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ORIGINAL ARTICLE

Residence time distribution in the Kirkgoz karst springs (Antalya-Turkey) as a tool for contamination vulnerability assessment

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Abstract Lumped parameter modeling of environmental tracer (tritium, CFCs and tritiogenic helium-3) transport in the Kirkgoz karst springs (Antalya-Turkey) appears to be a useful tool for assessing the vulnerability to contamination. Based on tritium observations between 1963 and 2000, the springs revealed a mean residence time (MRT) of 120 years. This suggests an active transport volume of 71 billion cubic meters for the aquifer, a value that is coherent with the estimated void volume of karst aquifer based on the mass of associated travertine deposits. The CFC-11 and CFC-12 MRTs are in agreement with tritium-based MRT, after correcting for excess air effect. Excess crustal and mantle helium flux hindered the use of tritiogenic helium-3 as a potential tracer. The residence time distribution (RTD) indicates a groundwater transport system that is fed by recharges extending back to past several hundred years. This wide RTD suggests that any recent contamination that may have entered the system could progress slowly within the entire aquifer but would be unnoticed in the early period because of the dilution effect of uncontaminated past recharge waters. Once the contamination is recognized, it may last for many centuries ahead even if the contamination practice is stopped. Thus, control of contaminant release to aquifer and monitoring of contaminant level in Kirkgoz springs is an immediate task for the associated public health authorities.

Keywords Lumped parameter · Modeling · Environmental tracer · Turkey

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Introduction

Karst aquifers are drained mostly by large springs that provide water for various uses. About one quarter of world's population is dependent on karst aquifers as the primary water resource (Ford and Williams 1989). However, compared to non-karstic groundwater systems, these aquifers are generally regarded as more prone to contamination because of their relatively high infiltration capacity. Therefore, a proper assessment of vulnerability to contamination is an important environmental and hydrogeologic task that is required for sustainable use of karst springs. Risk assessment maps based on data, such as geologic and hydrogeologic structure, soil cover, and land use, and interpretation methodologies, such as DRASTIC, are used increasingly for this purpose (e.g. Yidirim and Topkaya 2006). However, the reliability of resultant vulnerability map is inversely dependent on the complexity of karstic system. More reliable information comes usually from tracer tests carried out between point recharge sources (e.g. sinkholes) and the spring(s). But, the results of tracer tests are representative only for the flow conditions of the part of the aquifer where they are applied.

One way to determine the vulnerability of karst springs to contamination is to analyze groundwater's residence time distribution (RTD) with the aid of environmental tracers (e.g. tritium, ^{3}H) by means of flow and transport modeling. Any water sample taken from a karst spring comprises water molecules that have different residence times because of different velocities they had and the different flow paths they followed. The mean residence time (MRT) is the mean of residence times of water molecules in the water sample. Both the MRT and RTD can be determined by numerical modeling of either distributed or lumped type. However, in many cases extreme complexity of flow domain in karst aquifers limits the use of distributed parameter models, whereas the lumped parameter (LP) models that use a single equation to describe the RTD provide a strong alternative. Once the RTD of water mass in a karst spring is firmly established, it can be used to estimate contaminant arrival times at the springs.

The purpose of this study is to determine the RTD in the Kirkgoz (Antalya-Turkey) karst springs (spelled as Kırkgöz in Turkish) that provides water for domestic use, irrigation and hydroelectricity production. Because surface waters are limited and the other groundwater resources have already been polluted by industrial and agricultural mispractice, the Kirkgoz springs with minimum discharge of 15 m^3/s constitute a strategic water resource for the nearby Antalya city where population reaches 2 million during the peak tourism season. Sustainable development of the area is critically dependent on the protection of Kirkgoz springs from contamination. Although, several studies (e.g. Yurtsever 1979; UNDP 1983; Tezcan 1993) have been carried out to determine the MRT of Kirkgoz springs, the conflicting results they present necessitates a comprehensive reanalysis. Therefore, the environmental tracer data available from literature (^3H, CFC-11, CFC-12 and tritiogenic helium-3: $^3He^*$) have been used in this study by means of a lumped parameter modeling technique to determine the springs' MRT. The RTD associated with the MRT found by model was then used to assess the vulnerability of springs to potential contamination in the recharge area.

Study area

Kirkgoz springs is located at 300 m elevation (36°50′N, 30°50′E) on the southern flank of Central Taurids Mountains that extend along the Mediterranean coast of Turkey (Fig. 1). The mountain belt where the elevation ranges between 300 and more than 1,500 m form a topographic barrier between coastal zone and inner plains of intra-mountain character. A simplified tectono-stratigraphic framework of geology includes autochthonous Beydaglari carbonates (limestone, dolomite, dolomitic limestone) at the bottom (Senel 1997). This unit is thrusted over by the mostly impermeable units of Elmali and Antalya nappes on the western and eastern sides, respectively. Beydaglari carbonates (the karst aquifer) is drained mainly by Kirkgoz springs, which extends in a 7 hectares large pond of 3 m depth. Part of the underground drainage is suspected to feed the neighboring travertine along its contact with carbonate rocks. The Antalya travertine plateau which has been formed by the Kirkgoz springs since late Pliocene (Glover and Robertson 2003) is the largest (>600 km^2) karstic travertine deposit of the world. The spring zone is

