heated up due to the high heat flow, and is up welling in highly fractured zones by the buoyancy effect. In the near-surface areas it is mixed with low mineralized waters of direct origin within the crystalline rocks.

5 CONCLUSIONS

- Dating with ^{36}Cl is only possible if the exact evolution is known. This includes a detailed knowledge of the rock environment along the flow path and the geological evolution of the area.
- The main effects of underground processes affecting the ^{36}Cl level in groundwater in tectonic active areas are: (i) underground production; (ii) leaching of rock salt and fluid inclusions due to water–rock interaction processes; (iii) dissolution of limestones, especially in areas of high CO_2 activity; and (iv) mixing of fluids of different origin/evolution caused by active tectonic processes.
- Additional information from independent hydrodynamic and coupled geothermal modelling, as well as the results of other environmental isotope studies, gives independent support to the interpretation presented herein.
- *Residence times of geothermal fluids*, especially in tectonically active areas, can be at odds with the actual water cycle, e.g. when considering the recharge under current climatic conditions.
- A sustainable use of these geothermal resources can be made only if a steady-state situation is maintained.
- These hot waters may come out of reservoirs which are closed under actual conditions to actual recharge. It is possible that they represent tectonically squeezed or pressurized fluids as suspected for the Kuzuluk waters flowing mainly due to the maintained CO_2 flux. Therefore, increased exploitation of such *waters, which cannot be in steady state* with recharge, may result in drastic changes in hydraulic head (e.g. loss of artesian over pressure), lowering of flow rate and eventually also long-term changes in the chemical composition. Together with the high CO_2 up-flow and the periodically strong seismic activity even a complete loss of the thermal water of a whole area under exploitation could result.

In this study only first and preliminary results of three study areas could be presented. A more complete study including other geothermal areas of this Marmara project is under preparation.

ACKNOWLEDGEMENTS

We thank our collegues within the Poly Project Marmara for the good collaboration and fruitful discussions and especially Professor Dr L. Rybach and Dr F. Medici for the radiometric measurements of the rock samples and Mrs Seelhofer for preparing the text of the manuscript for printing. We also thank Dr J.L. Michelot of the University of Paris-Sud for the review and the constructive remarks.

This work is supported by the ETH research funds as interdisciplinary Polyproject and also in parts by the Swiss National Science Foundation.

REFERENCES

Andrews J.N., Fontes J.Ch., Michelot J.L. and Elmore D. (1986) In situ neutron flux, ^{36}Cl production and groundwater evolution in crystalline rocks at Stripa, Sweden, *Earth Planet. Sci. Letts*, **77**, 49.

Andrews J.N., Davis S.N., Fabryika-Martin J., Fontes J.Ch., Lehmann B.E., Loosli H.H., Michelot J.L., Moser H., Smith B. and Wolf M. (1989) The in-situ production of radioisotopes in rock matrices with particular reference to the Stripa granite, *Geochim. Cosmochim. Acta*, **53**, 1803–1815.

Airey P.L., Bentley H.W., Calf G.E., Davis S.N., Elmore D., Gove H.E., Habermehl H.A., Phillips F.M., Smith J.W. and Torgersen T. (1983) Isotope Hydrology of the Great Artesian Basin. In: *Proc. Int. Conf. Sidney 1983*. Aust. Govt. Publ. Serv., Canberra.

Balderer W., Fontes J.Ch., Michelot J.L. and Elmore D. (1987) Isotopic Investigations of the Water-Rock System in the deep Crystalline Rock of Northern Switzerland. In: *Saline Water and Gases in Crystalline Rocks* (ed. by P. Fritz and S.K. Frape). *Spec. Pap. Geol. Ass. Can.*, **33**, 175–195.

Balderer W., Greber E., Imbach Th., Rauert W., Trimborn P., Güler S. (1992) Environmental Isotope Study of Thermal-, Mineral- and Normal Groundwater within the Bursa and Kuzuluk/Adapazari Area, North Western Turkey. *IAEA-SM-319/52P*, International Atomic Energy Agency, IAEA, Vienna, Austria.

Balderer W. (1993) Conclusions on the possible variations of chemical and isotopic composition of groundwater systems in response to changed hydrodynamic conditions (based on investigations of deep groundwater systems and thermal-, mineral waters and brines in tectonic active areas). IAEA Technical Report of the Advisory Group on 'Isotope and Geochemical Precursors of Earthquakes and Volcanic Eruptions', *IAEA-TECDOC-726*, International Atomic Agency, Vienna.

Balderer W. (1994) A Multidisciplinary Approach for the Study of the Effects of Active Tectonics along the North Anatolian Fault Zone – Possibilities for the Application of the Electrical Self Potential Method. In: *Proc. IV Workshop Nazionale Di Geo-Elettro-Magnetismo, Dip. Di Geofisica e Vulcanologia, Università Federico II Napoli, Capri, 16–18 Sep. 1992* (ed. by A. Meloni and D. Patella). *Ann. Geofis.*, **XXXVII**, Suppl. 5, 1269–1282.

