20 pages (19) #73689

ELSEVIER

Journal of Volcanology and Geothermal Research 67 (1995) 187–205

Journal of volcanology and geothermal research

The use of tritium in groundwater to determine fluid mean residence times of Valles caldera hydrothermal fluids, New Mexico, USA

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Received 12 October 1992; accepted 29 September 1994

Abstract

Naturally and artificially produced ^3H in precipitation is used to place limits on mean residence times of fluids associated with the Valles caldera geothermal reservoir. The ^3H concentrations in precipitation are used to calculate fluid mean residence times using two end-member cases: piston-flow and well-mixed reservoirs. These simplified models using ^3H yield relative fluid mean residence times in different portions of the system. In-situ ^3H production in the reservoir through neutron interaction with ^6Li is considered, and only very low levels of ^3H (≤ 0.01 T.U) are contributed to the waters by this process. Calculations using the end-member cases at Valles caldera indicate that mean residence times of geothermal waters in the reservoir are between 3000 and 10,000 years. The results also show that the two distinct subsystems of the main reservoir are associated with different fluid mean residence times. Waters in the Redondo Creek subsystem are older (~4300 to > 10,000 years) than waters in the Sulphur Springs subsystem (~2000–4400 years). Comparison of the results of the end-member cases with those obtained using more sophisticated methods indicates that the two end-member cases, with the use of ^3H, can provide acceptable limits (order of magnitude) on a fluid's mean residence time and volumes within a reservoir.

1. Introduction

Tritium is a radio-isotope of hydrogen useful in determining the ages and mixing relationships of surface and groundwater systems. Because tritium (^3H) has a half-life of 12.43 years, and it generally behaves conservatively, the ^3H content of waters is a reliable indicator of mixing and relative groundwater ages.

Following the previous work of Pearson and Truesdell (1978), C.O. Grigsby (in Goff et al., 1987) and Shevenell (1991), the ^3H model to be discussed in this report involves a procedure that places limits on groundwater mean residence times and reservoir volumes by calculating two end-member cases utilizing known ^3H input into the system. The end-members are the piston-flow model, which requires that no mixing occurs in the reservoir, and the well-mixed model which assumes that the reservoir fluid is completely mixed with all fluids which enter the system. The two end-member cases provide upper and lower limits on mean residence times of fluids in a system, which can be useful information when studying a system in which the hydrologic characteristics are poorly known (i.e. Mount St. Helens; Shevenell, 1991).

Though our final results may be less accurate, the current model does not explicitly investigate dispersive

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SSDI 0377-0273(94)00102-2

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mixing along the flow path. A limiting case for the process of dispersion is instead simulated by assuming that the repeated, yearly recharge to a system, with variable ^3H year to year, is introduced at numerous points in the reservoir such that previously recharged fluids in the reservoir will become completely mixed each year with every new influx of recharged water. Deeper flow represented by streamlines at greater depths will, in reality, have different ^3H contents than shallower zones. In the current method, the assumption is made that these zones become mixed to form the discharge concentrations measured in the field. This well-mixed assumption will not necessarily yield accurate fluid ages in the system given the possibility of some amount of chemical stratification in the reservoir. The current procedure tends to overestimate the amount of hydrodynamic dispersion occurring in a system, yet the objectives of the model are to estimate upper and lower limits on mean residence times of fluids in a reservoir. With the current approach, this information can be gained without prior knowledge of dispersion coefficients, reservoir volumes, or other aquifer parameters. Hence, the method can provide an order of magnitude estimate on mean residence times of fluids in different portions of a system, requiring considerably less data and modeling effort than a spatially distributed advection–dispersion model.

The purpose of the current paper is to present the two end-member cases, to develop ^3H input functions representative of precipitation near Valles caldera, to estimate in-situ production of ^3H in the reservoir, to present ^3H data of thermal waters in and around Valles caldera and to test the limits and applicability of the described method by comparing the results with previous estimates on mean residence times of fluids within the reservoir.

2. Previous studies

Numerous studies of surface-and groundwater ages (or residence times) and mixing rates have been conducted over the years with the use of ^3H (Begemann and Libby, 1957; Eriksson, 1958; Nir, 1964; Carmi and Gat, 1973; Simpson and Carmi, 1983; Egboka et al., 1983; Vuataz and Goff, 1986). Discussions of well-mixed versus piston-flow behavior have been abundant in these and other studies, with several different methods of treating the cases being presented over the years. For instance, studies by Simpson and Carmi (1983) focused on the simple exponential model of piston-flow while studies by Nir (1964) discussed the concepts of well-mixed and piston-flow reservoirs, utilizing hydrodynamic dispersion coefficients in describing the well-mixed end-member. Carmi and Gat (1973) simulated well-mixed behavior with the use of an age function which incorporates a recharge weighting function to determine ages from the combination of ^3H input over a given number of years.

Experimental studies have demonstrated that ^3H can be weakly adsorbed as water flows under unsaturated conditions through sandstones and highly developed soils such as oxisols and sesquioxides (Wierenga et al., 1975; Van Genuchten and Wierenga, 1977; Nkedi-Kizza et al., 1982; Nkedi-Kizza et al., 1983). Some of the retardation of ^3H observed in these studies can be attributed to exchange of ^3H with crystal-lattice hydroxyls. Only very minor adsorption or retardation of ^3H can be expected in rocks and soils which contain little or no hydrated minerals. Hence, in most environments, ^3H is a very good tracer.

In the previous studies, Pearson and Truesdell (1978) applied the limiting models discussed here to the groundwater system at Yellowstone National Park. These authors applied the models using ^3H, but no derivation or input functions were included in the paper. Later, C.O. Grigsby (in Goff et al., 1987) applied the model to the Platanares, Honduras geothermal system. In forming input functions representative of Honduras precipitation for the model, it was assumed that no ^3H was added to the system for years prior to 1963. Later, Shevenell (1991) applied the models to the Mount St. Helens geothermal system and estimated ^3H in precipitation from 1953 to 1989. In the present paper, ^3H input functions will also be estimated for all years in which there has been a significant artificial ^3H input (1953 to present). For the time period prior to 1953, a constant value of ^3H input is assumed.

3. Geology and hydrogeology of Valles caldera

The Jemez volcanic field is located at the intersection of the NE-trending Jemez lineament and the Rio Grande rift (Mayo, 1958; Laughlin et al., 1976). The geology of the Jemez Mountains consists of about 2000

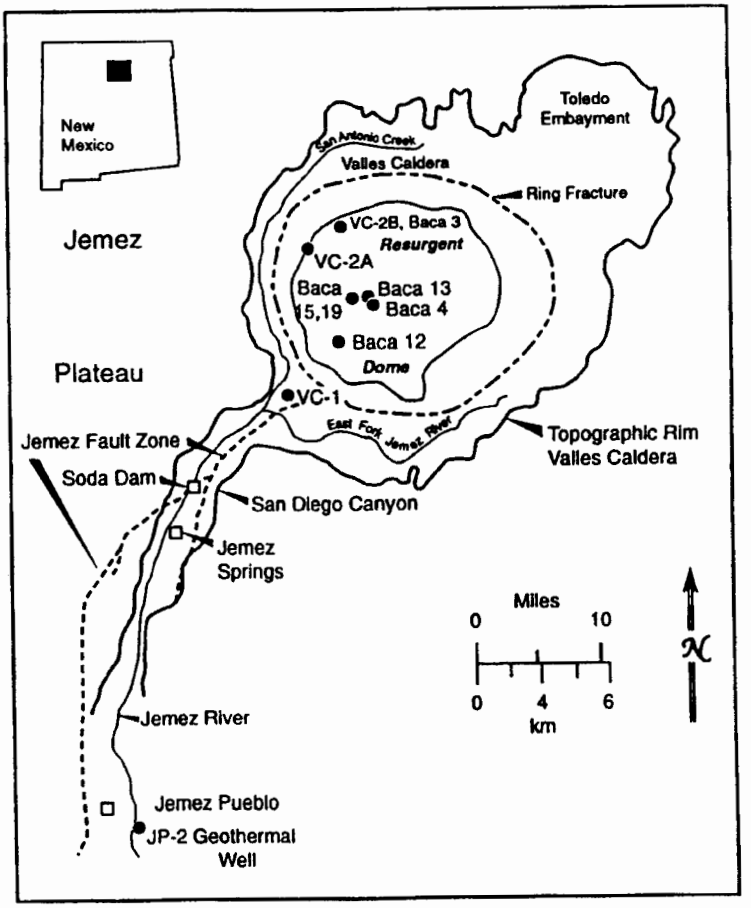


Fig. 1. Map showing geothermal water sampling locations in and near Valles caldera, New Mexico.

km^3 of Tertiary to Quaternary volcanic rocks that overlie Tertiary basin-fill sedimentary rocks within the rift, and Paleozoic and Mesozoic sedimentary rocks and Precambrian basement west of the rift margin. During the 1960's and 1970's, Union Oil Company of California drilled 24 deep geothermal wells within Valles caldera (Baca location No. 1, Fig. 1; Union Oil Company of California and Public Service Company of New Mexico, 1978; Union Oil Company of California, 1982) to evaluate the geothermal potential of the area. Numerous studies on the geology, structure and geothermal hydrology of the region have been conducted, partly with the use of data from these wells and partly from Continental Scientific Drilling Program coreholes (i.e. Mills et al., 1985; Goff and Gardner, 1988; Goff et al., 1989, 1992). The reservoir within Valles caldera largely resides in caldera fill tuffs and tuffaceous sediments and locally extends into underlying pre-caldera volcanics and basin sediments of the Rio Grande Rift.