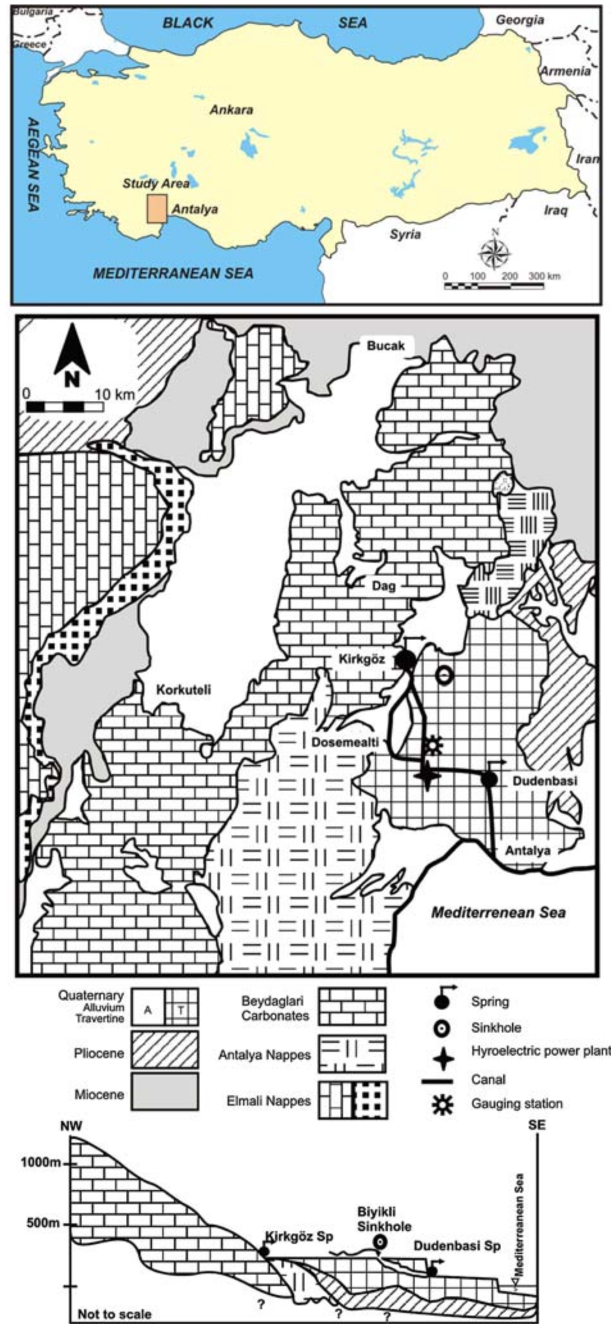

Fig. 1 Location and simplified geologic map of the study area (modified after Senel 1997)

located along the boundary between the Beydaglari carbonates and the impermeable ophiolitic rocks of Antalya nappes (see Fig. 1). This boundary is currently masked mostly by lacustrine deposits. Quaternary lacustrine deposits spreading around the spring zone imply that the springs' pond has expanded and shrinked several times in the past, probably because of climate changes that affected discharge regime. Currently, the pond water is diverted into two canals that transmit water for agricultural use (Vakif canal) and hydropower generation (Kepez canal). Until 1961, the springs' water was being naturally drained into the Biyikli sinkhole located nearby the pond area (Denizman 1989). Sinking water was proven, by a dye tracing test, to arrive at Dudenbasi spring (see Fig. 1) located at 20 km southeast of Kirkgoz springs (Gunay and Yayan 1979; Coskun et al. 1985). Beyond the pond area, Kirkgoz springs host one of the largest submerged conduits systems (ca. 478,000 m^3) in the world (Kincaid 1999). The largest single submerged conduit within the system is as large as a stadium.

The climate in the study area is of Mediterranean type with hot–dry summers and mild–wet winters. Mean annual temperature is around 12°C at the inferred mean recharge area elevation of 1,000 m. Based on the records of surrounding meteorological stations between the years 1929 and 2006, the mean annual gross precipitation in the recharge area is estimated as 627 mm, whereas the net recharge to aquifer is estimated, from Thornthwaite's (1944) equation to be 496 mm. Although rainfall constitutes the dominant precipitation type in the recharge area, snowfall is also observed above 800 m elevation during the winter. Kirkgoz springs are characterized by a highly regulated flow regime. According to observations between 1971 and 1986, the mean annual discharge of springs is 18.5 m^3/s. Maximum (22 to 27 m^3/s) and minimum (10 to 15 m^3/s) discharges are observed around January and September, and the ratio of maximum to minimum flow varies between 3/1 and 4/1 (UNDP 1983).

Previous studies indicated an increasing industrial and agricultural contamination in the springs issuing from Antalya travertine plateau (e.g. Karaguzel et al. 1999; Muhammetoglu and Yalcin 2003) still, to the knowledge of authors, notable contamination has not been reported for Kirkgoz springs so far. However, Ekmekci (2005) reports presence of some pesticide compounds in two water samples collected from the pond during the peak water season (March 1998). Because no pesticides were detected in a nearby well drilled in the same aquifer, it is likely that observed pesticides might have transported from the neighboring cultivated lands by way of overland flow. Another possibility appears to be the transport of these chemicals from cultivated lands of intramountain plains by the fast flow component of groundwater. An analysis (Gunay et al. 1995) of few trace metals (e.g. Pb, Ni and Cd) with concentrations close to atomic absorption spectrometer analytical detection limits deserves further investigation by techniques that are more precise. Obviously, further systematic and temporal observations are required to better characterize the potential pollution in Kirkgoz springs.

Materials and methods

RTD model

An unsteady lumped parameter (USLP) model of environmental tracer transport, which is based on Niemi's (1990) approach, has been used in steady mode to determine the RTD in Kirkgoz springs. Details of modeling algorithm and its use are described by Ozyurt and Bayari (2005a). Deterministic modeling of flow and transport in Kirkgoz karst aquifer is practically impossible at this stage because of the unavailability of data required to efficiently describe the characteristics of flow and transport domain (e.g. spatio-temporal head and hydraulic conductivity distribution). The LP model uses a single kernel function that lumps all factors affecting flow and transport so that the model requires only temporal environmental tracer input and output series along with corresponding recharge and discharge data. Steady state runs of model can be done only with mean discharge, which is assumed equal to recharge. Because flow and transport of water and tracer mass in karst aquifers is inherently a complex phenomenon that includes advective, dispersive and diffusive processes, a serially connected piston and well-mixed flow configuration has been used in this study. The piston and well-mixed flow components in the model are roughly analogous to advective and dispersive–diffuse flow, respectively. In the model, the value 0.056262 year–1 has been used as tritium decay and tritiogenic helium growth constant, whereas no degradation for CFCs was assumed.

The LP model used calculates temporal tracer output concentrations for every possible combination of initial reservoir volumes that can be freely selected by the user. Then, the degree of resemblance between calculated and observed tracer contents are determined based on Pearson's correlation coefficient and the mean difference between the calculated and observed values. The mean difference is determined by the following equation in which C_{out}_t and C_{obs}_t represent calculated and observed tracer contents at time(s) t, respectively, and the number of compared data sets is defined by n.

$$\text{Difference} = \sqrt{\frac{\sum (C_{\text{out}\_t} - C_{\text{obs}\_t})^2}{n}} \quad (1)$$

The MRT and RTD are calculated based on reservoir volume and flux rate values corresponding to the best-fitted model, by using the associated kernel function (see Ozyurt and Bayari 2005a)

Modeling approach

While the USLP model used in this study normally requires long-term annual recharge and discharge values, discharge observations of Kirkgoz springs are limited to 1973–1976 and 1980–1986 periods. Moreover, estimation of long-term annual discharge values from a potential relationship between recharge and discharge were found to be practically impossible (Korkmaz 1990). For this reason, the USLP model were first run for steady state condition by using available mean annual discharge rate data (584.8×10^6 m^3/year). The mean annual recharge is assumed equal to mean annual discharge. To determine the effect of unsteadiness, the model was also run for unsteady state conditions by using artificially created recharge and discharge data sets. Annual recharge and discharge data were produced by a random number generation technique in a manner that the produced data ranges between minimum and maximum observed discharge rates and their mean is about the same as the observed values. To refrain from any statistical bias that may arise in random number generation, ten artificial data tests were produced independently.

