Origin of Thermal Waters in Budapest Based on Chemical and Isotope Investigations Including Chlorine-36

Werner Balderer, H. Arno Synal, J. Deák, I. Fórizs and Fanny Leuenberger

Abstract Budapest is a major spa center with numerous thermal baths that are open to the public. Thermal spas in Budapest were first developed by the Romans and followed by the Turks, present spas were built mainly in the 19th and 20th centuries. At the city of Budapest the Danube River flows along a geological fault which separates the Buda Hills from the Great Plain. Within this fault zone in the vicinity of the Danube more than 100 thermal springs are arising yielding totally about 40,000 m^3 per day of warm mineral water. In this study the results of thermal, chemical and isotope analyses (including tritium and chlorine-36) of 12 thermal springs and wells are presented. These results are interpreted with respect to the origin and recharge conditions of the investigated thermal waters.

Keywords Thermal waters · Hydrogeological processes · Isotopes · Budapest

W. Balderer (✉)
Swiss Geotechnical Commission, ETH Zurich, SGTK Sonneggstr. 5,
8092 Zurich, Switzerland
e-mail: werner.balderer@erdw.ethz.ch

H. A. Synal
Institute of Particle Physics, ETH Zurich, Schafmatt Str. 20,
8093 Zurich, Switzerland

J. Deák
GWIS Ltd, Alkotmány Street 45, Dunakeszi 2120, Hungary

I. Fórizs
Hungarian Academy of Sciences, Institute for Geochemical Research,
Budapest, Budaörsi út 45, Budapest 1112, Hungary

F. Leuenberger
Geological Institute, Engineering Geology, ETH Zurich, Sonneggstr. 5,
8092 Zurich, Switzerland

1 Introduction

The capital of Hungary is situated along the Danube River, in the heart of the Carpathian basin. Budapest is divided by the Danube in two parts, the higher hilly side of Buda and the lower plain named Pest on the other side; therefore, both sides together form Budapest. Hilly Buda, which comprises one-third of the city's area of 525 km^2, is located along the right bank of the Danube surrounded by low mountains up to an altitude of 529 m above msl.

Budapest is a world known famous spa center with numerous thermal baths (Fig. 1).

The origin of these naturally outflowing thermal waters is due to the special geological features of this area in central Hungary. A conceptual hydrogeological model is presented in Fig. 2.

At the city of Budapest, the Danube River flows along a geological fault of north–south direction, which separates the Buda Hills from the Great Plain (Fig. 2). Within this fault zone in the vicinity of the Danube more than 100 thermal springs are arising, yielding a total of about 40,000 m^3 per day of warm mineral water.

As shown on the geological cross section of Fig. 3, the geological situation can be summarized as follows: the Danube (thermal) fault zone divides the city of Budapest in two distinct areas. In the Buda Hill at the Western bank of the Danube, Late Triassic dolomites are exposed forming a horst-anticline structure. On the other side of the Danube River the Pest plain extends to the east. In this area the Triassic dolomites and Eocene limestone are covered by several 100 m thick Paleogene shelf margin deposits and Quaternary alluvium of the Danube. In previous publications (Alföldi et al. 1978; Korpás et al. 1999), the mechanism of the ascending thermal waters is explained by the following theory: the karst water circulation within these dolomitic limestone formations is controlled partly by depositional features (unconformities, caves and clastic horizons) and partly by tectonic features such as faults and related fractures. "Ascending thermal water (along faults) mixes with cooler meteoric water giving the thermal springs and spas along the Danube" (Alföldi et al. 1978; Korpás et al. 1999).

1.1 Aim of the Present Study

The hydrogeological situation of the thermal springs is explained by the above-mentioned mixing theory; however, it remains still to prove these postulated hydrological mixing processes by investigation of the properties of the outflowing groundwater itself.