Recharge to the geothermal system is believed to occur within the northeastern portion of the caldera depression and highlands surrounding the caldera (Vuataz and Goff, 1986; Sass and Morgan, 1988), and possibly along the ring fracture faults (Faust et al., 1984). Meteoric waters circulate deeply within the caldera and are heated to temperatures of up to 300°C. Two up-flow zones representing two geochemically distinct subsystems of the reservoir have been identified within the caldera: (1) the Sulphur Springs subsystem, near the western margin of the resurgent dome (at VC-

2A on Fig. 1); and (2) a subsystem within the keystone graben of the resurgent dome (referred to as the Redondo Creek reservoir; i.e. Smith and Kennedy, 1985; Truesdell and Janik, 1986). The two subsystems are fault-controlled reservoirs separated from each other by 2–3 km of relatively permeable, hydrothermally altered, caldera-fill rocks. Geochemically, Sulphur Springs fluids are more concentrated and heavier in $\delta^{18}O$ than Redondo Creek Fluids (Goff et al., 1992).

Researchers have estimated the average thickness of the Redondo Creek subsystem to be between 610 (Bodvarsson et al., 1982) and 1830 m (Union Oil Company of California, 1982) with porosities ranging from 0.03 to 0.05 (Bodvarsson et al., 1982; Faust et al., 1984). Discharge from the system is through a hydrothermal outflow plume where the flow is dominantly fault controlled, with only minor stratigraphically controlled flow. Up to 50% of the total discharge from the system is along the Jemez fault zone at Soda Dam Springs and Jemez Springs (Fig. 1) where thermal fluids become mixed with young meteoric waters (Goff et al., 1988).

Several studies have been conducted which yield estimates on discharge rates from the system and volumes of fluid within the reservoir. The various estimates indicate that the volume of fluid discharging from the system ranges from 5.07×10^{-4} to 1.77×10^{-3} km^3/yr, and the reservoir volume ranges from 1.21 to 2.69 km^3 of fluid (Balleau, 1980; Bodvarsson et al., 1982; Union Oil Company of California and Public Service Company of New Mexico, 1978; Union Oil Company of California, 1982; Faust et al., 1984). None of the estimates of reservoir extent or fluid volume distinguishes between the Sulphur Springs and Redondo Creek subsystems of the Valles geothermal system. Both Faust et al. (1984) and Bodvarsson et al. (1982) assumed relatively small lateral extents of the reservoir (31.08 and 40 km^2) and modeled only the "producible", hot region surrounding Redondo Creek. Although Union Oil also modeled the "producible" portion of the reservoir, they assumed that the reservoir resides within most of the 144 km^2 of the caldera.

4. Methods

4.1. Sampling and analysis

Numerous water samples have been collected within and near Valles caldera since 1982 for ^3H analysis (White, 1986; Shevenell et al., 1987). Unfiltered 500–1000-ml samples were placed in un-rinsed, glass bottles and capped with polyseal caps. All springs were sampled at their sources. Well waters were collected using several different methods, with samples being of the following types: bailer samples; mini-separator samples (water and steam); total flow samples from a weir box or a sample port; samples collected using an in-situ, down-hole sampler; and water samples collected during swabbing operations. The sample types for each well water collected are noted in the data table appearing in section 5.2. The ^3H analyses were performed by Dr. H. Gote Ostlund (Tritium Laboratory, University of Miami) by electrolytic enrichment (Ostlund and Dorsey, 1977).

Three permanent rain collectors (locations LA, SFA and SFSB in Fig. 2) were installed in the Jemez Mountains–Sangre de Cristo Range–Espanola Basin region in 1990 to collect samples of precipitation for chemistry, stable isotopes, and ^3H as part of an environmental study of Los Alamos National Laboratory (Adams and Goff, 1991). The collectors are modeled after those described by Claassen et al. (1986) and White et al. (1990). Samples are removed every 3 to 5 months and the total volume of precipitation is measured. These rain gauge samples were analyzed for their ^3H contents, and the data are incorporated into the ^3H input functions describing the Valles caldera area. Incorporation of these analyses into the model allows estimation of average fluid age for samples collected up to 1991.

4.2. Procedure for estimation of in-situ tritium production

Tritium can be produced within a reservoir through the neutron-induced reaction:

$$^6Li(n,\alpha)^3H. \quad (1)$$

Because measured concentrations of ^3H in groundwaters at Valles caldera are quite low (see section 5), possible in-situ production of ^3H by this reaction must be considered. In order to evaluate ^3H production, the neutron production rate (neutrons g^{-1} yr^{-1}) due to spontaneous fission and (α, n) reactions is estimated using expressions presented in Andrews et al. (1989), which allow calculation of neutron flux as a function of total uranium and thorium contents in the rock. The fraction (F) of these produced neutrons which encoun-

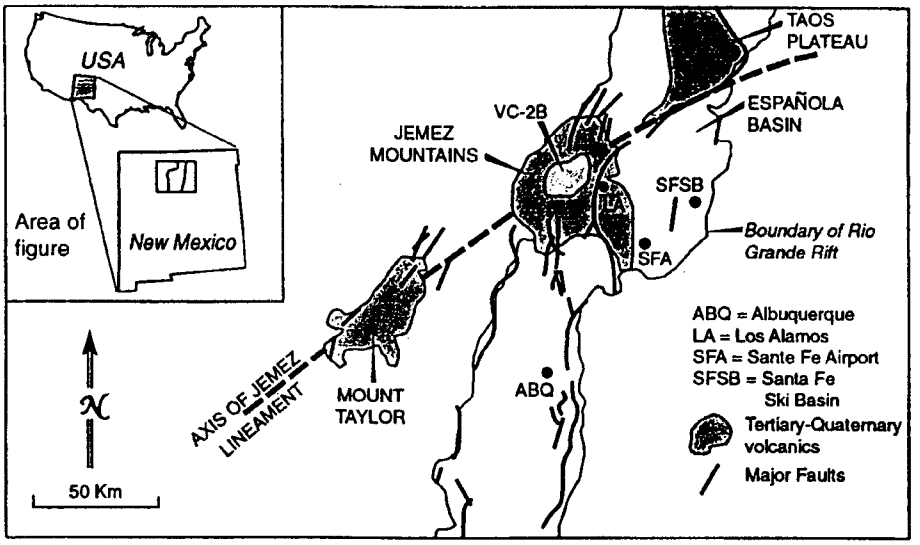


Fig. 2. Regional map showing locations of rain water collectors (*LA*, *SFA* and *SFSB*) and the Jemez Mountains, New Mexico.

ter Li in the rock matrix is estimated by the following (Andrews and Kay, 1982):

$$F = \frac{\sigma_{Li} N_{Li}}{\Sigma \sigma_i N_i} \tag{2}$$

where σ_{Li} is the total neutron absorption cross-section, N_{Li} is the Li abundance, σ_i is the total neutron absorption cross-section for all elements in the matrix and N_i is the abundance of all elements in the matrix.

Factor F is multiplied by the neutron production rate to obtain the ^3H production rate in atoms $g^{-1}\ yr^{-1}$. Note that one neutron will interact with one Li atom in the matrix to produce one ^3H atom. High concentrations of U, Th and Li could result in significant concentrations of ^3H being produced in the reservoir. However, high concentrations of B significantly reduce the number of neutrons interacting with Li because the adsorption cross-section of B (755 barn) is ten times larger than that for Li (71 barn; Andrews and Kay, 1982). The ^3H content in pore waters is calculated from the ^3H production rate (P) by the equation (Andrews and Kay, 1982):

$$^3H\ (T.U.) = \frac{18 \times 10^{18} P}{\lambda \times \phi \times 2 \times 6.02 \times 10^{23}} \tag{3}$$

where λ(0.05576 yr^{-1}) is the ^3H decay constant, and ϕ is the total water content of the matrix (structurally bound water and pore water). The other factors result because there are $2 \times 6.02 \times 10^{23}$ hydrogen atoms in one mole (18 g) of water, and one ^3H atom in 10^{18} hydrogen atoms is the definition of 1 T.U.

4.3. Procedure for estimation of input tritium functions

Background

Derivations of the piston-flow and well-mixed models appear in the Appendix. In order to evaluate end-member Eqs. (A-1) and (A-6), the ^3H concentration of recharged water before and after nuclear testing must be estimated. Although there are very few ^3H data for years prior to 1952, a few measurements were made on lake waters, groundwaters and wines from the Chicago and New York areas from which an estimate of pre-bomb ^3H concentrations can be made. These measurements indicate that the average background ^3H value for the interior of North America is ~6 T.U. (Kaufman and Libby, 1954; Craig and Lal, 1961).