Discharge data from gauging station (Yesilbayir ID no: DSI-9–80) located on Kepez canal have been used to determine the mean annual total discharge of Kirkgoz springs (Table 1; Fig. 2). Data from this station seem to realistically represent the spring's discharge because only a negligible amount of water is used for the irrigation of lands to the upstream of gauging station.

Tracer input functions and tracer observations

Tritium has been used as the primary tracer to determine the RTD, whereas chlorofluorocarbons (CFC-11 and CFC-12) and tritiogenic helium (^{3}He*) have also been used to test the applicability of these tracers in this karst aquifer. Kirkgoz springs have a long ^{3}H observation set that spreads between the years 1963 and 2000 (Table 2). Part of the data set for net ^{3}H input function calculations were taken from Tezcan (1993) which is based on the ^{3}H observations of the Antalya station (IAEA station ID 173000) of WMO-IAEA GNIP network (GNIP 2007). This station has an almost complete record of monthly ^{3}H observations between 1963 and 1993. The small number of missing data within this period was completed by regression with the data from other neighboring GNIP network stations. The data for 1954–1963 period were derived by regression with Ottawa station (Tezcan 1993). ^{3}H observations at Antalya station between 1994 and 1999 indicate a stable ^{3}H background content in atmospheric precipitation with mean and standard deviation values of 5.6 and 1.8 TU, respectively. This background concentration has been randomly attributed to the years prior to 1954 and after 1999 for which observation is not available. Because the LP model run at annual time steps, monthly ^{3}H values of Antalya station were converted to net annual ^{3}H input values ($^3H_{\text{net}}$) with the following equation.

$$^3H_{\text{net}} = \frac{\sum_{i=1}^{12} (P_{\text{grossAntalya\_i}} * 0.58 * F_{\text{ETP\_i}} * {}^3H_{\text{Antalya\_i}})}{\sum_{i=1}^{12} (P_{\text{grossAntalya\_i}} * 0.58 * F_{\text{ETP\_i}})} \quad (2)$$

where $F_{\text{ETP\_i}}$ is a monthly variable factor for the recharge area that converts gross precipitation to net precipitation by means of Thornthwaite (1944) equation, $P_{\text{grossAntalya\_i}}$ and $^3H_{\text{Antalya\_i}}$ are the observed monthly gross precipitation and ^{3}H in the Antalya meteorological station, respectively. The coefficient 0.58 is used to convert gross Antalya precipitation (1076.5 mm for 1972–1986 period) to gross precipitation at the mean elevation of Kirkgoz springs' recharge area (1,000 m). The mean annual gross precipitation in the recharge area (623.6 mm) was determined from a linear relationship established among the elevations and mean annual gross precipitations of the Antalya (42 m, 1076.5 mm), Dösemealti (265 m, 1033.7 mm) and Dag (775 m, 724.8 mm) meteorological stations (see Fig. 1).

$$P(\text{mm}) = -0.50277^{*}\text{elevation}(\text{m}) + 1125.8 \quad (\text{R}^2 = 0.964) \quad (3)$$

The mean annual net precipitation for the recharge area was determined as 496 mm by Thornthwaite's equation.

Historical atmospheric CFCs' records that is representative for northern hemisphere (NOAA 2007) have been used as input function for these tracers, whereas the net annual 3H input to aquifer was used internally by the model to determine temporal 3He* input. The CFCs concentrations used in models (i.e. CFC-11 = 0.84 pico mol/

Table 1 Statistics of total and base flow of Kirkgoz springs

	Total flow		Base flow	
	10^6 m^3/year	m^3/s	10^6 m^3/year	m^3/s
Mean	584.8	18.5	480.5	15.7
Standard deviation	71.1	2.3	127.1	2.2
Minimum	473.8	15.0	240.0	12.5
Maximum	685.9	21.7	764.0	19.2

Note: Statistics are based on observations during periods between 1971–1977 and 1978–1986

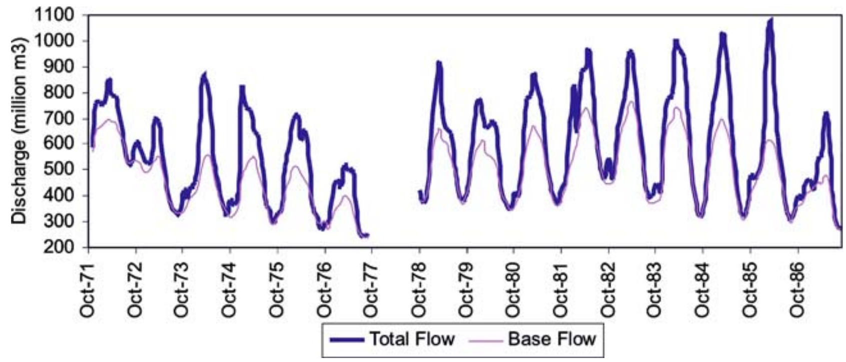

Fig. 2 Observations of monthly total and base flow discharge rate in Kirkgoz springs

Table 2 ^{3}H observations of Kirkgoz springs

	Months												
Years	1	2	3	4	5	6	7	8	9	10	11	12	Source
1963				186						46			a, b
1964							30			19*			a, b
1965		20			19*								a, b
1966			24		35	31			26	26*		79	a, b
1967		28		27								26*	a, b
1968				23		28*							a, b
1969										29*			a, b
1970				23									a, b
1978						16*							a, b
1979					18*								a, b
1988								9*					b, c
1993												6*	b, c
1994					5.9				5.5*				b, c
1995				5		4.7	4.2	4.5	4.5*		4.2	4.6	d
1996	4.3		4.4*										d
2000				3.6						3.7*			e

Note: Data sources are as follows. a: Yurtsever 1979; b: Tezcan 1993; DSI 2004, c: Gunay et al. 1995; d: Nativ et al. 1999; e: DSI 2004. Tritium analyses have been realized by the isotope hydrology laboratories of IAEA-Vienna and DSI-Ankara. Annually representative data used in this study are shown with an asterisk

kg H_2O, CFC-12 = 0.73 pico mol/kg H_2O) represent the concentrations in Kirkgoz springs as of summer 1995 (Nativ et al. 1999). The calculated 3He* content has been calculated from the data given by the same authors for 1995. All environmental tracer input values are provided in Table 3, and their temporal variation is shown on Fig. 3.