As demonstrated in Balderer et al. (2004), for the infiltration of the Danube River in western Hungary (Szigetköz area) the two radionuclide tritium (^{3}H) and Chlorine-36 (^{36}Cl) are well suited to study the infiltration process of recent
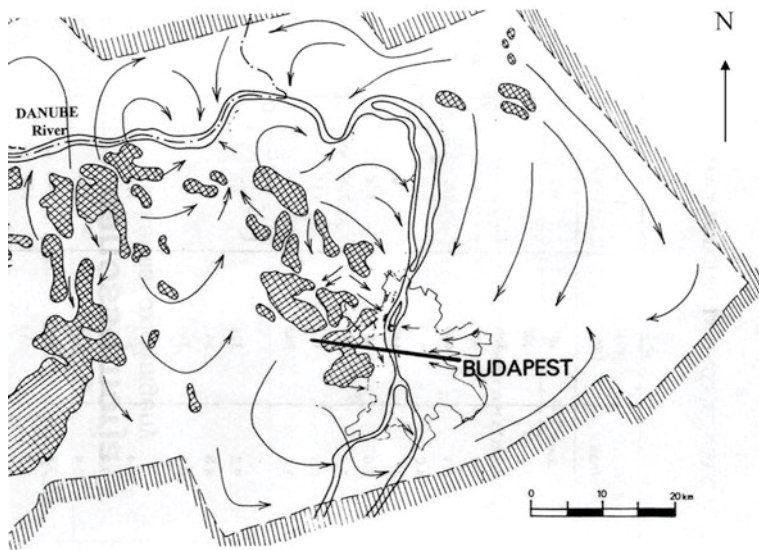
Fig. 1 Map with the Spa area of Budapest

Fig. 2 Conceptual model of Budapest thermal karst-water regime after Alföldi et al. (1978) and Deák (1979). The bold straight line presents the orientation of the cross-section presented in Fig. 3. Karstified rocks are on the surface on the grated areas (recharge). Arrows show the possible flow paths of karst-water
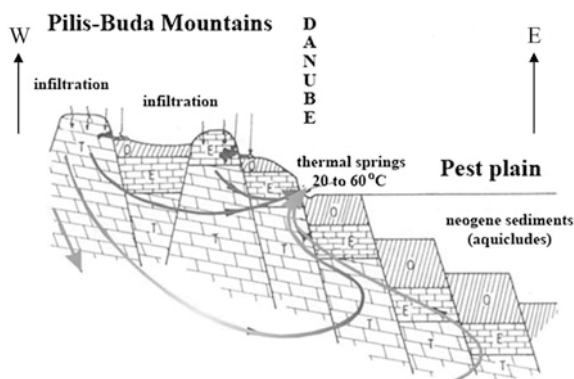
Fig. 3 Hydrogeological cross section presenting the water circulation in the Budapest thermal karst regime (after Kovács and Müller 1980). Arrows indicate schematic flow paths which are 3-dimensional and step out from the cross section in both the south and north direction (See Fig. 2). Used Terms of lithological units: *T* Triassic dolomite; *E* Eocene limestone; *O* Oligocene clay

groundwater along a groundwater flow path as still some bomb-produced nuclides are remaining within the water cycle.

In the present situation of mixing recent recharged karst groundwater with postulated groundwater of deep origin at higher temperatures and also of different chemical composition, the two mentioned radionuclides provide additional properties which are well suited to check for proposed hydrogeological processes of the formation of the Budapest thermal waters.

In a previous investigation of the groundwaters of the quaternary aquifer of the Great Hungarian Plain, the ^{36}Cl method proved to be applicable also for groundwater of recharge within the last glacial period; and it was also in agreement with the results of the ^{14}C and the stable isotopes ^{18}O and ^{2}H (Balderer et al. 1998).