Bentley H.W. (1978) Some comments on the use of Chlorine-36 for dating very old groundwaters. In: *Proc. Workshop on Dating Old Groundwater, Tucson, Arizona, 16–18 March 1978* (ed. by S.N. Davis). U.S. Department of Energy, 138 pp.

Bentley H.W. and Davis S.N. (1981) Applications of AMS to Hydrology. In: *Symposium on Accelerator Mass Spectrometry* (ed. by W. Kutschera *et al.*). Argonne National Laboratory, Argonne, Illinois, Pub. ANL/PHY-81-1, pp. 193–227.

Bentley H.W., Phillips F.M., Davis S.N., Gifford S., Elmore D., Tubbs L.E. and Gove H.E. (1982) *Thermonuclear Cl-36 Pulse in Natural Water*. University of Rochester, N.Y.

Bentley H.W., Phillips F.M. and Davis S.N. (1986) Chlorine-36 in the terrestrial environment. In: eds., *Handbook of Environmental Isotope Geochemistry,, 2, The Terrestrial Environment, B.* (ed. by P. Fritz and J.Ch. Fontes), pp. 427–480. Amsterdam, Elsevier.

Calf G.E. and Habermehl M.A. (1983) *Isotope Hydrology and Hydrochemistry of the Great Artesian Basin, Australia. IAEA-M270/19* International Atomic Energy Agency, IAEA, Vienna, Austria.

Elmore D., Tubbs L.E., Newman D., Ma X.Z., Finkel R., Nishizumi K., Oeschger H. and Andée M. (1982) ^{36}Cl bomb pulse measured in a shallow ice core from Dye 3, Greenland, *Nature*, **300**, 735–737.

Eriksson E. (1960) The yearly circulation of Chloride an Sulfur in nature, II. Meteorological, geochemical and pedological implications, *Tellus*, **12**, 63–109.

Feige J., Oltmann B.G. and Kastner J. (1968) Production rates of neutrons in soils due to natural radioactivity, *J. geophys. Res.*, **73**, 3135–3142.

Fontes J.Ch. (1985) Méthode au chlore-36. Datation des aeux. In: *Méthodes de Datation par les phénomènes Nucléaires Naturels Applications* (ed. by E. Roth and B. Pothy), pp. 401–418. Masson, Paris.

Fontes J.Ch. and Michelot J.L. (1983) Stable isotope geochemistry in groundwater systems from Stripa. In: *Geochemical and Isotope Characterisation of the Stripa Groundwater – Progress Report*. Stripa Project I.R. 83–01, SKBF/KBS, Stockholm, 74–104.

Fontes J.Ch., Brissand I. and Michelot J.L. (1984) Hydrological Implications of deep production of Chlorine-36. Nucl. Instr. Meth. Phys. Res., **B5**, 303–307.

Greber E. (1992) Das Geothermalfeld von Kuzuluk/Adapazari (NW-Türkei). Geologie, aktive Tektonik, Hydrogeologie, Hydrochemie, Gase und Isotope, *Diss. ETH-Zürich Nr. 9984.*

Greber E. (1994) Deep Circulation of CO$_2$-rich Palarowaters in a Seismically Active Zone (Kuzuluk/Adapazari, North Western Turkey), *Geothermics*, **23**, 151–174.

Imbach Th. (1992) Thermalwässer von Bursa. Geologische und hydrogeologische Untersuchungen am Berg Uludag (NW-Türkei). *Diss. ETH-Zürich Nr. 9988.*

Imbach Th. and Balderer W. (1990) Environmental hydrogeology of a karstic system with thermal and normal groundwaters Examples from the Bursa Region (Turkey). In: *Proc. Int. Symp. & Field Seminar on Hydrogeological Processes in Karstic Terranes, 7–17 October 1990 Antalya, Turkey*, IAHS Publication no. 207.

Kubik P.W. (1983) Beschleuniger-Massenspektrometrie mit nachgestripptem ^{36}Cl, *Inaugural-Dissertation*, Technische Universität München.

Kubik P.W., Korschinek G., Nolte E., Ratzinger U., Ernst H., Teichmann S. and Moringa H. (1984) Accelerator mass spectrometry of 36Cl in limestone and some paleotological samples using completely stripped ions, *Nucl. Instr. & Methods*, **B5**, 326.

Lal D. and Peters B. (1967) Cosmic ray produced radioactivity on the earth. *Handbuch der Physik* XLVI/2.

Lehmann B.E. & Loosli H.H. (1989) Subsurface production of 3He, ^{36}Cl, 37Ar, 39Ar, 40Ar, 129I and 222Rn in the crystalline basement and the sediments of Northern Switzerland. In: *Water-Rock Interaction*, (ed. by Miles). Balkema, Rotterdam.