Results

Preliminary analysis of ^{3}H observations

A visual analysis of available ^{3}H observations in Kirkgoz springs implies a ''well-mixed'' karst system in which the tracer input for each year is almost perfectly homogenized with the tracer content available in aquifer (see Table 2). Consequently, monthly ^{3}H observations in a given year are very similar, except for the period between 1963 and 1965. The annual ^{3}H content decreases in every passing year towards recent years. Inter-monthly ^{3}H variations observed between 1963 and 1965 is thought to have caused by atmospheric inhomogeneity of tritium content since the banning of thermo-nuclear bomb tests in 1963. These inhomogeneities might have been also caused by thermo-nuclear bomb tests carried out by China and France after 1963. The perfectness of tracer homogenization in the aquifer observed after 1965 leads to the fact that the ^{3}H content in karst aquifer varies temporally because of the decay of ^{3}H in a well-homogenized reservoir. Therefore, any observed ^{3}H at any time can be used to estimate the ^{3}H

Table 3 Environmental tracer input data used in this study

Years	Pnet (mm)	3H (TU)	CFC-12 (pptv)	CFC-11 (pptv)	Years	Pnet (mm)	3H (TU)	CFC-12 (pptv)	CFC-11 (pptv)
1929	187.5	4.5	0.36	0.05	1968	593.3	71.4	102.28	44.99
1930	512.7	6.0	0.36	0.05	1969	997.2	65.1	116.04	52.52
1931	700.6	4.3	0.36	0.05	1970	449.8	57.1	131.11	61.10
1932	349.7	5.0	0.36	0.05	1971	502.0	52.9	147.27	70.52
1933	359.1	4.5	0.36	0.05	1972	223.5	57.6	164.76	81.05
1934	347.7	4.6	0.36	0.05	1973	233.4	23.9	184.03	93.02
1935	618.5	5.4	0.36	0.05	1974	643.3	28.8	204.93	106.24
1936	716.1	4.3	0.36	0.05	1975	608.1	43.2	225.49	119.10
1937	363.0	5.4	0.36	0.05	1976	454.5	34.8	245.10	132.88
1938	551.8	4.6	0.36	0.05	1977	445.0	33.3	263.56	145.33
1939	526.4	6.0	0.36	0.05	1978	695.5	21.1	282.99	154.22
1940	453.7	6.0	0.36	0.05	1979	621.4	15.2	294.81	162.26
1941	255.9	4.3	0.51	0.05	1980	341.9	12.0	309.25	171.80
1942	506.5	4.3	0.70	0.05	1981	847.9	21.9	322.97	179.01
1943	425.9	4.3	0.93	0.05	1982	328.0	20.5	342.55	187.30
1944	655.6	4.3	1.24	0.05	1983	542.8	17.0	361.00	196.92
1945	645.9	5.4	1.64	0.05	1984	583.5	10.4	376.24	205.30
1946	546.8	4.5	2.31	0.08	1985	535.8	7.7	392.88	215.63
1947	394.0	4.6	3.35	0.13	1986	422.9	8.4	412.28	226.90
1948	249.3	6.0	4.63	0.23	1987	279.7	8.2	434.33	238.79
1949	543.1	4.5	6.03	0.39	1988	508.0	6.7	456.79	252.93
1950	311.4	4.5	7.55	0.62	1989	260.5	5.7	472.60	261.39
1951	568.1	4.3	9.22	0.95	1990	243.5	3.7	487.21	267.80
1952	824.9	4.3	10.97	1.42	1991	536.2	0.0	497.94	271.05
1953	469.5	5.1	12.89	2.06	1992	292.1	5.1	511.86	273.05
1954	556.7	186.2	15.06	2.87	1993	359.8	5.6	515.91	273.93
1955	255.1	31.1	17.50	3.86	1994	588.6	5.1	522.39	273.97
1956	504.9	58.6	20.31	5.09	1995	611.9	4.6	526.38	273.24
1957	156.3	101.7	23.52	6.49	1996	693.8	4.8	529.07	272.10
1958	508.0	433.0	26.94	7.84	1997	617.9	5.0	533.50	269.89
1959	364.7	481.7	30.70	9.15	1998	627.9	4.9	535.81	268.03
1960	635.5	97.9	35.11	10.80	1999	372.5	5.3	536.90	265.82
1961	431.8	368.4	40.13	12.94	2000	336.4	5.4	538.43	264.09
1962	418.4	1087.2	45.85	15.67	2001	976.6	4.3	540.15	263.45
1963	424.8	722.5	52.51	19.02	2002	437.7	4.5	540.60	262.80
1964	244.4	445.4	60.28	23.02	2003	876.0	5.0	540.15	262.20
1965	654.4	315.0	69.09	27.60	2004	632.0	4.3	539.70	261.60
1966	641.0	114.9	78.91	32.71	2005	444.7	4.6	539.25	261.00
1967	530.8	109.7	89.93	38.47	2006	510.0	4.5	538.80	260.40

content in the following observation period (Fig. 4a). For example, the decay-predicted ^{3}H content for 1978 (i.e. 14.5 TU) estimated from what is observed in 1970 (i.e. 22.9 TU) resembles closely to observed ^{3}H content in 1978 (i.e. 16 TU). The observed and radioactive decay predicted ^{3}H contents in Kirkgoz springs have a strong linear relationship (Fig. 4b). Similar situations have also been encountered by Ozyurt (2005) in four different springs of Aladag basin, located 350 km to the east of study area. This homogenization is probably the result of a wide range of groundwater velocity distribution that is inherent to many karst systems. Such a wide velocity distribution obviously implies a wide residence time distribution. The ^{3}H decay in well-homogenized Kirkgoz aquifer implies that the amount of this isotope in springs' water will arrive at its analytical detection limit (ca. 0.2 TU for liquid scintillation counting) around 2050.

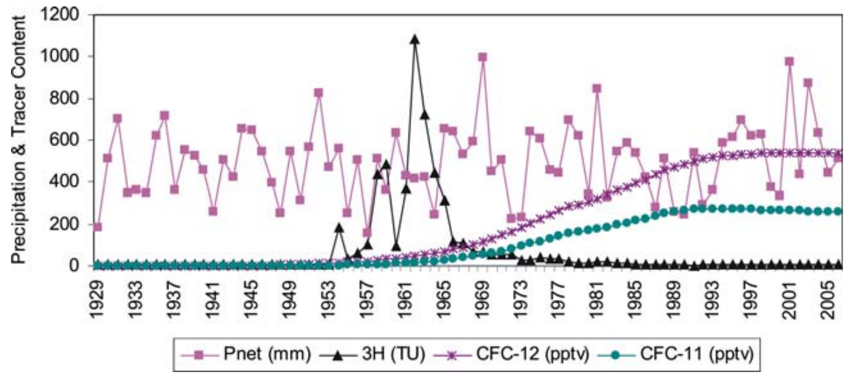

Fig. 3 Input functions of 3H and CFCs and the net precipitation input for the study area