In a more recent study, Robertson and Cherry (1989) studied the ^3H distribution in a sand aquifer near Sturgeon Falls, Ontario and found that the ^3H

distribution was accurately simulated when a pre-bomb ^3H value of 3 T.U. was used. The 3 T.U. value is a simulated value, subject to the uncertainties associated with their one-and two-dimensional advection and dispersion modeling. In addition, it appears that pre-bomb background ^3H concentrations may be greater than 6 T.U. in northern New Mexico (see Table 1), thus we select the pre-1953, background ^3H value of 6 T.U. for use in the current study.

Estimation of post-1953 tritium concentrations

Precipitation data from Albuquerque, New Mexico are used to estimate input functions to the Valles caldera system, because Albuquerque is the station closest (~ 100 km) to the caldera. The Albuquerque station is missing data for the years 1953–1961, hence, the Albuquerque data are compared to the Ottawa (Canada) station because this station has a complete record of ^3H in precipitation after 1953 (IAEA data). The IAEA data at Ottawa have often been used to formulate ^3H input functions at other stations (i.e. Rabinowitz et al., 1977; Pearson and Truesdell, 1978; Campana and Mahin, 1985).

The IAEA data are reported as monthly concentrations of ^3H for a known amount of precipitation. Because it is convenient to express the input functions as ^3H concentration per year which enters the system, yearly weighted mean ^3H concentrations are calculated at the two stations (Table 1). The percentage of total yearly precipitation data available to calculate the weighted mean ^3H concentrations is listed in Table 1 in the columns "% of precip".

In order to estimate the missing ^3H data at the station between 1953 and 1961, the natural logarithm of ^3H at the two stations is compared, with the two being linearly correlated. The best-fit linear regression equation for this data set is:

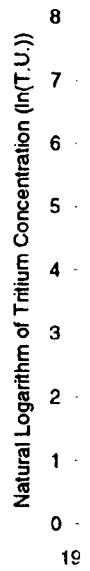
$$\ln(^3H_{ABQ}) = 1.0967[\ln(^3H_{Ottawa})] - 0.8998 \qquad (4)$$

which has a correlation coefficient (R^2) of 0.9411 and a standard deviation for the Albuquerque (ABQ) ^3H data of ± 3.76 T.U. Using this linear regression equation, ^3H concentrations were calculated for each year requiring ^3H data. The estimated and measured values are listed in Table 1 and illustrated in Fig. 3, where the dots represent the Ottawa data and the dashed line and open dots represent the Albuquerque data. Note that the illustrated lines are not linear least-squares lines but

Table 1
Tritium in precipitation for Albuquerque and Ottawa for the years 1952–1991

Time	Albuquerque		Ottawa	
(years)	^3H (T.U.)	% of precip.	^3H (T.U.)	% of precip.
1952	6[a]	–	6[a]	–
1953	14.7[b]	–	26.4	43.0
1954	202.3[b]	–	287.7	92.3
1955	24.1[b]	–	41.3	100
1956	123.7[b]	–	183.8	100
1957	76.1[b]	–	118	100
1958	442.3[b]	–	587.2	100
1959	331.7[b]	–	451.6	100
1960	103.6[b]	–	156.3	100
1961	156.2[b]	–	227.3	100
1962	413.3	70.3	992.4	100
1963	1898.7	98.4	2900.1	100
1964	1688.3	99.5	1532.8	100
1965	484.1	96.6	778.2	100
1966	282.2	100	560.8	100
1967	237.6	97.1	324.2	100
1968	188.1	100	216.9	100
1969	193.6	100	253.7	55.8
1970	200.8	100	190.8	100
1971	163.8	100	206.1	86.6
1972	53.1	92.6	92.3	100
1973	71.0	100	90.4	100
1974	52.7	77.3	98.1	100
1975	50[c]	–	75.9	95.2
1976	63.4	90.9	58.9	100
1977	45.3	100	73.9	100
1978	46.9	100	73.6	99.8
1979	23.4	63.9	49.6	100
1980	23.3	100	49.5	100
1981	35.7	100	55.1	100
1982	28.9	100	39.7	100
1983	16.2	100	50.5	100
1984	15.1	100		
1985	19.7	100		
1986	17.3	100		
1987	12.2	–		
1990	11.8[d]	100		
1991	11.3[d]	100		

All measured values are yearly weighted mean ^3H concentrations from data reported by the IAEA; "% of precip" is the amount of total yearly precipitation at a site which was available for calculating weighted mean ^3H concentrations.
[a]Assumed background values (see text)
[b]Values calculated using known ^3H in Ottawa precipitation.
[c]Calculated using linear relationship of $\ln(^3H)$ vs. time at the Albuquerque station between 1972 and 1991.
[d]Weighted mean ^3H concentration from three precipitation collectors near Valles caldera.



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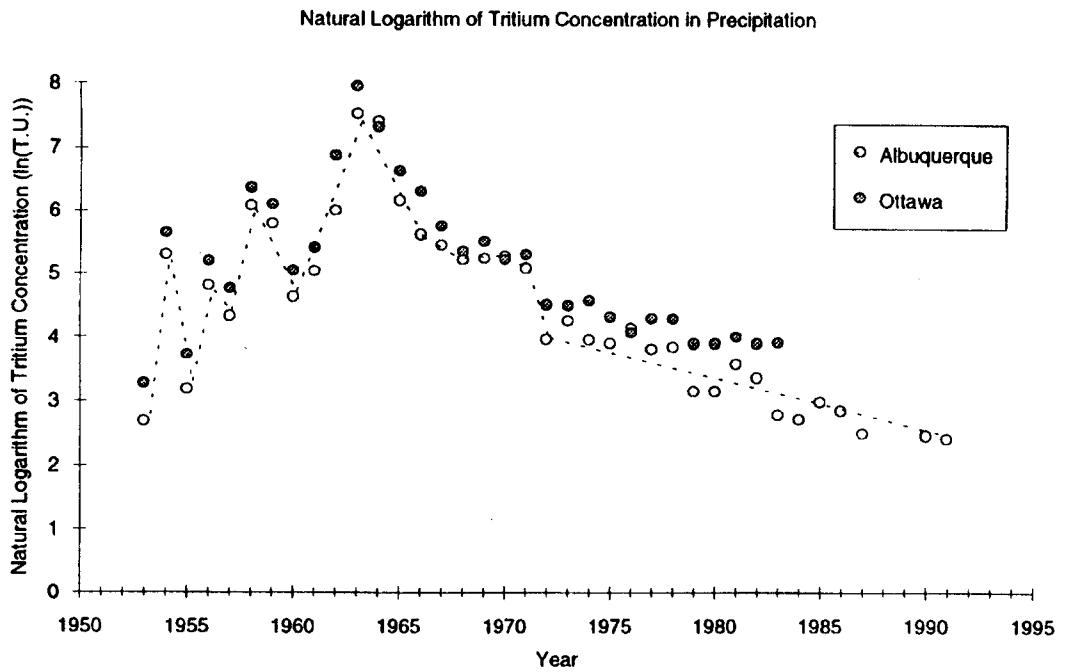

Fig. 3. Distribution of the natural logarithm of tritium concentrations in precipitation for the Albuquerque, New Mexico and the Ottawa, Canada stations for the years 1953–1991.

lines which intersect in the years in which a change in slope occurs. These lines are drawn merely for illustrative purposes.

The simple linear regression method estimates the missing ^3H data values quite well and the small standard deviation of ± 3.76 T.U. is acceptable because the values being estimated lie between 14.7 and 442.3 T.U., and significant error could only be produced on one of the estimated values (in 1953, Table 1). On Table 1, note that the 1975 ^3H value of 50 T.U. is calculated. A ^3H value of 78.4 T.U. for 1975 was reported by the IAEA, yet this value represents only 39% of the total yearly precipitation. The 50 T.U. value was calculated based on the ^3H versus time trend between 1972 and 1991 at the Albuquerque station.

Tritium input functions

It is necessary to find a function which best describes each segment on the plot of Fig. 3, and a linear least-squares regression was performed on each discrete line. Choice of the line segments illustrated in Fig. 3 was accomplished in order to yield the minimum error in calculation of input functions. The choice of each segment is physically valid for two reasons. First, incomplete records on atmospheric nuclear tests by the USA, USSR and Great Britain (Telegadas, 1959; Martell, 1963) indicate that maximum and minimum fallouts of ^3H from atmospheric nuclear tests should occur in the years suggested by the points in the plot of Fig. 3. Second, although very limited ^3H data in precipitation with time are available for most stations around the world in the earlier years, trends of ^3H concentration seen at several stations for specific segments of time show similar trends to those observed and calculated at the Albuquerque station (Table 2). Table 2 lists linear least-squares slopes calculated from $\ln(^3H)$ versus time data at several stations for three of the segments illustrated on Fig. 3 (1957–1958, 1958–1960 and 1960–1963). For each segment considered, slopes of the $\ln(^3H)$ versus time lines are positive for the 1957–1958 and the 1960–1963 time periods at all stations. Negative slopes are found for the 1958–1960 time period at all stations, and the values of the slopes are similar between stations. Hence, the lines drawn in Fig.

