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19 April 2013

Environment Canterbury
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Attention: Matt Dodson

Dear Matt

Groundwater age interpretation for Ashley-Waimakariri springs

This report provides the results of age-tracer analyses for five Ashley-Waimakariri springs and presents a calculation of the mean groundwater residence times for these waters. Site details are given in Table 1. Analytical results are presented in Tables 2 and 3. Calculated ages are presented in Table 4.

Table 1 Site details.

Site ID	Easting [1]	Northing [1]	Site description [2]	Sampling comments [3]
BW24/0023	1568021	5192526	Not specified	None given
M35/7450	1570342	5206836	"Spring" is the outflow from a pipe, which is draining the paddock.	Sampled using 12v supertwister up pipe.
M35/7493	1565982	5203859	Spring has a CRC weir and recorder installed 50m downstream	Did not sample CFCs, SF_6. Sample taken from near the weir
M35/7494	1565982	5203859	"Spring" is the outflow from a pipe, which is draining the paddock	Sampled using 12v supertwister.
M35/7500	1565959	5196779	"Spring" is the outflow from a pipe, which is draining the paddock.	Sampled discharge from broken section of the drain using 12v supertwister up pipe.

1. Coordinates are NZTM.
2. Site descriptions from the Environment Canterbury well card database.
3. Sampling comments provided by Environment Canterbury.

Table 2 Tracer concentrations.

Site ID	Sampling date	CFC Lab no.	CFC-11 [1] pmol/L	CFC-12 [1] pmol/L	CFC-113 [1] pmol/L	SF_6 Lab no.	SF_6 [2] fmol/L	Tritium Lab no.	Tritium TR [3]
BW24/0023	2/04/2012	FC484	2.26 ± 0.07	2.71 ± 0.11	0.21 ± 0.03	SC314	2.84 ± 0.08	TCB792	1.680 ± 0.034
BW24/0023	19/07/2012	FC505	2.15 ± 0.02	2.54 ± 0.14	0.20 ± 0.00	SC336	2.80 ± 0.08	TCB814	1.686 ± 0.035
M35/7450	2/04/2012	FC485	10.3 ± 0.2	ND [4]	0.48 ± 0.02	SC315	4.57 ± 0.12	TCB793	2.335 ± 0.042
M35/7450	19/07/2012	FC506	13.5 ± 0.8	ND	0.48 ± 0.01	SC337	4.71 ± 0.12	TCB815	2.227 ± 0.041
M35/7493	2/04/2012	NS [5]	NS	NS	NS	NS	NS	TCB794	2.160 ± 0.040
M35/7493	19/07/2012	NS	NS	NS	NS	NS	NS	TCB816	2.199 ± 0.044
M35/7494	2/04/2012	FC487	3.67 ± 0.08	3.81 ± 0.12	0.28 ± 0.02	SC316	2.75 ± 0.07	TCB795	1.912 ± 0.039
M35/7494	19/07/2012	FC507	3.33 ± 0.07	3.54 ± 0.11	0.24 ± 0.02	SC339	2.93 ± 0.08	TCB818	1.832 ± 0.037
M35/7500	2/04/2012	FC486	4.07 ± 0.08	2.84 ± 0.10	0.34 ± 0.02	SC317	2.79 ± 0.08	TCB796	1.733 ± 0.037
M35/7500	19/07/2012	FC508	3.75 ± 0.05	2.74 ± 0.14	0.26 ± 0.02	SC338	3.05 ± 0.08	TCB817	1.640 ± 0.037

1. Dissolved CFC concentrations are expressed in pmol/L where 1 pmol = 1×10^{-12} mol.
2. Dissolved SF_6 concentrations are expressed in fmol/L where 1 fmol = 1×10^{-15} mol.
3. Tritium concentrations are expressed as ^3H:^1H ratios where 1 tritium unit (TR) signifies a ratio of $1:1\times10^{18}$.
4. ND = not determined as above calibrated range of analytical technique.
5. NS = no sample taken.

Table 3 Calculated atmospheric partial pressures of trace gases.