2 Introduction to the Application of ^{36}Cl in Groundwater Studies

2.1 Origin of Chlorine-36 in Groundwater

^{36}Cl with a half-life of about 301,000 years is one of the most promising isotopes for environmental studies. The ^{36}Cl content is usually expressed as concentration with respect to the volume of water (number N of ^{36}Cl atoms per litre of H_2O) or as the atomic ratio R of ^{36}Cl with respect to the total chloride.

$$\text{The conversion factors are: } N = 1.7 \cdot 10^{19} \cdot R \cdot C \tag{1}$$

$$\text{or: } R \cdot C = N \cdot 5.89 \cdot 10^{-20} \tag{2}$$

where, C is the chloride content of the water in mg/l. The principles of the ^{36}Cl method are well described by several authors as reviewed in Balderer and Synal (1996, 1997).

The main cycle in groundwater is related to the following processes and reservoirs.

2.1.1 Atmospheric Input

Natural ^{36}Cl is primarily produced 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 latitude dependence (Bentley et al. 1986). New ^{36}Cl measurements on ice cores from Greenland at latitudes between 60° and 70°N result ^{36}Cl fallout rates of about 20 atoms/(m^{-2}/s) (for the period not affected by the anthropogenic thermo nuclear production; Synal et al. 1990).

This is approximately a factor of 2 higher than the expected fallout rates according to Bentley et al. (1986).

The ^{36}Cl concentration N_o for the infiltration water is given by the following equation:

$$No = F/P \cdot 3.156 \cdot 10^7 \cdot 100/(100 - E) \tag{3}$$

with:
F   Fallout rate of ^{36}Cl (at $m^{-2} \ s^{-1}$)
P   Mean annual precipitation of the considered catchment area (mm)
E   Mean annual evapotranspiration rate (in % of P).

2.1.2 Anthropogenic Thermo Nuclear Production

Nuclear weapon tests in the South Pacific in the years 1952–1959 produced large amounts of ^{36}Cl through the reaction:

^{35}Cl (n,γ) ^{36}Cl by neutron activation of chloride contained in sea water. ^{36}Cl contents, which are about three orders of magnitude above the normal level in precipitation waters, have been observed in ice cores from Dye-3 in Greenland between 1952 and 1956 (Synal et al. 1990).

In shallow groundwater also anthropogenic produced tritium and increased ^{36}Cl concentration were measured as reported in Bentley et al. (1986).

Table 1 ^{36}Cl/Cl—ratios of achieved secular equilibrium of underground production

Rock type	^{36}Cl/Cl—ratio
Vulcanite	$10\ (\pm 1.7)\cdot 10^{-15}$
Rhyodacite	$19\ (\pm 1.1)\cdot 10^{-15}$
Marble (limestone)	$5.6\ (\pm 0.4)\cdot 10^{-15}$
Travertine	$0.9\ (\pm 0.3)\cdot 10^{-15}$

2.1.3 Near Surface Production

In case of calcium carbonate formations, ^{36}Cl production from cosmic myons is of importance down to depths of 100 m below surface.

2.1.4 Radiogenic Production in the Deep Subsurface

Within the geological environment ^{36}Cl is naturally produced by the radiogenic reaction ^{35}Cl (n,γ) ^{36}Cl and expressed by the following equation:

$$R_{eq} \cdot C_o \cdot (1 - e - \lambda t) \tag{4}$$

where C_o is the chlorine content of the recharge groundwater and R_{eq} the ^{36}Cl/Cl ratio for achieved equilibrium of underground production (depending on the radio element content of the aquifer rock). An additional source presents dissolved chloride originating from the aquifer rocks which is contained in minerals, fluid inclusions and as inter granular salt in pore spaces. 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.

In order to give the magnitude of the possible range of underground production for a groundwater of long residence time, the following ^{36}Cl/Cl ratios of achieved secular equilibrium of underground production (that means a residence time of more than 5 half-lives, that means more than 1.5 million years) are given in Table 1, according to Balderer and Synal (1997).