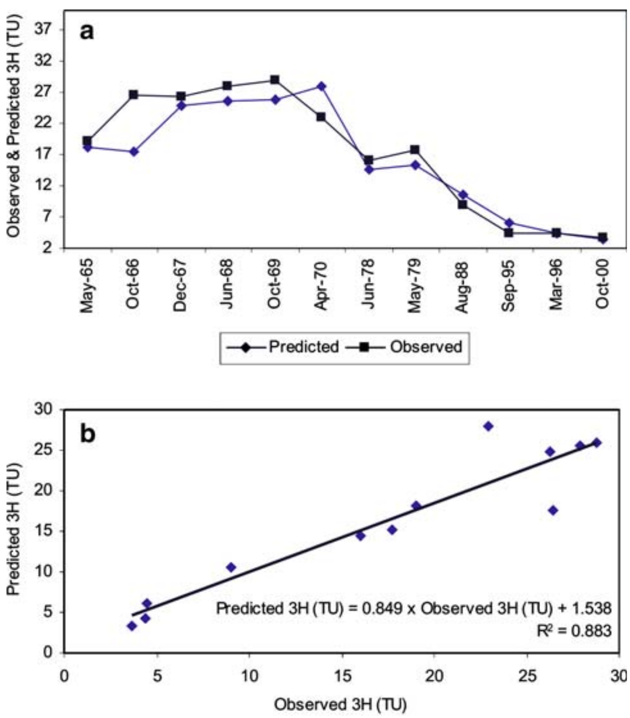

Fig. 4 **a** Temporal variation of observed and radioactive decay-predicted 3H contents in Kirkgoz springs, **b** linear relationship between observed and predicted 3H contents

Tritium-based MRT and residence time distribution

For the determination of tritium-based MRT and its distribution the serially combined well-mixed and piston-type USLP model has been run in steady state mode with the input data between 1929 and 2006 (Fig. 5). Test runs with data sets extending back to the year 1600 did not reveal any significant deviation from the results of models with 1929–2006 data set. A parallel model run with a similar software of well-mixed flow (i.e. FLOPWC, Maloszewski 1996) did also provide the same MRT (Fig. 6). The model provided the best fit to observed ^{3}H contents for MRT = 120 years for the flow system comprising well-mixed and piston flow reservoir volumes of 70×10^9 m^3 and 1×10^9 m^3, respectively (Fig. 5). For this model, the mean difference and the Pearson's correlation coefficient between the observed and calculated ^{3}H series are 2.009 TU and 0.980, respectively. Next three best models provided MRTs as 137, 103 and 103 years with correlation coefficient and difference values ranging as 0.981, 0.914, 0.980 and 2.693 TU, 3.760 TU, 3.802 TU, respectively. Accordingly, the respective well-mixed and piston flow reservoir volumes range between 60–80 $\times$ 10^9 and 1–2 $\times$ 10^9 m^3. Although, all models provided similar MRT and reservoir volumes within the range of uncertainty of input variables, the first model is accepted to be more realistic because it apparently provided the best fit to observed values. Major deviations of observed ^{3}H content from the model predicted values are observed in 1968, 1969 and in 1980 years probably because of the incomplete homogenization of annual recharge and available storage in these years.

To investigate the effect of unsteady flow conditions on tritium transport within the Kirkgoz system, further modeling runs have also been carried out by using the artificially created unsteady influx and outflux series. The ten unsteady model runs provided the same MRT as predicted by the steady state model while their difference and correlation coefficient values vary slightly (Table 4). This resemblance indicates that the variations in annual water mass influx and outflux are damped effectively by the Kirkgoz springs' aquifer, as expected from a flow system with a long MRT and reservoir volume. Because all steady and unsteady model runs provided results that fit to observed data equally well, the soundness of the combined reservoir model and its parameters (i.e. MRT and reservoir volumes) are interpreted to be justified.

The high ratio of well mixed to piston flow reservoir volumes offers some important implications on the flow system of Kirkgoz springs. Long-term observations carried out by Ozyurt (2005) on ^{3}H and specific conductivity response of various karst springs with varying recharge conditions indicate that the dominance of well mixed or piston flow systems in a karst aquifer is linked closely with the recharge regime. Karstic systems tend piston flow when

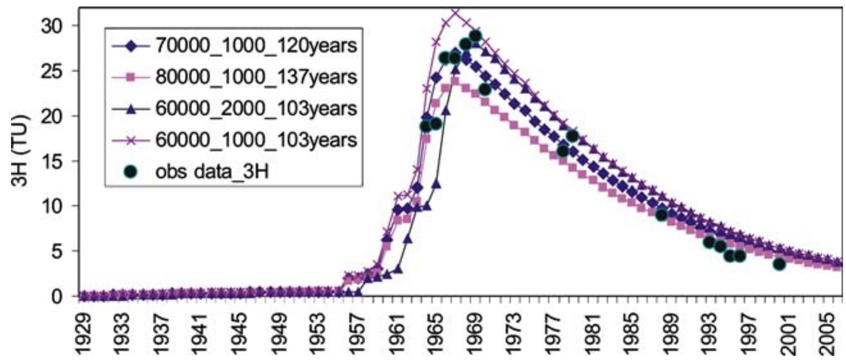

Fig. 5 Comparison of observed and modeled 3H content

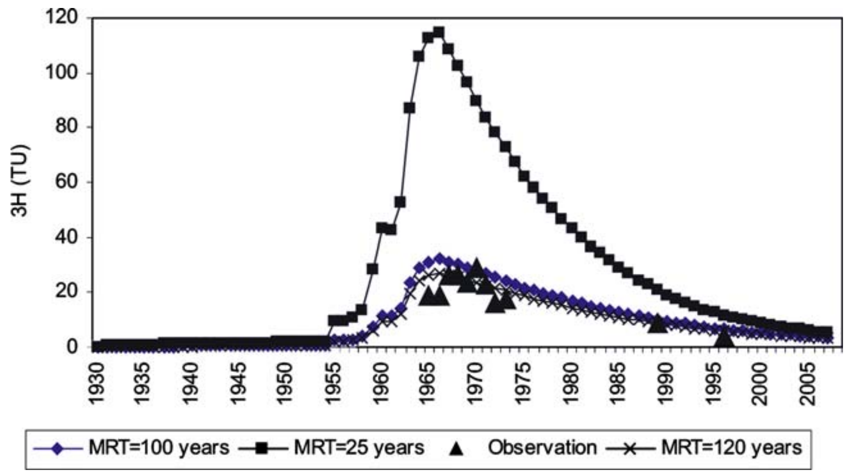

Fig. 6 Comparison of observed and modeled 3H content by FLOWPC model

Table 4 Comparison of model predicted parameters for steady state and unsteady state model runs for ^{3}H

	Vwm (10^9 m^3)	Vp (10^9 m^3)	Difference	Corr. coef.	MRT	Mean annual recharge, MAR (10^6 m^3)	Standard deviation of MAR (10^6 m^3)
SS	70,000	1000	2.00	0.980	120	584.8	–
1	70,000	1000	1.96	0.979	120	586.0	63.4
2	70,000	1000	2.08	0.979	120	585.9	55.7
3	70,000	1000	2.10	0.975	120	584.8	62.1
4	70,000	1000	2.40	0.976	120	585.0	63.7
5	70,000	1000	2.39	0.974	120	584.7	59.9
6	70,000	1000	2.05	0.977	120	584.7	65.4
7	70,000	1000	2.01	0.980	120	584.9	64.0
8	70,000	1000	2.18	0.978	120	585.5	59.5
9	70,000	1000	2.71	0.958	120	584.6	63.8
10	70,000	1000	2.33	0.976	120	584.7	64.3