Site ID	Sampling date	Ar mL(STP)/kg [1]	N_2 mL(STP)/kg [1]	Recharge temp °C [2]	Excess Air [1,2]	CFC-11 ppt [3]	CFC-12 ppt [3]	CFC-113 ppt [3]	SF_6 ppt [3]
BW24/0023	2/04/2012	0.421 ± 0.011	17.06 ± 0.57	9.1 ± 2.5	2.8 ± 1.6	103 ± 15	468 ± 61	30.2 ± 6.1	5.23 ± 0.78
BW24/0023	19/07/2012	0.404 ± 0.006	16.67 ± 0.22	11.5 ± 1.4	3.3 ± 0.7	111 ± 9.0	491 ± 43	32.4 ± 2.8	5.35 ± 0.42
M35/7450	2/04/2012	0.397 ± 0.007	15.41 ± 0.16	9.8 ± 1.4	1.0 ± 0.7	485 ± 39	ND	72.6 ± 6.9	10.15 ± 0.9
M35/7450	19/07/2012	0.399 ± 0.007	16.4 ± 0.41	11.8 ± 1.8	3 ± 1.1	710 ± 81	ND	80.3 ± 8.6	9.25 ± 0.97
M35/7493	2/04/2012	ND	ND	ND	ND	ND	ND	ND	ND
M35/7493	19/07/2012	ND	ND	ND	ND	ND	ND	ND	ND
M35/7494	2/04/2012	0.411 ± 0.014	16.71 ± 1.32	10.1 ± 2.8	2.8 ± 3.5	176 ± 27	690 ± 97	42.8 ± 7.8	5.32 ± 1.47
M35/7494	19/07/2012	0.356 ± 0.006	14.77 ± 0.52	17.1 ± 2.3	2.7 ± 1.3	229 ± 25	884 ± 91	54.5 ± 7.7	7.16 ± 0.92
M35/7500	2/04/2012	0.392 ± 0.007	15.35 ± 0.16	10.6 ± 1.5	1.3 ± 0.7	202 ± 16	537 ± 43	54.4 ± 5.5	6.14 ± 0.54
M35/7500	19/07/2012	0.356 ± 0.009	14.47 ± 0.53	16.1 ± 2.8	2.1 ± 1.4	247 ± 34	661 ± 87	56.5 ± 9.2	7.19 ± 1.14

1. Ar, N_2 and excess air concentrations are expressed in mL of gas at standard temperature and pressure per kg of water.
2. Recharge temperatures and excess air concentrations are derived from measured argon and nitrogen concentrations.
3. CFC and SF_6 partial pressures are expressed in parts per trillion (ppt) where 1 ppt signifies a volumetric ratio of 1×10^{-12}.
4. ND = not determined.

Age Calculation

Calculated groundwater model ages (Table 4) are based on an exponential-piston flow model matched to the tracer concentrations presented in Tables 2 and 3. An overview of the age-dating methodology is provided in Appendix 2.

Springs and streams are often assumed to integrate flow paths from a large catchment area resulting in a high proportion of mixed flow (Manga 2001), therefore to calculate ages for the water from the five springs a value of 80% exponential mixed flow was initially used.

Table 4 Groundwater model ages.

		EPM with 80% exponential mixed flow mean age (years)				
Site ID	**Sampling date**	**CFC-11**	**CFC-12**	**CFC-113**	**SF_6**	**Tritium**
BW24/0023	2/04/2012	57 (44 - 72) [1]	16 (0 - 31)	47 (34 - 67)	8 (3 - 17)	7 (6 - 8) or 41-52 [2]
BW24/0023	19/07/2012	52 (46 - 62)	13 (0 - 23)	45 (39 - 52)	7 (5 - 12)	7 (6 - 8) or 41-52 [2]
M35/7450	2/04/2012	C [3]	C	11 (0 - 21)	C	1 (0 - 2)
M35/7450	19/07/2012	C	C	(0 - 18)	C	2 (1 - 3)
M35/7493	2/04/2012	ND [4]	ND	ND	ND	2 (1 - 3)
M35/7493	19/07/2012	ND	ND	ND	ND	2 (1 - 3)
M35/7494	2/04/2012	29 (16 - 47)	C	33 (22 - 52)	7 (0 - 29)	4 (3 - 5) or 46-47 [2]
M35/7494	19/07/2012	15 (0 - 28)	C	24 (14 - 37)	0 (0 - 7)	5 (4 - 6) or 45-50 [2]
M35/7500	2/04/2012	22 (14 - 32)	0 (0 - 18)	24 (18 - 32)	4 (0 - 9)	6.5 (6 - 7) or 42-51 [2]
M35/7500	19/07/2012	8 (0 - 28)	C	22 (0 - 37)	0 (0 - 10)	7.5 (6 - 9) or 41-52 [2]