2.1.5 Radioactive Decay During Residence in the Aquifer Along Flow Path

Within the groundwater the atmospheric component is subject to radioactive decay.

The corresponding equations are:

$$\text{if expressed as ratios: } R = R_o \cdot e^{-\lambda t} \tag{5}$$

and,

$$\text{if expressed as concentrations: } N = N_o \cdot e^{-\lambda t} \tag{6}$$

$$\text{according to the equation: } RC = R_o \cdot C_o \cdot e^{-\lambda t} \tag{7}$$

2.1.6 Residence Time of the ^{36}Cl in Groundwater

The resulting residence time of the ^{36}Cl in groundwater is determined by taking into account all these processes by the following equation derived from mass balance a mass balance approach:

$$t = -1/\lambda \cdot \ln\{C/C_o \cdot (R - R_{eq})/(R_o - R_{eq})\} \tag{8}$$

where:
λ $\ln 2/T_{1/2}$ = decay constant of ^{36}Cl,
$T_{1/2}$ half-life of ^{36}Cl equal to 301,000 years
R ^{36}Cl/Cl ratio of water sample (R),
R_o ^{36}Cl/Cl ratio of infiltrating water
R_{eq} ^{36}Cl/Cl ratio of chloride in secular equilibrium of production
C_o chloride concentration of the infiltration water (directly from precipitations)
C   chloride concentration of the water sample.

3 Interpretation of the Results of Analyses of the Sampled Waters

According to the obtained data of the chemical and isotope analyses as presented in Table 2 the following characteristics can be deduced:

- The water of the cold spring of some km NW to Budapest on the hilly recharge area (Csobánka, Szentkút OBP21) yields the lowest water temperature of 10 °C, the highest tritium concentration of 4.3 TU, and the highest ^{36}Cl/Cl ratio of 1007 $\cdot$ 10^{-15}. This component of cold, low chloride water contains water originating from the nuclear bomb period (Balderer et al. 2004). It is therefore considered as most representative of a groundwater of recent recharge containing no component of the deep thermal water.
- The water of three deep wells may be considered as the possible end-member of the hot thermal water ascending along deep fault zones. The water of Széchenyi-spa (OBP24), Paskál-spa (OBP 12), and Palatinus-spa Margitsziget II. (OBP1) is tritium-free (<0.5 TU), which have the highest temperature (68–78 °C) and the lowest ^{36}Cl/Cl—ratio of 9.2 $\cdot$ 10^{-15}–19.4 $\cdot$ 10^{-15}. These wells lying on the Pest Plain provide groundwater from limestone and dolomite aquifers covered by thick (300–1,700 m) aquitard sediments.

Table 2 Results of chemical and isotope analyses of the investigated thermal waters

Sample location	Nr.	Type	$^{36}Cl/Cl * (10^{-15})$	Tritium (TU)	T (°C)	F⁻ (ppb)	Cl⁻ (ppb)	Br⁻ (ppb)	NO₃⁻ (ppb)	SO₄²⁻ (ppb)
Budapest area										
Széchenyi-spa II	OBP 24	W	9	<0.5	76.8	3.31	189	0.55	n.d.	195
Paskál-spa	OBP 12	W	19	<0.5	69.7	2.69	96	0.25	n.d.	148
Palatinus spa, Margitsziget II	OBP 01	W	17	<0.5	68.6	2.81	166	0.51	n.d.	202
Lukács-spa IV	OBP 26	Sp/W	31	1.5	52.5	2.29	129	0.29	n.d.	161
Csepel-spa II	OBP 20	W	26	<0.5	45.2	1.71	186	0.43	n.d.	321
Gellért-spa GT-I	OBP 15	Sp/W	24	1.5	44.5	2.23	151	0.33	1.2	366
Rudas-spa, Juventus	OBP 06	Sp/W	30	1.3	42.7	2.23	148	0.38	n.d.	283
Dagály-spa, Béke-well	OBP 11	W	23	0.6	37.5	1.34	75	0.24	n.d.	110
Palatinus spa, Margitsziget IV	OBP 03	W	25	0.5	36.9	1.35	76	0.23	n.d.	120
Csillaghegy-spa, József	OBP 10	W	199	1.0	27.8	0.40	18	n.a.	1.7	71
Lukács-spa, Római-spring	OBP 29	Sp	358	4.3	20.8	0.48	34	n.a.	6.3	75
Surrounding area of Budapest										
Csobánka, Szentkút-spring	OBP 21	Sp	1,007	4.3	10.0	0.09	14	n.a.	n.a.	247