Notes: *SS* steady state model. Numbers 1 through 10 refer to unsteady models. Vwm: well-mixed flow reservoir volume, Vp: piston flow reservoir volume

recharge is either weak or slow, whereas well-mixed flow becomes dominant when recharge is rapidly transferred into the flow system. In other words, a karst aquifer favors well-mixed flow in the case of a continuous recharge, which is in the form of rainfall that spreads into entire wet period. Contrarily, when recharge is slow as in the case of slow snow melt or when recharge ceases as in dry period, piston flow condition becomes dominant in the flow system. In the case of Kirkgoz springs, the bulk of the recharge is in the form of rainfall, 90% of which occurs between October and May so that, dominance of well-mixed flow is an expected behavior.

Figure 7 shows the temporal variation of cumulative tracer weighting function for the steady flow model of Kirkgoz springs that is based on serially combined well-mixed and piston flow reservoirs with a MRT of 120 years. While the weighting graphs show the situation for the year 2006, it can also be used for any observation year if graph's time scale is shifted accordingly. Because the ^{3}H is a part of natural water molecule, its transport in the karst system can safely be assumed to represent the transport of karstic water mass that accompany this tracer. Therefore, the weights of past tritium inputs on observed ^{3}H content of any year (e.g. 2006) constitutes a reliable indicator of the contribution rates of past water mass inputs (i.e. recharge). The cumulative weighting function indicates that past recharges in the periods of 2006–1980 (20%), 1979–1943 (20%), 1942–1840 (20%) and 1983–1805 (20%) comprises 80% of spring's discharge in 2006, whereas the recharges prior to 1805 account for the rest. Such a wide residence time distribution does also explain why the Kirkgoz springs have always been supersaturated with respect to calcite throughout its history so that it formed the world's largest karst-water travertine deposit. While many factors such as temperature, initial carbon-dioxide content is effective, the length of water–rock contact time is also known to increase calcite supersaturation. The residence time distribution also shows the vulnerability of Kirkgoz springs to contamination events. For example, any pollutant that entered the system only between 1980 and 2006 should be diluted five times because the water mass that carries it comprises only 20% of the total discharge. If the year 1960 is assumed as the onset of anthropogenic pollutant use in the recharge area of Kirkgoz springs, a 30% dilution should be expected as of 2006. Similarly, a pollutant contribution rate of 40% should be expected for the year 2025. These interpretations are obviously based on the assumption that the transport of chemical is exactly similar to that of accompanying water mass. If the contaminant is adsorbed by the aquifer rock or degraded during its transport, lower concentrations would be observed at the springs.

Verification of tritium-based model with CFCs

As a further check of the results obtained from ^{3}H modeling, the same steady state tracer transport model (MRT = 120 years, Vwm = 70×10^9 m^3 and Vp = 1×10^9 m^3) has been also used for CFC-11 and CFC-12 tracers. Use of CFCs as environmental tracer is cumbersome because their initial concentration may be changed because of processes such as sorption, degradation and anthropogenic contamination. Furthermore, their atmospheric input function needs to be converted to dissolved concentration that depends on the temperature and the atmospheric pressure (or altitude) in the environment where the atmosphere equilibrates with recharge water. Other processes such as, partial equilibration and involvement of excess air in recharge water further complicates the use of CFCs. Excess air involvement increases the dissolved concentration whereas, sorption and biochemical decay cause a decrease. To determine the equilibrium concentration of CFCs in recharge water the required equilibrium temperature (ET) and atmospheric pressure (EP) values have been determined from a relationship (Cakir 1998) between mean annual air temperature (MAAT) and elevation of the meteorological stations that encompasses the recharge area of Kirkgoz springs.

$$\mathrm{MAAT}\ (^\circ\mathrm{C}) = -0.006095\ \mathrm{elevation}\ (\mathrm{m}) + 18.026 \quad (R^2 = 0.967) \tag{4}$$

It was assumed that the atmospheric CFCs are introduced in recharge water during the entire year, and the equilibrium temperature is equal to the MAAT at the elevation of recharge area for which the equilibrium pressure (P) has been estimated by the following equation (Manual of Barometry 1963).

$$P\ (\mathrm{atm}) = (1 - 0.0065\ \mathrm{elevation}\ (\mathrm{m})/288.16)^{5.2561} \tag{5}$$

Based on the these equations, the mean annual temperature and air pressure for the mean topographic elevation of

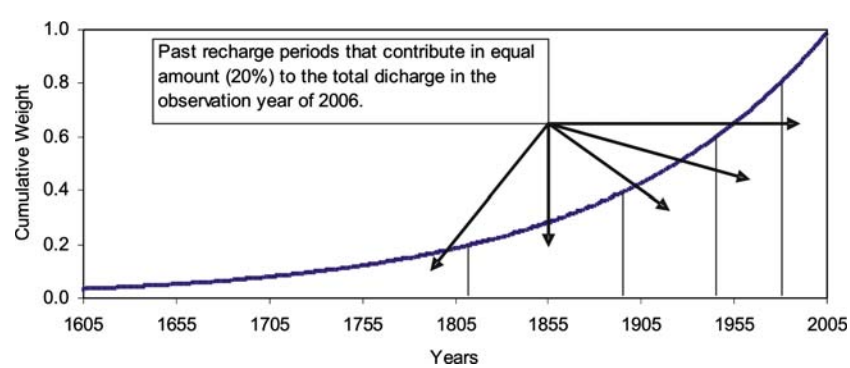

Fig. 7 Temporal variation of cumulative 3H weighting function

recharge area (1,000 m) were found to be 11.9°C and 0.89 atm, respectively. To determine the effect of errors in estimating the magnitude of these variables on model calculations, different values have also been used.

The CFC-11 model run for several plausible ET and EP values shows a good match between observed and model-derived concentrations (Fig. 8). While the model is based on only a single observation, it appears that the CFC-11 may have a potential use as a supplement to ^{3}H modeling in karst systems. However, the same model did not reveal a satisfactory fit between the observed and model-predicted CFC-12 values (Fig. 9). A good fit between observed (raw CFC-12) data and model predicted value could only be obtained for significantly changed CFC-12 input function that corresponds to air–water equilibration at 2,300 m and 4°C, a condition that is practically impossible. However, if the raw CFC-12 observation is corrected for inclusion of 15 cm^3 of excess air, a good fit between predicted and corrected CFC-12 contents could be obtained. A similar correction for CFC-11 does not significantly affect the goodness of fit (see Fig. 8). The excess air volume that is supposed to have involved in Kirkgoz water is about three times greater than the amount that is generally observed in aquifers (Plummer and Busenberg 1999). Greater amount of excess air inclusion may be associated with the complexity of infiltration process in the Kirkgoz aquifer.