1. The stated model age ranges (in brackets) result from the 95% confidence interval based on the uncertainty in analytical measurements only and do not account for uncertainty in model selection.
2. The older age ranges are only possible for proportions of exponential mixed flow less than 30%.?
3. C denotes contamination whereby the derived atmospheric partial pressure of the respective gas tracer is above that possible for water in equilibrium with modern air.
4. ND = not determined.

Groundwater from springs M35/7450 and M35/7493 is young, with mean ages of 1 to 2 years. There is little difference in age between the April and July sampling rounds. Gas tracer concentrations in water from M35/7450, except for CFC-113, are affected by contamination. Similar contamination has been observed in bores downgradient of this spring (van der Raaij 2011)

The age-tracer data from the other three springs (BW23/0023, M35/7494 and M35/7500) are ambiguous. Tritium data indicates either a young mean age of 4 to 8 years, or an older mean age of 40 to 50 years. The older age possibility can only be attained for proportions of exponential mixed flow less than 30%. As stated previously, springs are commonly assumed

to integrate flow paths over a large catchment and therefore have high proportions of mixed flow. Whether the older ages and low proportions of exponential mixed flow are realistic depends on the hydrogeological context of each site.

Gas tracer results for BW23/0023, and in part for M35/7494 and M35/7500, appear to support the older age interpretations. However the gas tracer results may be unreliable due to the nature of the sampling points. Samples taken from pipes draining the paddocks where the springs are situated are likely to have had some contact with air prior to collection and the dissolved gases will be in a state of partial re-equilibration to the temperature at the time of sampling. The extent of re-equilibration will depend on a number of factors such as the nature of the sampling site, the extent of air contact, changes in water temperature which occur between the spring and sampling point and the initial dissolved gas concentrations.

Recharge temperatures derived from measurements of dissolved argon and nitrogen (Figure 1) could also be affected by partial re-equilibration, although the extent of this appears to be limited. Observed field temperatures in April are roughly 4°C higher than the Ar-N_2 recharge temperatures, while field temperatures in July are mostly lower than the Ar-N_2 temperatures. The Ar-N_2 derived temperatures are close to the mean annual air temperature of 11.4°C observed at Rangiora for the 30 year period from 1971 to 2000 (National Climate Database 2013), except for the measurements for springs M35/7494 and M35/7500 from July 2012, which are higher.

The combination of above effects is a possible cause of the apparent difference in model ages derived from CFCs and tritium, most notably for BW24/0023 but also for M35/7494 and M35/7500. Model ages derived from SF_6 are generally in better agreement with the tritium derived ages but these too have probably been affected by partial re-equilibration. CFC-12 concentrations are also affected by contamination in springs M35/7494 and M35/7500.