Table 2
Comparison of the slopes of tritium functions of selected line segments of Fig. 1 with calculated slopes at other stations around the world

Station	Latitude	1957–1958	1958–1960	1960–1963
Valentia, Ireland	51.93°N	1.740	−0.546	1.069
Sindorf, western Germany	50.90°N			0.848
Khartoum, Sudan	15.60°N			0.998
Reykjavik, Iceland	64.13°N			1.419
Lista, Norway	58.10°N			1.635
Whitehorse, Canada	53.32°N			1.434
Goose Bay, Canada	53.32°N			1.489
Tokyo, Japan	35.68°N			1.362
Portland[a], OR, USA	45.60°N	1.791	−0.739	1.107
Waco[a], TX, USA	31.62°N	1.923	−0.793	0.968
Albuquerque[a], NM, USA	35.05°N	1.760	−0.726	0.970
Ottawa, Canada	45.32°N	1.604	−0.662	1.024

[a]calculated using Ottawa data.

Table 3
Tritium input functions for Albuquerque, New Mexico

Year	Input functions	R^2
1953–1954	$C_{in}(t) = e^{2.6219t + 2.6878}$	–
1954–1955	$C_{in}(t) = e^{-2.1275t + 7.4373}$	–
1955–1956	$C_{in}(t) = e^{1.6356t - 0.0891}$	–
1956–1957	$C_{in}(t) = e^{-0.4858t + 6.2753}$	–
1957–1958	$C_{in}(t) = e^{1.7599t - 2.7077}$	–
1958–1960	$C_{in}(t) = e^{-0.7257t + 9.8666}$	0.89
1960–1963	$C_{in}(t) = e^{0.9698t - 2.4273}$	0.94
1963–1966	$C_{in}(t) = e^{-0.6964t + 14.7101}$	0.92
1966–1968	$C_{in}(t) = e^{-0.2035t + 8.2999}$	0.99
1968–1970	$C_{in}(t) = e^{0.0327t + 4.7457}$	0.99
1970–1971	$C_{in}(t) = e^{-0.2037t + 8.7646}$	–
1971–1972	$C_{in}(t) = e^{-1.1265t + 25.3751}$	–
1972–1991	$C_{in}(t) = e^{-0.1021t + 6.5162}$	0.88

3 have physical significance in that the indicated trends occurred as a result of the varying atmospheric nuclear tests of the 1950's and 1960's.

Using these data to calculate input functions, a best-fit line between data points is constructed such that an input function was obtained for the years 1953–1954, 1954–1955, ..., and 1972–1991. The calculated input functions [$C_{in}(t)$] are of the form:

$$C_{in}(t) = e^{mt + b} \tag{5}$$

where m is the slope and b is the intercept in ln(T.U.). $C_{in}(t)$ is in T.U. for each interval, and correlation coefficients range from 0.88 to 0.99 (Table 3). Because significant amounts of ^3H began to fall in precipitation in 1953, the year zero was assigned to 1953 (1953 = 0, 1954 = 1, ...) and all calculated intercepts are those at the year 1953. These $C_{in}(t)$ values for each period of years are substituted directly into Eq. (A-1) for the piston-flow model. The appropriate C_{in} expressions for the corresponding residence times are used for the piston-flow calculations. For instance, when $19 \leq \tau < 22$, the C_{in} for 1960–1963 is used. The designation for τ in this example is made for samples collected in 1982.

For the well-mixed model of Eq. (A-6), it is first necessary to multiply each $C_{in}(t)$ term by $e^{(1/\tau+\lambda)t}$ and integrate with respect to "t" over the interval of interest. Each $C_{in}t)e^{(1/\tau+\lambda)t}$ product is integrated over its interval of applicability {i.e. the definite integral of $e^{-0.7385t+9.2731}[e^{(1/\tau+\lambda)t}]$ is evaluated with lower and upper limits of 5 and 7 for 1958 and 1960, respectively}. The definite integrals for each segment of years are substituted into Eq. (A-6), each of which has the form:

$$\frac{a}{\frac{1}{\tau} + \lambda + b}\left[e^{(1/\tau+\lambda+b)t1} - e^{(1/\tau+\lambda+b)t0}\right] \tag{6}$$

where a is the exponent of the intercept of the input line with the year 1953, b is the slope of the ^3H input line, $t1$ is the upper limit of integration (year, where 1953 = 0, etc.) and $t0$ is the lower limit of integration (year).

Therefore, thirteen terms for the thirteen line segments represented by Fig. 3 are added together and substituted into Eq. (A-6) in order to calculate the upper limit of mean residence times.

5. Results

5.1. In-situ tritium production

Using expressions presented in Andrews et al. (1989) and Eqn. (2) and (3) from section 4.2, ^3H production in the Bandelier Tuff was estimated. A representative chemical composition for the Bandelier Tuff was utilized based on data in Gardner et al. (1986,

table 3, weight percent analyses $SiO_2 = 72.7$, $Al_2O_3 = 12.2$, $Fe_2O_3 = 1.47$, $MnO = 0.08$, $MgO = 0.05$, $CaO = 0.33$, $Na_2O = 3.08$ and $K_2O = 5.36$). Because the U, Th, Li and B contents of a rock are most important in determining the production of ^3H, several values for each of these parameters were used in different computations in order to obtain the maximum and minimum possible production in the rock. The minimum and maximum measured values for these parameters in the Bandelier Tuff are as follows: U = 11.8–16 ppm; Th = 40–43 ppm; Li = 14–47 ppm; and B = 16–29 ppm. The maximum amount of ^3H which can be produced in a rock with this composition is 0.019 T.U., whereas the minimum is 0.010 T.U. It is unlikely that all produced ^3H atoms will diffuse from the matrix into fracture and intergranular porosity to be trapped by the fluids. Hence, these values are maxima. Clearly, the low values of in-situ produced ^3H will not influence groundwater dating using ^3H because the maximum possible production rate is near the analytical ^3H detection limit. In-situ production of ^3H will not be considered further.

5.2. Mean residence times

A plot of the results of calculated ^3H concentrations versus mean residence times for the two end-member cases for samples collected in the Valles caldera area in 1991 is shown in Fig. 4. Table 4 Table 5 list expected ^3H contents associated with fluids of varying mean residence times for well-mixed and piston-flow type reservoirs for samples collected in several years up to 1992. These mean residence times are applicable for fluids derived from aquifers of all types within the Four Corners region of the USA.

Table 6 lists ^3H data for selected geothermal fluids sampled at Valles caldera between 1982 and 1992. The table also lists estimated mean residence times of fluids, and fluid volumes, for both the well-mixed and piston-flow models. Fluids from geothermal wells in the

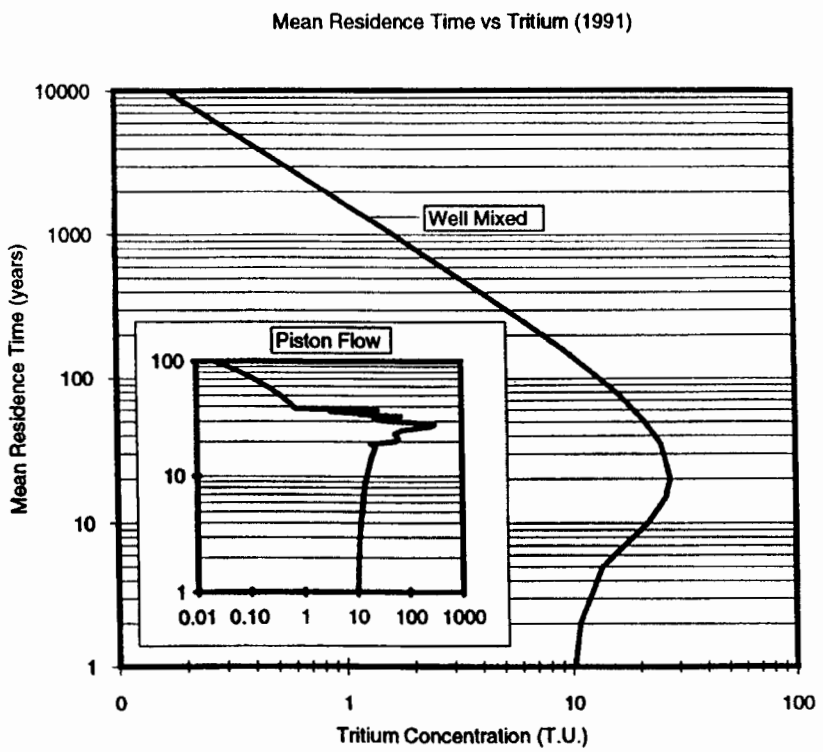

Fig. 4. Plot showing the results of the well-mixed and piston-flow models for the Albuquerque region for samples collected in 1991.