The analytical error of the ^{36}Cl measurement made by the Accelerator Mass Spectrometry (AMS) Technique is in the order of 10–20 %. The anion concentrations were determined by ion-chromatography
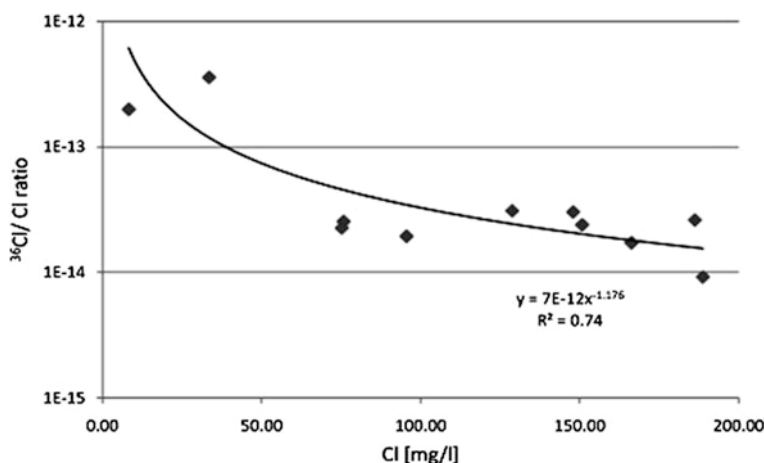
Fig. 4 ^{36}Cl/Cl ratio and Chloride concentration of investigated thermal waters of Budapest

- The other investigated wells and springs are at the vicinity of the fault zone; therefore, these are mixtures of the above-mentioned two components.

From the presented results in Table 2 it can also be deduced that there is no clear systematic trend for the analyzed chemical parameters such as fluoride, chloride, bromide, nitrate and sulfate. This may be due to the fact that the chemical compounds are more related to the local mineralogical composition of the rocks within the groundwater flow path and not only to origin and related mixing processes within the hydrodynamic flow field. For this purpose the two considered radioisotopes present a great advantage, as only related to atmospheric input and groundwater residence time.

## 4 Evaluation of the Mixing Components of the Budapest Thermal Water

According Eq. (1) the concentration N of atoms of ^{36}Cl in 1 liter of water is determined as: $N = 1.7 \cdot 10^{19} \quad R \cdot C$;
where, R is the measured ^{36}Cl/Cl ratio and C is the concentration of chloride of the investigated water.

The same relationship is represented by the diagram of the ^{36}Cl/Cl ratio against the chloride concentration of the investigated waters (Fig. 4). For this relation results in a regression coefficient r^2 of 0.74, the resulting relative mixing proportions by the application of this relationship are presented in Table 3. The next possibility to test this mixing relation of shallow karst groundwater with deep hot thermal water is the combination with the tritium data.