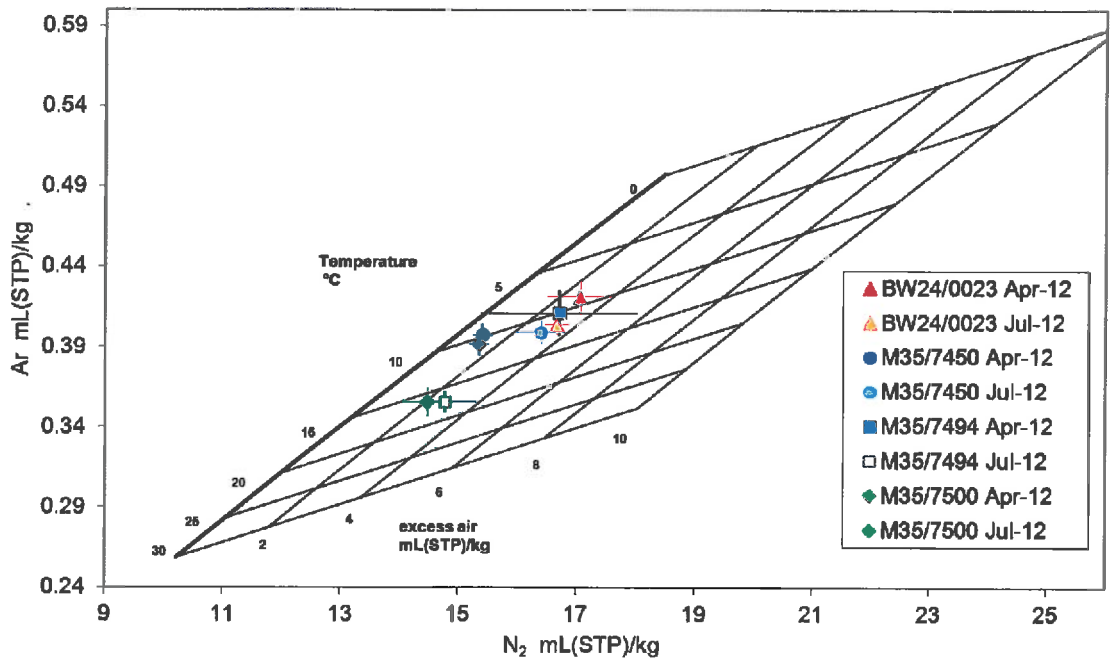

Figure 1 Plot of nitrogen versus argon concentrations. The positions of the samples within the grid indicate their recharge temperatures and excess air concentrations. The bold line on the left of the grid is for gas concentrations in water which are in equilibrium with the atmosphere.

Summary

Groundwater from springs M35/7450 and M35/7493 is young, with mean ages of 1 to 2 years. There is little difference in age between the April and July sampling rounds.

Groundwater age data for BW23/0023, M35/7494 and M35/7500 are ambiguous. There is currently insufficient age-tracer data to determine whether the younger or older model age is correct. If the springs are assumed to perform an integrating function over a variety of flow paths from a large catchment area (as seems probable) then the younger age is the most likely. Whether this assumption is reasonable should be determined through closer examination of the hydrogeological setting of each spring.

Yours sincerely

Rob van der Raaij
Scientist, Isotope Hydrology

Mike Stewart
(Reviewer)
(pp: C Vedder - Administrator)

Appendix 1. Determination of Groundwater Age using Tritium, CFCs and SF_6

Chlorofluorocarbons (CFCs) are entirely synthetic compounds. Significant production of CFCs began in the 1930s. Sulphur hexafluoride (SF_6) is predominantly anthropogenic with industrial production beginning in the 1950s. However, a small amount of SF_6 is also produced in certain volcanic minerals and fluids. Groundwater age-dating using CFCs and SF_6 is possible due to the steady increase in atmospheric concentrations of these gases since production began (Figure A 1.1). These gases are dissolved in recharge waters and are isolated from the atmosphere when this recharge enters the groundwater zone. Thus the gases hold a record in the groundwater of past atmospheric concentrations. CFCs have been measured continuously in the atmosphere at various sites worldwide since the late 1970s but their concentrations have begun to decline since use of them was phased out following the Montreal Protocol in 1987 thus losing effectiveness for age-dating over this period (IAEA, 2006).