Another potential reason for higher than expected CFC-12 concentration could be the contamination of spring water by the CFC-12 bearing pesticides. The latter reason also seems likely because CFCs have been used as propellant in pesticide sprays, and the pesticides are suspected to have contributed into the Kirkgoz aquifer (e.g. Ekmekci 2005). Further CFCs and pesticide observations would help to understand the behavior of CFCs in Kirkgoz karst system.

Verification of tritium-based model with ^{3}He*

Tritiogenic helium-3 accumulates in aquifers due to decay of environmental tritium that had already entered the flow system. Based on this fact, ^{3}He* has been proposed as a substitute for ^{3}H which has been depleted in aquifers due to radioactive decay, and the atmospheric environmental tritium as a feeder has already reached its background value in many places in the world. To test this proposal, ^{3}He* has also been used in this study. Common use of ^{3}He* in aquifers as an age-dating tool is based on the following equation in which ^{3}He* and ^{3}H contents are expressed in TU (Kamenski et al. 1991).

$$t^3H/^3\text{He}*(\text{year}) = \lambda^{-1}\ln(^3\text{He}*/^3\text{H}+1) \tag{6}$$

This equation assumes that a simple piston flow system is dominant in the aquifer, and the resultant value is regarded as ''tritiogenic helium-3 age'' which is different from the real mean age of groundwater because the groundwater flow rarely obeys piston flow. A different approach is the use of lumped parameter model to predict the amount of ^{3}He* to be observed in the sampling point. The model uses the past ^{3}H inputs and their respective residence times to calculate the amount of ^{3}He* to be produced within the aquifer. In theory, for a realistic model, the predicted ^{3}He* value must match the calculated ^{3}He* content which is determined from noble gas measurements. Previous studies carried out on karstic springs (Ozyurt 2005; Ozyurt and Bayari 2005b) have shown that lumped parameter models calibrated for spring's outflux provide the same MRTs both for ^{3}H and ^{3}He*.

The ^{3}He* content of Kirkgoz springs has been calculated as 880 TU from the noble gas (e.g. ^{3}He, ^{4}He, ^{40}Ar, Ne_{total}) data of Nativ et al. (1999) by using the procedures given by Solomon and Cook (1999). The procedures account for the contributions of crustal, radiogenic, atmospheric etc. components, and the success of calculations depends very much on the correct estimation of immeasurable isotope fluxes. Radiogenic and crustal helium contributions are the major complicating factors. Figure 10 shows the temporal variation of ^{3}He* content in Kirkgoz springs as predicted by the steady state model which considerably underestimates the calculated (''observed'') ^{3}He* content. The predicted ^{3}He* content seems reasonable when the amount of ^{3}H input to the aquifer is considered. In other words, there is practically no way for the ^{3}H to

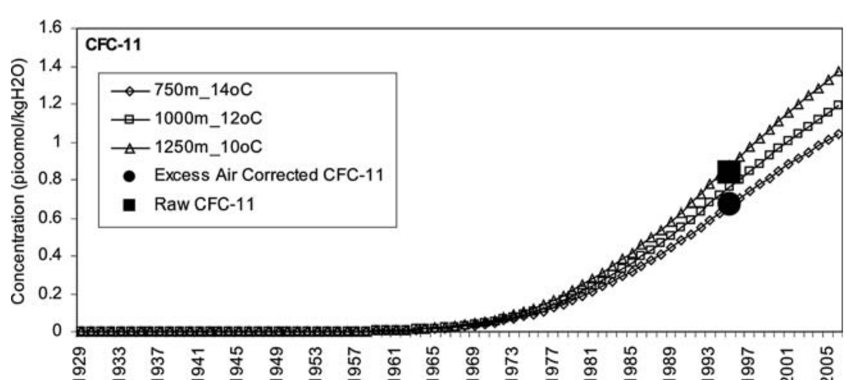

Fig. 8 Comparison of CFC-11 observation with model outputs for various recharge elevation and temperatures

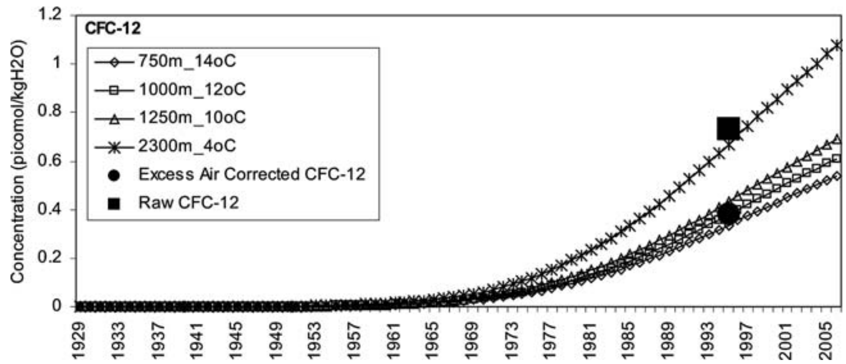

Fig. 9 Comparison of CFC-12 observation with model outputs for various recharge elevation and temperatures

produce ^{3}He* as big as the calculated ^{3}He* based on noble gas data. This discrepancy is caused by the fact that the calculated ^{3}He* is unrealistically high because of inevitable errors associated with the unusually high mantle-crustal or radiogenic helium flux in the recharge area of Kirkgoz springs. This fact is also pointed out by Nativ et al. (1999) based on high ^{3}He/^{4}He ratio (R/Ra = 2.602). While a substantial radiogenic helium is not expected in Kirkgoz carbonate aquifer, excess flux of mantle and crustal helium seems very likely because the earthquakes occurring around Antalya at depths >60 km imply a disrupted lithosphere. On the other hand, use of calculated ^{3}He* and the observed ^{3}H content (4.4 TU) by Nativ et al. (1999) in Eq. 6 gives a ^{3}He* piston flow age of 101 years which is comparable to aforementioned tritium-based MRT. However, this similarity is very coincidental.

Overall, comparison of predicted and calculated ^{3}He* in Kirkgoz springs implies that successful use of ^{3}He* in groundwater age-dating in karst systems requires correct calculation of ^{3}He* that depends on the realistic determination of helium sources in the flow system. Thus, success of ^{3}He* for age-dating in karst aquifers appears to be a site-dependent practice.