Table 4
Tritium concentrations (T.U.) calculated with the piston flow model for selected base years, Albuquerque Region, USA

Fluid age (yr)	Year 1960	1965	1970	1975	1980	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992
1	234	1090	184	52	31	26	23	21	19	17	15	14	13	11	10	9.2
2	396	1286	170	55	33	27	24	22	20	18	16	15	13	12	11	9.7
3	64	461	197	45	34	28	25	23	21	19	17	15	14	12	11	10.1
4	99	165	229	131	36	29	27	24	22	20	18	16	14	13	12	10.6
5	18	91	435	152	38	31	28	25	23	20	19	17	15	14	12	11.1
6	145	177	825	139	40	32	29	26	24	21	19	17	16	14	13	11.6
7	4.1	299	973	129	41	34	31	28	25	22	20	18	17	15	13	12
8	3.8	49	349	149	34	35	32	29	26	24	21	19	17	16	14	13
9	3.6	75	125	173	99	37	33	30	27	25	22	20	18	16	15	13
10	3.4	14	69	329	115	30	35	32	29	26	23	21	19	17	16	14
11	3.3	110	134	624	105	89	29	33	30	27	24	22	20	18	16	15
12	3.1	3.1	226	736	97	103	84	27	31	28	26	23	21	19	17	15
13	2.9	2.9	37	264	113	94	97	79	26	30	27	24	22	20	18	16
14	2.8	2.8	57	95	131	87	89	92	75	24	28	25	23	21	19	17
15	2.6	2.6	10	52	249	101	82	84	87	71	23	27	24	22	20	18
16	2.5	2.5	83	102	472	117	95	78	80	82	67	22	25	23	20	18
17	2.3	2.3	2.3	171	557	223	111	90	74	75	78	63	21	24	21	19
18	2.2	2.2	2.2	28	200	422	211	105	85	70	71	74	60	19	22	20
19	2.1	2.1	2.1	43	72	498	400	199	99	81	66	67	70	57	18	21
20	2.0	2.0	2.0	7.9	39	179	471	378	188	94	76	62	64	66	54	17
21	1.9	1.9	1.9	63	77	64	169	446	357	178	89	72	59	60	62	51
22	1.8	1.8	1.8	1.8	130	35	61	160	422	338	168	84	68	56	57	59
23	1.7	1.7	1.7	1.7	21	69	33	57	151	399	320	159	79	65	53	54
24	1.6	1.6	1.6	1.6	32	116	65	31	54	143	377	302	151	75	61	50
25	1.5	1.5	1.5	1.5	6.0	19	110	61	30	51	135	357	286	143	71	58
26	1.4	1.4	1.4	1.4	47	29	18	104	58	28	49	128	337	270	135	67
27	1.3	1.3	1.3	1.3	1.3	5.4	27	17	98	55	27	46	121	319	256	127
28	1.3	1.3	1.3	1.3	1.3	42	5.1	26	16	93	52	25	43	114	302	242
29	1.19	1.19	1.19	1.19	1.19	1.19	40	4.8	25	15	88	49	24	41	108	285
30	1.13	1.13	1.13	1.13	1.13	1.13	1.13	38	4.5	23	14	83	47	23	39	102
31	1.07	1.07	1.07	1.07	1.07	1.07	1.07	1.07	35.9	4.3	22	14	79	44	21	37
32	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01	34.0	4.1	21	13	74	42	20
33	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.95	32	3.8	20	12	70	39
34	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	30	3.6	19	11	66
35	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	29	3.4	18	11
36	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	0.81	27	3.2	17
37	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	26	3.1
38	0.72	0.72	0.72	0.72	0.72	0.72	0.72	0.72	0.72	0.72	0.72	0.72	0.72	0.72	0.72	24
39	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68
40	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64	0.64
41	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61	0.61
42	0.58	0.58	0.58	0.58	0.58	0.58	0.58	0.58	0.58	0.58	0.58	0.58	0.58	0.58	0.58	0.58
43	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55	0.55
44	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52
45	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49	0.49
46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46
47	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44
48	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41	0.41
49	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.39
50	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37
60	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21
70	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
80	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
90	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
100	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
110	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

Table 5
Tritium conce

Fluid age (yr)	Ye 19
1	19
2	18
5	12
10	7
15	5
20	4
35	2
50	1
75	1
100	
150	
200	
300	
400	
500	
750	
1000	
1500	
2000	
3000	
4000	
5000	
6000	
7000	
8000	
9000	
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Table 5
Tritium concentrations (T.U.) calculated with the well-mixed model for selected base years in the Albuquerque Region, USA

Fluid age (yr)	Year 1960	1965	1970	1975	1980	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992
1	197	1598	194	54	31	26	23	21	19	17	15	14	13	11	10	9.2
2	184	1096	231	70	34	27	25	22	20	18	16	15	13	12	11	10
5	121	633	280	121	55	41	36	32	28	25	22	19	17	15	14	12
10	74	376	235	136	76	60	54	48	43	38	34	30	27	24	22	19
15	53	268	190	124	77	63	57	52	47	43	39	35	32	29	26	24
20	41	208	157	109	72	60	55	51	47	43	39	36	33	30	28	25
35	25	125	102	77	55	48	45	42	39	36	34	31	29	27	25	23
50	18	89	75	59	44	38	36	34	32	30	28	26	24	23	21	20
75	12	60	52	42	32	28	27	25	24	23	21	20	19	18	17	16
100	9.1	45	40	33	25	23	21	20	19	18	17	16	15	14	14	13
150	6.1	31	27	23	18	16	15	14	14	13	12	12	11	10	9.8	9.2
200	4.6	23	21	17	14	12	12	11	10	9.9	9.4	8.9	8.5	8.0	7.6	7.2
300	3.1	15	14	12	9	8	8.0	7.6	7.2	6.9	6.5	6.2	5.9	5.6	5.3	5.0
400	2.3	12	11	8.8	7.0	6.4	6.1	5.8	5.5	5.2	5.0	4.7	4.5	4.3	4.0	3.8
500	1.9	9.3	8.5	7.1	5.7	5.1	4.9	4.7	4.4	4.2	4.0	3.8	3.6	3.4	3.3	3.1
750	1.2	6.2	5.7	4.8	3.8	3.5	3.3	3.1	3.0	2.9	2.7	2.6	2.5	2.3	2.2	2.1
1000	0.93	4.6	4.3	3.6	2.9	2.6	2.5	2.4	2.3	2.2	2.0	2.0	1.9	1.8	1.7	1.6
1500	0.62	3.1	2.8	2.4	1.9	1.8	1.7	1.6	1.5	1.4	1.4	1.3	1.2	1.2	1.1	1.1
2000	0.46	2.3	2.1	1.8	1.4	1.3	1.3	1.2	1.1	1.1	1.04	0.99	0.94	0.89	0.85	0.81
3000	0.31	1.6	1.4	1.2	0.97	0.88	0.84	0.80	0.76	0.73	0.69	0.66	0.63	0.60	0.57	0.54
4000	0.23	1.16	1.07	0.90	0.73	0.66	0.63	0.60	0.57	0.55	0.52	0.50	0.47	0.45	0.43	0.41
5000	0.19	0.93	0.86	0.72	0.58	0.53	0.51	0.48	0.46	0.44	0.42	0.40	0.38	0.36	0.34	0.33
6000	0.16	0.78	0.71	0.60	0.48	0.44	0.42	0.40	0.38	0.36	0.35	0.33	0.31	0.30	0.29	0.27
7000	0.13	0.67	0.61	0.52	0.42	0.38	0.36	0.34	0.33	0.31	0.30	0.28	0.27	0.26	0.24	0.23
8000	0.12	0.58	0.54	0.45	0.36	0.33	0.32	0.30	0.29	0.27	0.26	0.25	0.24	0.23	0.21	0.20
9000	0.10	0.52	0.48	0.40	0.32	0.29	0.28	0.27	0.26	0.24	0.23	0.22	0.21	0.20	0.19	0.18
10000	0.09	0.47	0.43	0.36	0.29	0.27	0.25	0.24	0.23	0.22	0.21	0.20	0.19	0.18	0.17	0.16

Redondo Creek and Sulphur Springs reservoirs have been sampled and consistently have ^3H concentrations between ~0.2 and 0.89 T.U. (±0.08–0.13 T.U.; Table 6) suggesting that reservoir fluids are quite old. Due to extensive flowing of these wells, it is assumed that there is no drilling fluid contamination.

The estimated mean residence times using the well-mixed model indicate differences in relative fluid ages between the two subsystems in Valles caldera. The fluids in the Redondo Creek area are generally older (4300 to > 10,000 years) than those in the Sulphur Springs area (2000–4400 years; all ages in Table 6 are rounded to the nearest 10 years), providing additional evidence that two distinct subsystems are present in Valles caldera.