After measured CFC and SF_6 concentrations in groundwater are corrected for excess air, they are used to calculate relative atmospheric concentrations using Henry's Law and an estimated recharge temperature. Excess air is air in excess of the equilibrium soluble amount at the given recharge temperature and is thought to originate by processes such as bubble entrapment occurring during recharge. The excess air correction and recharge temperature are calculated from the ratio of dissolved nitrogen and argon concentrations (Heaton & Vogel, 1981). These nitrogen and argon concentrations are measured simultaneously with the CFC concentrations. The calculated atmospheric concentrations are then used to calculate the CFC and SF_6 model ages of the groundwater (Plummer & Busenberg, 2000).

Under certain circumstances, CFCs and SF_6 can undergo diffusive exchange processes in the unsaturated zone, increasing their concentrations in groundwater. In these cases the model ages derived from the CFC and SF_6 concentrations should be regarded as minimum ages for groundwater. CFCs are also susceptible to degradation processes underground, particularly in anoxic environments, and to contamination. SF_6 is less susceptible to these but is affected more by excess air and diffusion.

Tritium (^3H) is a component of the water molecule and thus forms an ideal tracer for groundwater studies. Age-dating using tritium is based on radioactive decay of tritium after rainwater penetrates the ground during recharge. The half-life of tritium is 12.32 years. Tritium is produced naturally by cosmic radiation in the upper atmosphere but was also released into the atmosphere by nuclear weapons testing. Figure A 1.1 shows the history of the tritium concentration in rainfall; the peak in tritium concentration in the 1960s and early 1970s is a result of this testing (Stewart & Morgenstern, 2001). Tritium data may give ambiguous ages, because of this irregularly shaped peak. Often this will be resolved by measuring the change in tritium concentration in groundwater over a time interval of a few years or by comparison to CFC and SF_6 ages.