Lehmann B.E., Loosli H.H., Balderer W., Fontes J.Ch., Michelot J.L. (1991) Chlorine-36. In: *Applied Isotope Hydrogeology – A Case Study in Northern Switzerland* (ed.

by F.J. Pearson, W. Balderer., H.H. Loosli, B.E. Lehmann, A. Matter, Tj. Peters, H. Schmassmann and A Gautschi). Studies in Environmental Science, 43.

Michelot J.L., Balderer W., Elmore D., Fontes J.Ch., Kubik P.W. and Soreau S. (1987) Teneurs en chlore 36 et problèmes de circulation des eaux profondes du socle de Suisse septentrionale. In: *International Symposium on the use of Isotope Techniques in Water Resources Development, IAEA-SM-299/738,* Vienna, Austria.

Michelot J.L., Fontes J.Ch., Soreau S., Lehmann B.E., Loosli H.H., Balderer W., Elmore D., Kubik P.W., Wölfli W., Beer J. and Synal A. (1989) Chlorine-36 in deep groundwaters and host-rocks of Northern Switzerland: Sources, evolution and hydrological implications. In: *Water-Rock Interaction* (ed. by Miles). Balkema, Rotterdam.

Michelot J.L. (1990) Hydrologie Isotopique des Circulations Lentes en milieu cristallin fracturé: Essai Methodologique, *Thèse de Doctorat ès Sciences Nr. 3446,* Université de Paris-Sud, Orsay, France.

Miserez J.C. (1971) Premier bilan des indices de saturation en carbonates dans le bassin supérieure de l'Areuse (NE). *Extrait des actes de 4e Cogrès de Spéléologie, Neuchâtel, sept. 1970,* Neuchâtel.

Mützenberg S. (1989) Westliche Biga-Halbinsel: Geologie, Tektonik und Thermalquellen (Canakkale, Türkei), *Mitt. Geol. Inst. ETH Univ. Zürich,* **287**.

Mützenberg S., Balderer W. and Rauert W. (1992) Environmental Isotope Study of Saline Geothermal Systems in Western Anatolia (Canakkale, Turkey). *Proc. of the 7th International Symposium on Water Rock Interaction, Park City, Utah.* A.A. Balkema, Rotterdam.

Pearson F.J., Balderer W., Loosli H.H., Lehmann B.E., Matter A., Peters Tj., Schmassmann H. and Gautschi A. (1991) Applied Isotope Hydrogeology – A Case Study in Northern Switzerland, *Studys in Environmental Science* **43**, Elsevier, Amsterdam.

Peters Tj. (1986) Structurally incorporated and water extractable chlorine in the Böttstein Granite (N. Switzerland) *Cont. Min. Petrogr.,* **94**, 305–322.

Pfister M. (1995) Geothermische Untersuchungen in der Region Marmara. *Diss. ETH-Z Nr. 11054,* 135 pp.

Rybach L. and Pfister M. (1993) Geothermal investigations, *Terra Nova,* **5**, 164–173.

Rybach *et al.* Radioelements measurements in rocks of the Marara Project areas in Western Turkey and implications for the heat flow distribution.

Schindler C., Balderer W., Greber E., Imbach, Kahle H.G., Marti U., Straub C., Aksoy A., Rybach L., Pfister M., Pavoni N. and Mayer-Rosa D. (1993) The MARMARA Poly Project: Tectonics and recent Crustal Movements Revealed by Space-Geodesy and Their Interaction with the Circulation of Groundwater, Heat Flow and Seismicity in Northwestern Turkey, *Terra Nova,* **5**, 164–173.

Straub Ch. and Kahle H.G. (1994) Global Positioning System (GPS) estimates of crustal deformation in the Marmara Sea region, Northwestern Anatolia, *Earth Planet. Sci. Letts,* **121**, 495–502.

Synal H.A., Beer J., Bonani G., Suter M. and Wölfli W. (1990) Atmospheric transport of bomb-produced ^{36}Cl, *Nucl. Instr. Meth. Phys. Res.,* **B52**, 483–488.

Synal H.A., Beer J., Lukasczyk Ch., Suter M. (1994) ^{36}Cl in Polar Ice Cores. In: *PSI Condensed Matter Research and Material Sciences: Progress Report 1993, Annex IIIA, Annual Report 1993.* Paul Scherrer Institut, Villigen PSI, Switzerland.

Synal H.A., Kubik P.W., Beer J., Lehmann B., Suter M. (1994) A ^{6}Cl Depth Profile of a Limestone Core from Vue des Alpes. In: *PSI Condensed Matter Research and Material Sciences: Progress Report 1993, Annex IIIA, Annual Report 1993.* Paul Scherrer Institut, Villigen PSI, Switzerland.

Received 21 December 1994; revision accepted 22 March 1995.