Tritium concentrations and average ages of fluids discharging from wells VC-1 and hot springs along the Jemez fault zone are also listed in Table 6. It has been repeatedly demonstrated that discharging thermal waters along the Jemez fault zone have been diluted with younger, near-surface, meteoric waters (Trainer, 1984; Goff and Shevenell, 1987; Goff et al., 1988). Higher ^3H values and lower average residence times between 720 and 3470 years (well mixed) also show that fluids originating within the caldera have been diluted with younger waters along the fault zone. Because geothermal fluids are diluted with young waters along the fault zone, the calculated reservoir volumes do not reflect the actual fluid volumes within Valles caldera. One manner in which to visualize the distribution of the measured ^3H contents as a function of calculated mean residence times is presented in Fig. 5. The plot shows that the reservoir waters in Redondo Creek and Sulphur Springs are clearly older than the waters in the outflow plume (Soda Dam and Travertine Mound) which are mixed with younger waters along the flow path from the caldera. The large range in ^3H in the spring waters through time reflects mixing with

1991	1992
10	9.2
11	9.7
11	10.1
12	10.6
12	11.1
13	11.6
13	12
14	13
15	13
16	14
16	15
17	15
18	16
19	17
20	18
20	18
21	19
22	20
18	21
54	17
62	51
57	59
53	54
61	50
71	58
135	67
256	127
302	242
108	285
39	102
21	37
42	20
70	39
11	66
18	11
3.2	17
26	3.1
0.72	24
0.68	0.68
0.64	0.64
0.61	0.61
0.58	0.58
0.55	0.55
0.52	0.52
0.49	0.49
0.46	0.46
0.44	0.44
0.41	0.41
0.39	0.39
0.37	0.37
0.21	0.21
0.12	0.12
0.07	0.07
0.04	0.04
0.02	0.02
0.01	0.01

Table 6
Reservoir/spring data and estimated fluid ages (in years) in Valles Caldera, New Mexico

Name	Date	Depth (m)	Temp (°C)	Cl[a] (mg/kg)	^{3}H (T.U.)	PF (yr)	WM (yr)	Vol. 1[b] (km^3)	Vol. 2[b] (km^3)	Ref[c]
Valles Reservoir, Redondo Creek subsystem										
Baca 4[d]	7/2/82	> 1000	297	2670	0.49	45	5400	2.74	9.56	V
Baca 13[d]	7/1/82	> 1000	279	2594	0.61	41	4340	2.20	7.68	V
Baca 15[d]	7/23/82	> 1000	267	3257	0.25	57	> 10,000	> 5.07	> 17.7	V
Baca 15[d]	9/7/82	> 1000	326	3302	0.18	63	> 10,000	> 5.07	> 17.7	V
Baca 19[d]	10/15/82	> 1000	223	3340	0.47	46	5630	2.85	9.97	V
Valles Reservoir, Sulphur Springs subsystem										
Baca 3[e]	6/22/88	518	190	2010	0.63	40	3140	1.59	5.56	Me
Baca 3[d]	6/22/88	335	165	1880	0.55	43	3600	1.83	6.37	Me
VC-2A[d]	5/12/87	490	210	1545	0.72	38	2880	1.46	5.10	Mu
VC-2A[d]	5/13/87	490	210	1400	0.64	40	3250	1.65	5.75	Mu
VC-2A[f]	5/14/87	490	210	2180	0.61	41	3410	1.73	6.04	Mu
VC-2A[d]	7/30/87	490	210	2620	0.47	46	4430	2.25	7.84	Mu
VC-2A[d,h]	8/27/87	490	210	2945	0.06(?)	82	> 10,000	> 5.07	> 17.7	Mu
VC-2A[d]	12/2/87	490	207	2250	0.75	37	2770	1.40	4.90	C
VC-2B[g]	6/21/89	1753	295	0.63	0.67	39	2800	1.42	4.96	C
VC-2B[j,k]	10/26/89	1753	295	6990	0.77	37	2440	1.24	4.32	C
VC-2B[j,k]	1/18/90	1753	295	8380	0.89	37	2000	1.01	3.54	C
VC-2B[f]	6/15/91	640–1457	225	3907	0.45	46	3790	1.92	6.71	C
VC-2B[d]	6/16/91	640–1457	225	2670	0.11	71	> 10,000	> 5.07	> 17.7	C
VC-2B[g]	6/16/91	640–1457	225	6.58	0.41	48	4160	2.11	7.36	C
VC-2B[f]	6/17/91	640–1457	225	3528	0.58	42	2940	1.49	5.20	C
VC-2B[i]	6/18/91	640–1457	225	3713	0.43	47	3970	2.01	7.03	C
VC-2B[f]	6/18/91	640–1457	225	4021	0.39	49	4380	2.22	7.75	C
VC-2B[l]	5/11/92	640–1457	225	3245	0.20	61	8140	4.13	14.4	C
VC-2B[m]	5/11/92	640–1457	225	4000	0.46	46	3530	1.79	6.24	C
VC-2B[n]	5/12/92	640–1457	225	5290	0.98	39	1640	0.83	2.90	C
VC-2B[o]	5/12/92	640–1457	225	3325	0.35	51	4640	2.35	8.21	C
VC-2B[p]	5/12/92	640–1457	225	4050	0.74	39	2180	1.11	3.86	C
Valles caldera outflow plume										
VC-1[j]	8/18/85	428	90	937	0.77	37	2970	1.51	5.26	Mu
VC-1[q]	9/5/85	428	90	964	0.66	39	3470	1.76	6.14	Mu
VC-1[j]	5/13/86	428	90	415	0.18	63	> 10,000	> 5.07	> 17.7	Mu
VC-1[j]	8/26/86	537	125	853	0.76	37	2870	1.46	5.08	Mu
Soda Dam Spring	3/82	–	47	1480	2.9	29	900	0.46	1.59	V
Soda Dam Spring	9/82	–	47.5	1614	1.33	29	1980	1.00	3.50	V
Soda Dam Spring	1/83	–	46.8	1536	1.48	30	1690	0.86	2.99	V
Soda Dam Spring	5/83	–	47	1477	1.62	30	1550	0.78	2.73	V
Soda Dam Spring	7/12/84	–	47	1480	1.29	31	1850	0.94	3.27	C
Soda Dam Spring	2/9/88	–	46.6	1540	1.64	34	1190	0.60	2.11	C
Soda Dam Spring	6/3/88	–	47.7	1540	0.88	35	2240	1.14	3.96	Me
Soda Dam Spring	8/3/88	–	47.0	1565	1.01	34	1950	0.99	3.45	Me
Soda Dam Spring	5/7/91	–	47.0	1507	0.73	38	2330	1.18	4.12	C
Soda Dam Spring	6/8/92	–	47.2	1530	0.84	39	1920	0.97	3.40	C
Main Jemez Spring	3/82	–	74	926	1.2	29	2200	1.12	3.89	V
Main Jemez Spring	6/8/92	–	68.4	932	1.6	39	950	0.48	1.69	C
Travertine	1/83	–	72.6	906	2.92	30	850	0.43	1.50	V

Name	Date	Depth (m)	Temp (°C)	Cl[a] (mg/kg)	^{3}H (T.U.)	PF (yr)	WM (yr)	Vol. 1[b] (km^3)	Vol. 2[b] (km^3)	Ref[c]
Mound Spring										
Travertine Mound Spring	7/13/84	–	72.0	952	3.22	31	730	0.37	1.30	C
Travertine Mound Spring	2/9/88	–	72.4	882	2.68	35	720	0.36	1.27	C
Travertine Mound Spring	6/3/88	–	73.3	862	2.34	35	830	0.42	1.46	Me
Travertine Mound Spring	5/13/91	–	72.5	910	1.59	19	1050	0.53	1.86	C
Travertine Mound Spring	6/8/92	–	73.3	910	1.77	39	900	0.46	1.59	C
Jemez Springs Well	10/20/86	24–150	74.0	890	1.75	33	1230	0.62	2.18	C
Jemez Pueblo Well (JP-2)	10/11/91	73.2	57.8	1196	0.07	80	> 10,000			C

[a]Cl values for well samples are corrected for steam flash unless otherwise noted.
[b]Volume 1 is calculated using the well-mixed (WM) age and a minimum discharge rate of 5.07×10^{-4} km^3/yr, and Volume 2 is calculated using the well-mixed age and the maximum discharge rate of 1.77×10^{-3} km^3/yr.
[c]V = Vuataz and Goff (1986); Me = Meeker et al. (1990); Mu = Musgrave et al. (1988); C = current work.
[d]Mini-separator sample (water).
[e]Bailer sample, Cl value is not flash corrected.
[h]Cl value calculated from average of five flash corrected analyses (Table 3; Goff et al., 1989).
[f]Weir sample.
[g]Mini-separator sample (steam).
[i]Total flow on surface sample port.
[j]In-situ sample collected with down-hole sampler.
[k]Based on the stable isotope data, these samples appear to be substantially evaporated ($\leq 50\%$).
[l]First mini-separator sample (water); flash temperature = 175°C; Cl not corrected for steam flash.
[m]Second mini-separator sample (water); flash temperature = 144°C; Cl not corrected for steam flash.
[n]Weirbox sample; temperature = 95°C.
[o]First mini-separator sample (water); flash temperature = 160°C; Cl not corrected for steam flash.
[p]Total flow from well.
[q]Water sample collected at surface during well swabbing operations.

a component of more recent precipitation in which the ^{3}H has been decreasing through time.