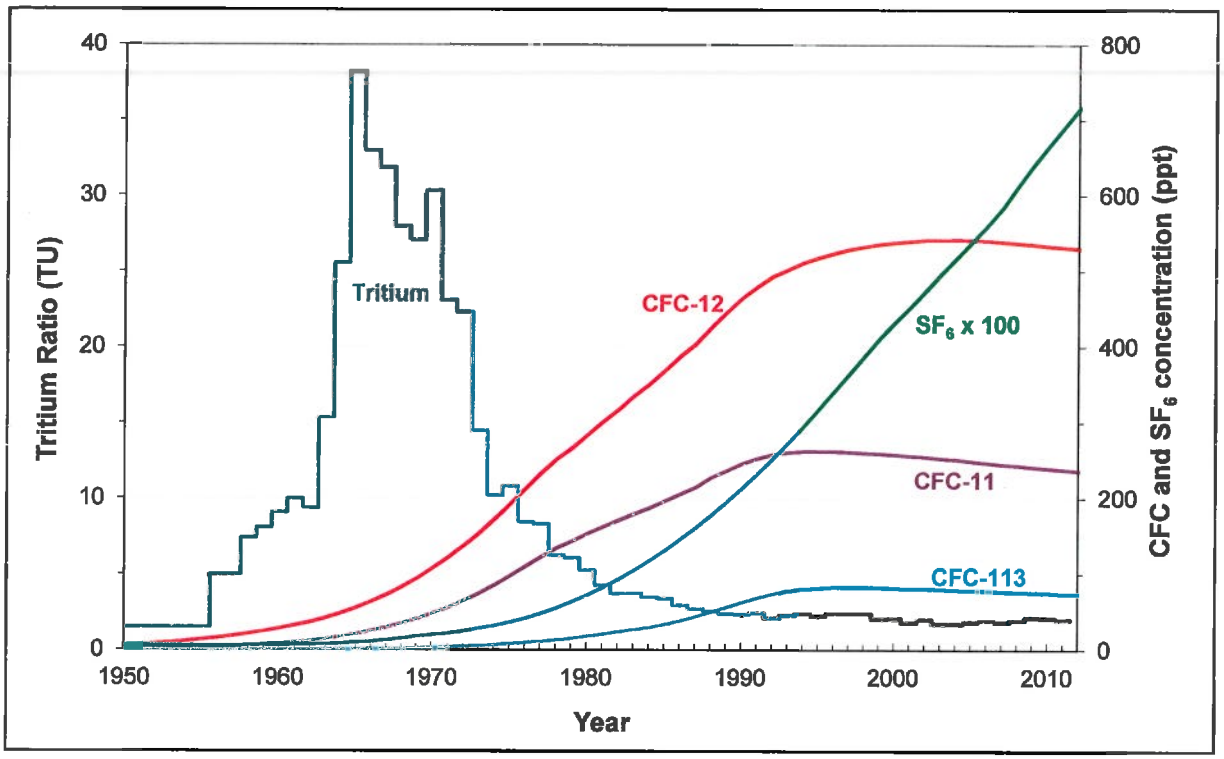

Figure A 1.1 Tracer input curves. The tritium concentrations are from rainfall at Kaitoke, New Zealand, and have been measured monthly since the 1960s. CFC and SF_6 concentrations are for southern hemispheric air (IAEA, 2006).

Groundwater extracted from a well or other discharge point is a mixture of water with different ages due to the convergence of different flow lines within the aquifer at the discharge point (Figure A 1.2). Groundwater age-dating therefore yields an average age of the water. To calculate the average age the distribution of groundwater age must also be determined. This distribution can be described using lumped-parameter mixing models. Piston flow is a simplified approximation of little mixing of flow lines and is suitable for aquifers in which the recharge zone is narrow with respect to the overall distance from recharge zone to sampling point, while the exponential model describes complete mixing of the flow lines within a system. The mixing of different flow lines occurs at the sampling point. For more realistic scenarios which are intermediate between piston flow and exponential mixing, the exponential-piston flow model (EPM) may be applied (Maloszewski & Zuber, 1982).

The EPM is described by two parameters – the mean age and the fraction of exponential mixed flow. The fraction of exponential mixed flow is a measure of the degree of mixing and reflects the distribution of travel-times of different components of groundwater around the mean age (Figure A 1.3). The fraction of exponential mixed flow observed at the bore depends on the characteristics of the sampling point as well as the hydrogeologic attributes of the aquifer concerned (which affect the variety of possible flow paths that may be intersected by the bore). This fraction is best estimated by matching to the tritium data using a series of measurements separated in time by several years. If such a time series is not available, comparison of the tritium data to CFC and SF_6 data can sometimes be used for less precise estimates of the mixing fraction, but should be confirmed by future sampling.