Discussion

The general results of this study indicate the RTD, which could be determined based on environmental tracer transport modeling, can be used to infer contamination vulnerability risk in karst aquifers. Lumped parameter models constitute a practical tool particularly for the case of karst aquifers in which parameters affecting flow and transport are difficult to determine. Moreover, environmental tritium appears to be the most reliable tracer in similar studies. Although, the modeling with CFC-11 provided results comparable to ^{3}H, reliable use of CFCs in determination of RTD in karst aquifers requires additional data on the processes that affect their transport in the modeling domain. Similar modeling attempts in previous studies (e.g. Ozyurt 2005; Ozyurt and Bayari 2005b) revealed that CFCs transport in karst aquifers has their own characteristics that are specific to each karst spring. Similarly, the successful use of ^{3}He* as a substitute for depleting ^{3}H in karst aquifers seems to depend very much on the reliable isolation of helium sources that affect the accurate calculation of ^{3}He* content.

The specific results of this study show that the Kirkgoz springs, as the strategic water resource for Antalya town, has a remarkably long MRT. The wide RTD associated with this MRT implies significant advantages and disadvantages as far as the vulnerability to contamination is concerned. This is because a wide RTD would lead to a long-range of contamination that progresses slowly within the entire aquifer but would be unnoticed in the early period because of the dilution effect of uncontaminated past recharge waters. The wide RTD would cause the contaminant concentration in Kirkgoz spring to rise slowly

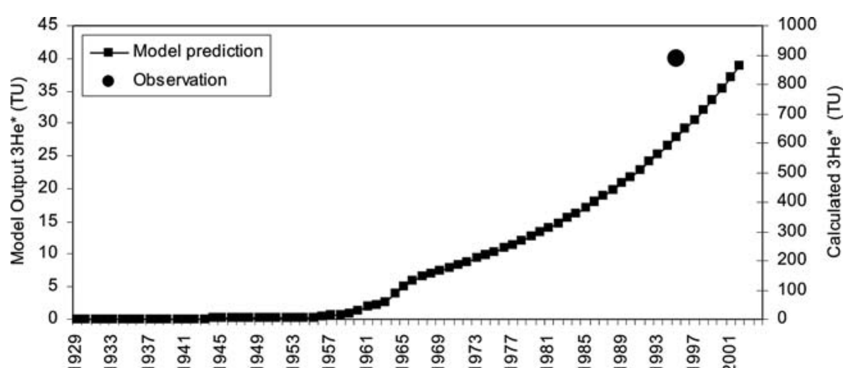

Fig. 10 Model predicted and observed tritiogenic helium-3

so that the water can still be used for some period until contaminant concentration reaches at harmful level. However, this advantage may turn out to be a major disadvantage because, even if the contaminant release into the aquifer were immediately stopped after recognition of risk, it would be present in the flow system for many decades ahead. The real risk of contamination would also be dependent on the mobility of tracer within the flow system. While contaminants with high sorptivity to aquifer rock would be retarded with respect to water mass transport, non-sorptive contaminants would arrive at springs along with the accompanying recharge water. In fact, the largeness of the Kirkgoz springs' reservoir and its effect to contaminant transport has already been recognized in a previous work by UNDP (1983). In this regard, although based on a single sample in high water season, observation of Ekmekci (2005) on presence of pesticides in Kirkgoz springs should be regarded as an early warning. Therefore, control of contaminant release to aquifer and monitoring of contaminant level in Kirkgoz springs is an immediate task for the associated public health authorities. Rising the public awareness on this critical issue should be an essential part of protecting these springs.

Previous studies report varying MRTs, which range between 25 and 120 years for the Kirkgoz springs. Tezcan (1993) argues that both the steady state, well-mixed lumped parameter model and the discrete state multi-cell tracer transport model revealed the same MRT of 25 years. In both modeling exercises, environmental ^{3}H data between 1954 and 1987 and spring's ^{3}H observations between 1963 and 1978 have been used. In another study by Yurtsever (1979), in which data between 1954 and 1979 seems to have been used, a MRT of 50 years was proposed. UNDP (1983) states that various studies to determine MRT in Kirkgoz springs revealed MRTs ranging between 40 and 120 years yet, a MRT of up to 120 years was probable. Different MRTs proposed by previous studies might be caused probably by the lack of data available to workers at that time or by the different net ^{3}H input functions they used. However, use of same data set given in Tezcan (1993) both in the model of this study and in the FLOWPC produced a MRT of 120 years. Furthermore, the remarkably low carbon-14 activities (i.e. 12.1 to 22.4 pmc) observed by Nativ et al. (1999) in Kirkgoz springs may also be regarded as an additional evidence for wide RTD in these springs. Meanwhile, an interesting point reported by UNDP (1983) is the Kirkgoz springs' aquifer volume, which was inferred from the volume (mass) of travertine deposited by these springs. Although the details of calculations are not given explicitly, the report states that the volume of travertine mass deposited by Kirkgoz springs corresponds to the void volume of aquifer in the range of 50–60 $\times$ 10^9 m^3. Not surprisingly, this volume is very close to the total flow volume of aquifer (71 $\times$ 10^9 m^3) as predicted in this study.

Another outcome of this study is the time range that can be represented by environmental ^{3}H in groundwater age-dating studies. Several literature sources regard the usable time range of environmental tritium to past 60 years (e.g. Kazemi et al. 2006) or up to 100 years (e.g. Gonfiantini et al. 2003). However, this study shows unambiguously that the environmental tritium and the CFCs may be used in systems with MRT greater than 100 years.

Protecting the Kirkgoz springs against contamination requires the information on the realistic extent of recharge area where the counter measures should be applied. Several studies suggest recharge area magnitudes that range between 4,300 km^2 (Tezcan 1993) and 1,800 km^2 (Korkmaz 1990). Analysis of springs' discharge in this study reveals a long-term mean annual discharge of 584 $\times$ 10^6 m^3. To meet the observed mean discharge, the proposed recharge area magnitudes of 4,300 and 1,800 km^2 would require effective mean annual precipitation values of 136 and 324 mm, respectively. Considering the high infiltration capacity of karst aquifer (up to 80%) and the net mean annual precipitation over the potential recharge of Kirkgoz springs (496 mm), a recharge area of about 1,200 km^2 is proposed in this study. Briefly, a roughly 1,500 km^2 large region extending from Korkuteli and Bucak towns towards the springs constitutes the most likely recharge area (see Fig. 1). Because a notable part of this area is occupied by agricultural lands nested in intramountain plains and karst poljes, the agrochemicals appear to be the most likely contaminants for Kirkgoz springs.

While this study reveals a wide RTD for the Kirkgoz springs, future studies should be carried out to determine more precisely the mass transport in the aquifer. Lumped parameter models are inherently incapable of accounting for the effect of fast flow component in karst aquifers. Such flows can occur because of intense areal or pointwise (i.e. via sinkholes) recharge events that may lead to instantaneous transfer of contaminants to springs. Flow and transport models, which can consider more precisely the non-linear and non-stationary behavior of karst systems should be developed and used to analyze the vulnerability of karst springs to contamination in a more accurate manner.

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