One additional sample was obtained from outside of the caldera area from a recently drilled geothermal well at Jemez Pueblo. Geochemical trends suggest that this Jemez Pueblo fluid may be composed partly of Valles caldera geothermal fluid which discharge through the Jemez fault zone. The data for the fluid are included for comparison with younger waters which flowed shorter distances along the Jemez fault zone and mixed with young, near-surface, meteoric waters. Due to the longer flow path, and perhaps, less mixing with younger waters, the Jemez Pueblo water is considerably older than the waters discharging at Jemez Springs and Soda Dam.

6. Discussion

Very few, if any, systems can be described by pure piston-flow or pure well-mixed conditions. Although ^{3}H, with its short half-life, can not be used rigorously to obtain accurate mean residence times of old waters, this work demonstrates that it can be used to obtain an order of magnitude estimate of fluid ages and help distinguish between different zones in a reservoir.

Presumably before 1953, the Valles caldera reservoirs had a ^{3}H content near zero, but the addition of some of the high ^{3}H water following 1953 elevated these concentrations to detectable levels. The similar ^{3}H concentrations measured in each of the geothermal wells in Valles caldera over time indicate that the reservoir may be relatively well mixed and may only have a very small piston-flow component. However, estimated mean residence times of fluids assuming well-mixed conditions are possibly too high because it is quite likely that some of the fluid recharged since atmospheric testing began has not yet reached the depths of the reservoir. If all post-bomb recharge (that is, all water precipitated from 1953 to the date of sample collection) had reached the reservoir and mixed with

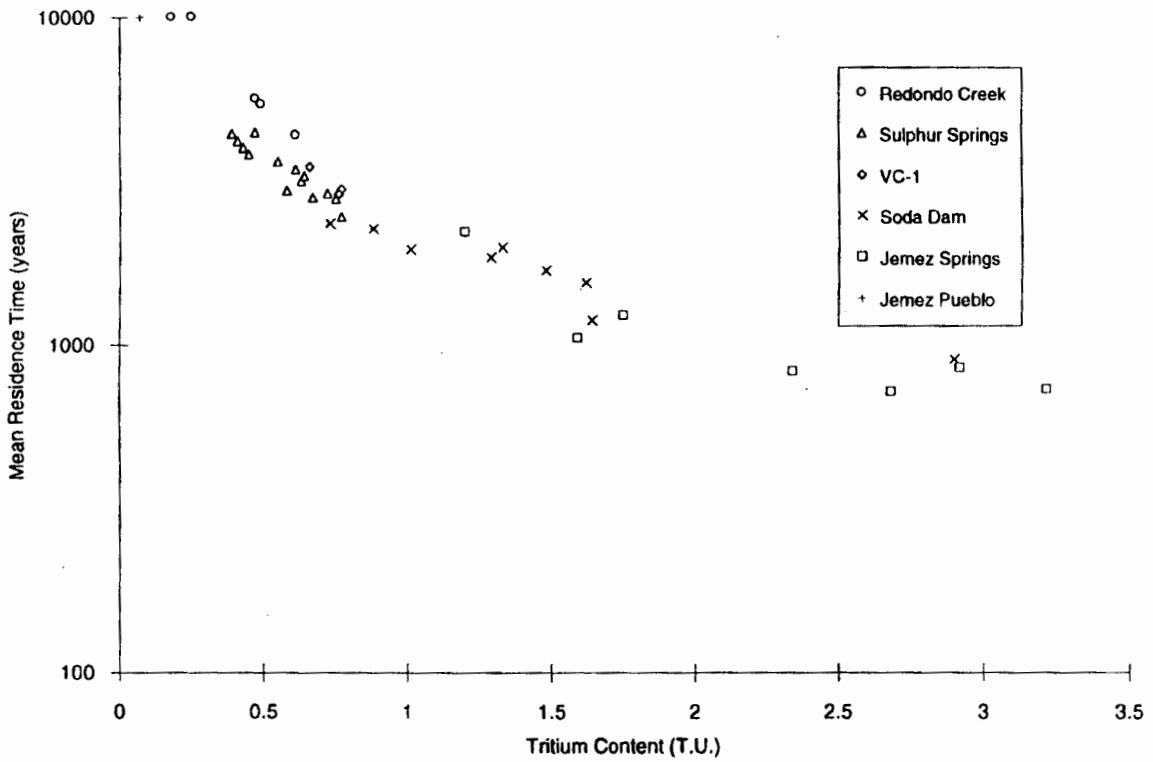

Fig. 5. Measured ^3H content in geothermal waters versus calculated mean residence times using the well-mixed model. Data for the plot are taken from Table 6.

Fig. 6. Lines sho
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Soda Dam Spring.

fluids within the reservoir, the required rate of vertical circulation would be quite high for welded, silicified tuff (6.6 m/d, assuming up to 2400 m for a circulation depth within one year). Also, due to the sluggish nature of the flow system and current views on the magnitude of dispersion, it is unlikely that the reservoir is strictly well mixed. Hence, estimated mean residence times using the current model are likely to be too old.

The Valles caldera reservoir has a fairly uniform distribution of low ^3H values within the system suggesting an old, perhaps well-mixed reservoir. The low measured ^3H concentrations in the wells of both subsystems ($\sim$0.2–0.75 T.U.) suggest maximum mean residence times between 3000 and $>$10,000 years (well mixed). These values disagree somewhat with estimates of previous investigators ($\sim$1900 years) who may have underestimated the total fluid volume of the Valles geothermal system by concentrating solely on the producible reservoir in their calculations (Union Oil Company of California and Public Service Company of New Mexico, 1978; Balleau, 1980; Union Oil Company of California, 1982, Bodvarsson et al., 1982; Faust et al., 1984).

Using the well-mixed model, the estimated volume of fluids residing within Valles caldera ranges from 1.41 to $\sim$18 km^3 (Table 6) which brackets the estimates of 1.21 and 2.69 km^3 found by previous groups. The upper limit on fluid volume estimated in this study is substantially greater than that estimated by previous workers. Yet the purpose of each of the previous studies was to estimate the volume of the producible, geothermal reservoir at Redondo Creek and the entire reservoir in the caldera depression may be substantially larger and reside in a greater portion of the caldera. For instance, even if the lateral extent of 40 km^2 (Bodvarsson et al., 1982) is used to estimate areal extent of the

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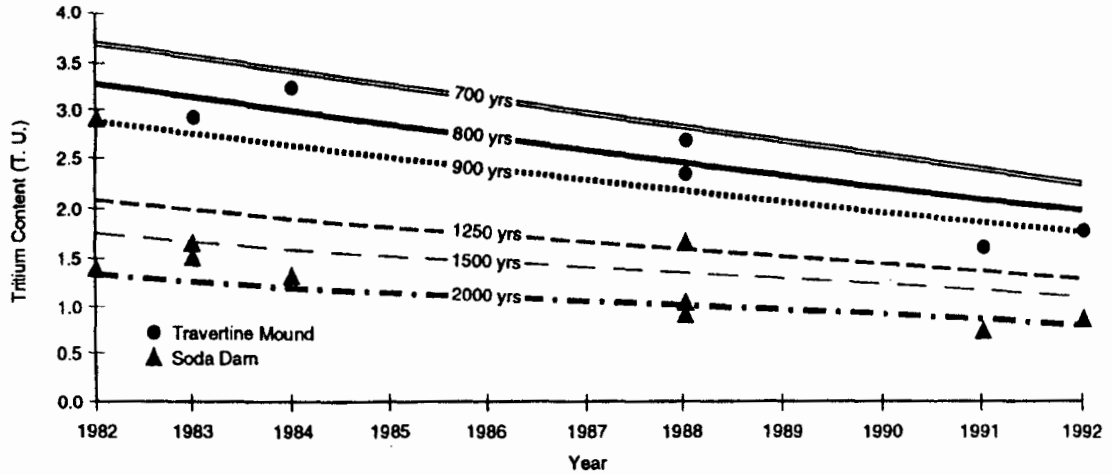

Fig. 6. Lines showing calculated ^3H content versus year for the well-mixed model. Individual lines show equal mean residence times for calculated ^3H contents in the years 1982–1992. ● and ▲ show measured ^3H contents in the indicated years for Travertine Mound Spring and Soda Dam Spring, respectively.

producible reservoir, a thermal fluid volume of 4 km^3 is found.

Several samples from Soda Dam and Travertine Mound springs have been collected between 1982 and 1992 allowing for temporal comparisons of calculated versus measured ^3H contents. Calculated ^3H contents using the well-mixed model for six mean residence times between 700 and 2000 years are illustrated in Fig. 6. Most of the Soda Dam samples plot between the 1500 and 2000 years mean residence time lines. The sample collected in 3/82 appears anomalous and may represent increased mixing with young waters during a heavy storm event, or the value may be in error. All other samples show a general decreasing trend in ^3H through time, reflecting the decreasing ^3H content in precipitation over the same time (see Fig. 3). A better fit is observed for the younger Travertine Mound Spring water where the decreasing ^3H through time indicates mean residence times between 700 and 900 years over the 10 yr sampling interval. Neither spring exhibits trends which precisely match calculated ^3H for a given mean residence time, yet the correspondence is good considering the limitations of the well-mixed model.