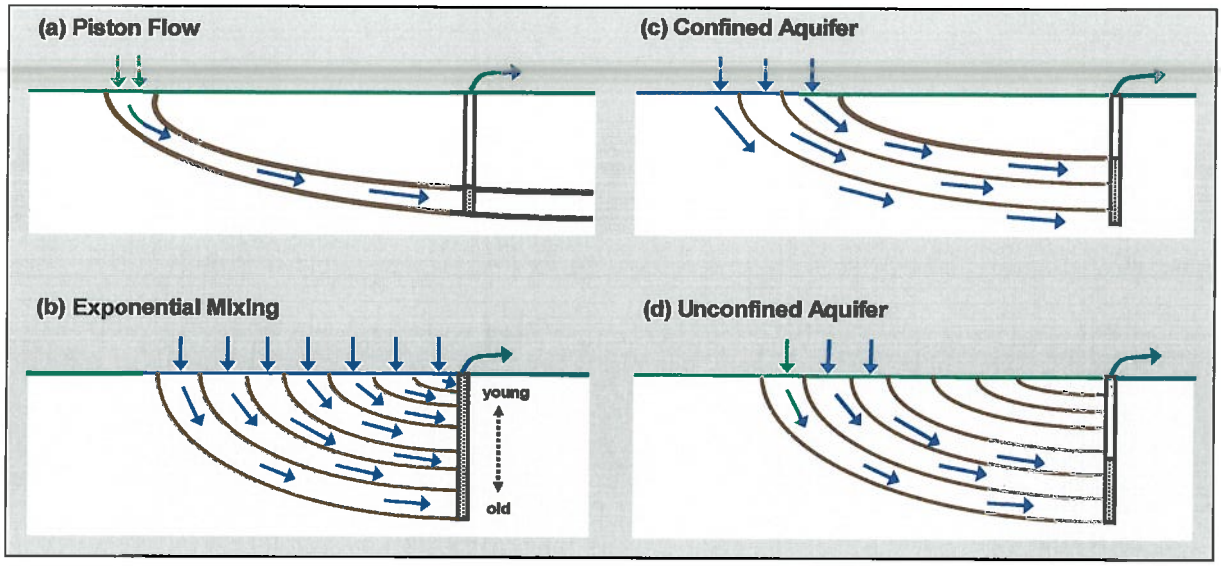

Figure A 1.2 Conceptual groundwater flow situations which can be described by lumped parameter mixing models.

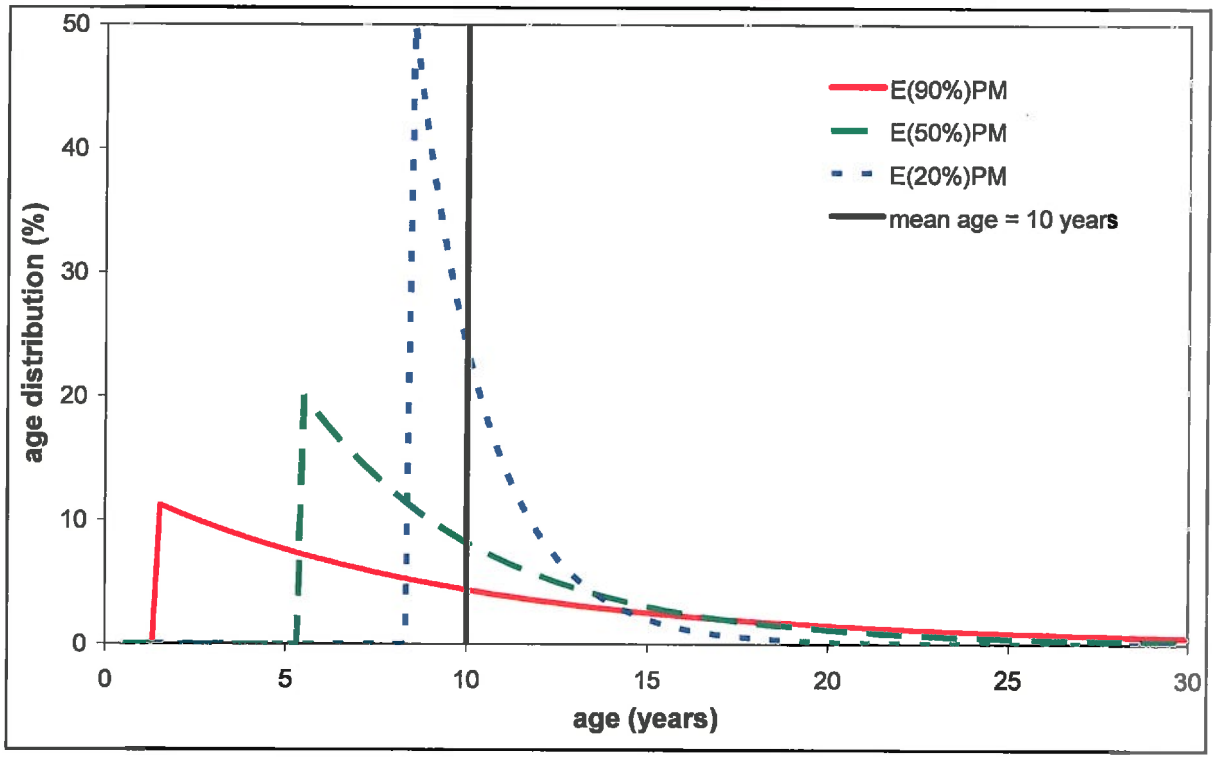

Figure A 1.3 Age frequency distributions for the exponential - piston flow model for mean age = 10 years, with typical parameter values (20%, 50% and 90% of the flow is exponential-mixed flow).

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