Table 3 Resulting relative mixing proportions as resulting from the ^{36}Cl concentration

Sample Nr.	N ($*10^7$at/l)	Mixing proportion of shallow water component
OBP 1	4.86	0.09
OBP 3	3.27	0.01
OBP 6	7.62	0.21
OBP 11	2.89	0.00
OBP 12	3.15	0.01
OBP 15	6.13	0.15
OBP 20	8.26	0.24
OBP 21	24.70	1.00
OBP 26	6.77	0.18
OBP 29	20.40	0.80
OBP 10	2.87	0.00
OBP 24	2.95	0.00

Fig. 5 Mixing ratios of shallow water component as determined from the ^{36}Cl concentration versus the tritium concentration of the investigated Budapest thermal waters
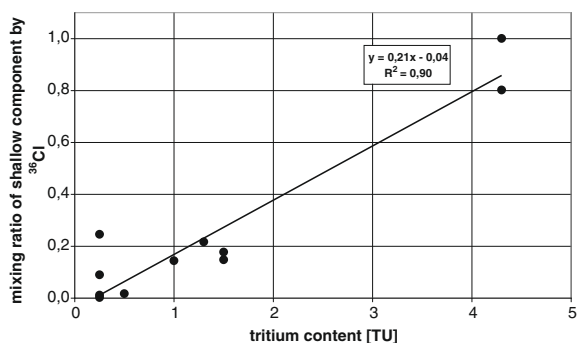
The resulting relation of these calculated mixing ratios with the corresponding tritium concentration (Fig. 5) is with $r^2 = 0.9$ quite good, although some uncertainties may be introduced by the fact that the tritium concentrations in the atmospheric cycle are quite low as the elapsed time as the atmospheric nuclear test activities is now more than 47 years, which equals about four times the half live of the tritium isotope.

The correlation of the $^{36}Cl/Cl$ ratio with the measured water temperature is represented in Fig. 6. Wells and springs in Table 2 are divided into two groups by their tritium content. In the first group where tritium could be detected (>0.5 TU, gray squares on Fig. 6) the $^{36}Cl/Cl$ ratio is decreasing via water temperature. This result can be interpreted as the cooler waters contain more post-bomb ^{36}Cl than the warmer ones because the ratio of fresh (coldest) component decreases via temperature.

In the other group containing tritium free waters (<0.5 TU) the presence of post-bomb ^{36}Cl can be excluded. Significantly lower $^{36}Cl/Cl$ ratio in the warmest waters ($9 \cdot 10^{-15}$–$19 \cdot 10^{-15}$) refers to very long transit time of groundwater or mixing of such an old component to the flow regime. Previous studies (Alföldi et al. 1978; Deák 1979) have demonstrated that the transit time of the Budapest

Fig. 6 Correlation of the ^{36}Cl/Cl ratio with the measured water temperature of the Budapest thermal waters
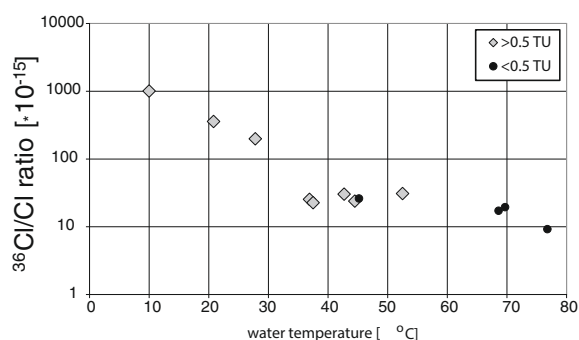
thermal karst-water regime is 20–30 thousand years. Accepting these results based on ^{14}C, δ^{18}O and δ^{2}H data, mixing of a very old component is more reliable than the extremely long transit time.

5 Conclusion

Based on the results of ^{36}Cl and tritium analyses as presented, the already established conceptual hydrogeological model (Fig. 2) can be confirmed:

- Cold groundwater of atmospheric origin infiltrates within the karstified recharge areas of Buda hills and is flowing within the limestone aquifer—according to the present hydraulic conditions—towards the Danube River which is parallel to an active tectonic fault zone. It supplies the cold component of springs rising along the hill slope. This cold water contains tritium and ^{36}Cl of anthropogenic origin.
- Thermal component originates from the ancient precipitation fallen in the Buda hills and Pilis mountains lying 100–400 m higher elevations as the thermal wells and springs. This high potential energy forces the karst water to follow the karstified rocks into high depths. Reaching the highest depths of the flow path (boundary of carbonate aquifers, see Fig. 2) the heated water will flow towards the springs.
- The deep hot water is characterized by a higher residence time (without any trace of anthropogenic tritium or ^{36}Cl) with ^{36}Cl/Cl -ratios at levels quite similar to the ratios of achieved equilibrium of underground production as of vulcanite rocks with $R = 10$ $(\pm 1.7) \cdot 10^{-15}$ up to Rhyodacite rocks with $R = 19$ $(\pm 1.1) \cdot 10^{-15}$. That would mean that the residence time of the deep water component could even reach time scales of up to 1.5 million years (for achieved equilibrium of underground production).

Such a rock environment is in quite good agreement with the observed geological features of the area whereas even volcanic intrusions of Senonian to Late Eocene age are present. The coeval volcanism produced volcano-clastics, shallow

intrusive bodies and dikes. The center of this volcanism was postulated as the Wein palaeovolcano located in the SE foreland of the Buda Hills as reported in Korpás et al. (1999). This hypothetical model is in contradiction with the former interpretation of isotope data (Deák 1979) presenting much younger groundwater ages to be less than 30,000 years. A more reliable hypothetic model can be developed presuming that a certain amount of very old, respectively stagnant (several millions of years old) groundwater is mixed to the relative young (20–30 thousand years) karst water. Mixing ratio depends on the Chlorine ion content of the hypothetic old component.

References

Alföldi L, Deák J, Liebe P, Lorberer Á (1978) Connection of cold and warm karstic water resources in the Hungarian Central Mountains with special reference to draining efforts of mining (in Hungarian). In: Proceedings of research activity of VITUKI, Report series (1976–1977) 3.15, pp 300–317

Balderer W, Synal HA (1996) Application of the chlorine-36 method for the characterization of the groundwater circulation in tectonically active areas: Examples from North Western Anatolia, Turkey. Terra Nova 8:324–333

Balderer W, Synal HA (1997) Use of chlorine-36 as tracer for the evolution of waters in geothermal and tectonically active areas in Western Turkey. Elsevier Sci 123:387–393

Balderer W, Synal HA, Deak J, Stichler W (1998) Application of the chlorine-36 method for the investigation of the infiltration conditions and evolution of the deep groundwaters of multilayer aquifer systems of the Great Hungarian Plain. In: IAEA-SM-349/2P, vol 2. International Atomic Energy Agency, Vienna, pp 431–437

Balderer W, Synal HA, Deak J (2004) Application of the chlorine-36 method for the delineation of groundwater recharge of large river systems: example of the Danube River in Western Hungary (Szigetköz Area). Env Geol 46(7):755–762

Bentley HW, Phillips FM, Davis SN (1986) Chlorine-36 in the terrestrial environment. In: Fritz P, Fontes JC (eds) Handbook of environmental isotope geochemistry, vol 2, The terrestrial environment, B, Elsevier, Amsterdam, pp 427–480

Deák J (1979) Environmental isotopes and water chemical studies for groundwater research in Hungary. In: IAEA Vienna, isotope hydrology 1978, vol 1, pp 221–249

Korpás L, Lantos M, Nagymarosy A (1999) Timing and genesis of early marine caymanites in the hydrothermal palaeokarst system of Buda Hills, Hungary. Sed Geol 123:9–29

Kovács J, Müller P (1980) Origin and traces of hydrothermal activities in the Buda Range (in Hungarian). In: Karszt és Barlang, 1980/II, pp 93–98

Synal HA, Beer J, Bonani G, Suter M, Wölfli W (1990) Atmospheric transport of bomb-produced ^{36}Cl. Nuclear instruments and methods in physics research, B(NIMB), vol 52. Elsevier, North Holland, pp 483–488