It should be noted that an error of ± 0.1 T.U. can have a dramatic affect on estimated mean residence times in systems with very low ^3H concentrations such as Valles. A measured ^3H content of 0.5 ± 0.1 T.U. yields large variations in fluid ages and volumes (i.e. 3940^{+989}_{-660} yr and $7.0^{+1.7}_{-1.2}$ km^3). At higher ^3H concentrations, the errors in fluid ages are much smaller. A fluid with a ^3H content of 1.9 ± 0.1 T.U. yields an age of 1019^{+57}_{-51} years. Note that ^3H values can currently be measured to 0.01 ± 0.02 T.U., and the quoted errors in these examples are unrealistically high.

Selection of the pre-bomb ^3H of 6 T.U. has negligible effects on the well-mixed model because the input function is overwhelmed by the high ^3H input in the 1950's and 1960's. However, variations from this value can have more substantial effects on calculated ages in the piston-flow model. For instance, a measured ^3H content of 1.12 T.U. in a sample collected in 1982 will yield an age of 30 years for a background value of 6 T.U., yet will yield an age of 17.7 years when a 3 T.U. background value is used.

Fig. 4 shows that non-unique mean residence times are obtained for ^3H contents greater than ~ 10 T.U. Although non-uniqueness does not present a difficulty in interpreting the Valles caldera data, other study areas having younger waters, and higher ^3H contents may suggest multiple mean residence times for which interpretations must be made using additional data. For instance, ^3H contents of hot springs at Mount St. Helens indicate mean residence times between ~ 2 and 7 years, or between ~ 100 and 184 years (Shevenell, 1991). Observations other than ^3H must be used in such cases

in order to eliminate one range from further consideration. At the Mount St. Helens site, the upper range of 100–184 years is inappropriate because hot springs in the summit area formed only 3 years following the 1980 eruptions, suggesting rapid initiation of hydrothermal circulation. Rapid fluid velocities of > 49 m/yr are also suggested based observed hydraulic gradients and conductivities. In addition, the permeability of the 1980 avalanche and pyroclastic deposits from which the hot spring discharge is higher than pre-1980 deposits suggesting preferential flow of young water in shallower deposits. One-dimensional advection–dispersion modeling was also conducted to verify the lower mean residence times of 2–7 years at this site (Shevenell, 1991). Hence, interpretation of ^{3}H data must be consistent with all other relevant hydrogeologic information.

Breaking the aquifer into subregions is appropriate in many systems due to the extreme variability in hydraulic parameters encountered. However, more rigorous models which account for spatial variability in hydrologic parameters would be more difficult to apply to a system in which there are very little hydrologic data available. With limited data, the system may be modeled in its entirety, rather than in subregions, and the current model yields acceptable results when interpreted with the knowledge that the well-mixed model yields excessive ages and volumes if the system has an appreciable piston-flow component.

7. Conclusions

This work shows that reliable input ^{3}H functions can be derived at specific localities having limited data sets by numerically comparing their data to the ^{3}H record at Ottawa, Canada. With these input functions, ^{3}H is used to define upper and lower limits on mean residence times of fluids within the Valles caldera reservoir using the well-mixed end-member model (3000–10,000 years). In-situ production of ^{3}H in the reservoir is very low (≤0.01 T.U.) and insufficient to change the estimated mean residence times at Valles caldera. Limits on reservoir volumes obtained with the well-mixed model bracket those estimated by other methods at Valles caldera (1.21–2.69 km^3), and this information required less data and modeling time than the more rigorous, numerical models. Relative differences in fluid mean residence times between various fluids in a system are also provided by this ^{3}H model. For instance, the ^{3}H data indicate that the hot springs discharging along the Jemez fault zone are mixtures of older, Valles caldera reservoir water and young meteoric water. The results also show that the waters in the Sulphur Springs subsystem of Valles caldera are younger (~2000–4400 years) than those in the Redondo Creek subsystem (~4300 to > 10,000 years).

Acknowledgements

We wish to thank Dr. F.D. Vuataz, Dr. R. Gonfiantini and Dr. D.K. Solomon for their review comments on an earlier version of this manuscript. We thank Drs. J.N. Andrews and D.J. Martel for providing useful comments on in-situ production of ^{3}H. Much of this work was conducted at the Desert Research Institute, Reno, Nevada with partial support from Mrs. B. Stout who provided the George Burke Maxey Fellowship. Work was also conducted at Oak Ridge National Laboratory which is managed by Martin Marietta Energy Systems, Inc. under contract DE-AC05-84OR21400 with the U.S. Department of Energy. Funding for the Valles caldera work was provided through a grant to the second author from the U.S. Department of Energy, Office of Basic Energy Sciences.

Appendix A. Reservoir model using tritium

The piston-flow model yields a lower limit of fluid age and reservoir volume. This model assumes that no mixing of recharged water occurs in the reservoir from the time of recharge to the time of discharge. Therefore, all molecules in the system have the same residence time, and the molecules travel through the system from recharge to discharge without being mixed with other sources. Output tritium concentrations depend only on the input concentration at recharge and on the fluid residence time (time since recharge). The relationship between input and output concentration is expressed by:

$$C_{out}(t) = C_{in}(t-\tau)e^{-\lambda\tau} \qquad \text{(A-1)}$$

where $C_{out}(t)$ is the output tritium concentration at time t, $C_{in}(t-\tau)$ is the tritium concentration of fluid

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recharging the system, τ is the residence time and λ is the tritium decay constant ($5.576 \times 10^{-2}/\mathrm{yr}^{-1}$).

Eqn. 1 is simply a standard decay equation and all that is needed to estimate age are the input and output concentrations.

Because the piston-flow model does not account for mixing, nor does it account for the possibility that the system may have many points of input, the well-mixed model must be used to calculate an upper limit on the age of the fluid. The well-mixed model assumes that all input to the reservoir is completely mixed with fluid already in the reservoir. Hence, fluid discharging from the system has the same composition as the mixed fluid in the reservoir. The mass balance equation presented by Pearson and Truesdell (1978) for a well-mixed reservoir is given by:

$$\frac{\mathrm{d}C(t)}{\mathrm{d}t} = \frac{Q_{\mathrm{in}}}{V} C_{\mathrm{in}}(t) - \frac{Q_{\mathrm{out}}}{V} C(t) - \lambda C(t) \qquad \text{(A-2)}$$

where $C(t)$ is the tritium level in the reservoir and at the discharge point, at time t, $C_{\mathrm{in}}(t)$ is the input tritium concentration, Q_{in} is the recharge flow rate, Q_{out} is the discharge flow rate and V is the volume of the reservoir.

Assuming that the volume of the reservoir remains unchanged with time and the recharge rate equals the discharge rate ($Q_{\mathrm{in}} = Q_{\mathrm{out}}$), and defining the mean residence time (τ) equal to V/Q, the equation takes the form of:

$$\frac{\mathrm{d}C(t)}{\mathrm{d}t} + \left(\frac{1}{\tau} + \lambda\right) C(t) = \frac{1}{\tau} C_{\mathrm{in}}(t) \qquad \text{(A-3)}$$

and:

$$\mathrm{d}C(t) + \left(\frac{1}{\tau} + \lambda\right) C(t)\ \mathrm{d}t = \frac{1}{\tau} C_{\mathrm{in}}(t)\ \mathrm{d}t$$

In order to find the solution to this equation we must multiply the equation by an integration factor. Multiplication by $\mathrm{e}^{(1/\tau+\lambda)t}$ transforms the previous expression into an exact equation given by:

$$\mathrm{e}^{(1/\tau+\lambda)t}\ \mathrm{d}C(t) + C(t)\left(\frac{1}{\tau} + \lambda\right)\mathrm{e}^{(1/\tau+\lambda)t}\ \mathrm{d}t = \qquad \text{(A-4)}$$

$$\frac{\mathrm{e}^{(1/\tau+\lambda)t}}{\tau} C_{\mathrm{in}}(t)\ \mathrm{d}t$$

where the left side of the equation is the first derivative of $\mathrm{e}^{(1/\tau+\lambda)t} C(t)$. Substituting the derivative of the previous expression into Eqn. 4 yields:

$$\left[\mathrm{e}^{(1/\tau+\lambda)t} C(t)\right]' = \frac{\mathrm{e}^{(1/\tau+\lambda)t}}{\tau} C_{\mathrm{in}}(t)\ \mathrm{d}t \qquad \text{(A-5)}$$

Integrating Eqn. 5 and then dividing by $\mathrm{e}^{(1/\tau+\lambda)t}$ results in the solution to Eqn. 2:

$$C(t) = \mathrm{e}^{-(1/\tau+\lambda)t}\left[\frac{1}{\tau}\left(\int C_{\mathrm{in}}(t)\mathrm{e}^{(1/\tau+\lambda)t}\ \mathrm{d}t + C\right)\right] \qquad \text{(A-6)}$$

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