The Conundrum of Incongruent Multiple Age Tracer Results in Mine Water

Devmi Kurukulasuriya[1], William Howcroft[1], Karina Meredith[2], Wendy Timms[1]

[1]*Deakin University, Waurn Ponds, VIC, 3216, Australia*

[2]*Australian Nuclear Science and Technology Organisation, Institute for Environmental Research, NSW 2232, and Australia.*

Abstract

The interpretation of multiple tracer data for a single sample of mine water can be challenging if it contains water molecules having a distribution of ages. Interpretation of tracer results may be complicated due to inter-aquifer connection, geochemical interactions, dispersive flow, and dual-domain effects from preferential flow paths created by mining operations. Lumped parameter models (LPMs) are commonly used to interpret age tracer results by estimating a mean residence time (MRT) for a given water sample. Furthermore, it is generally recommended to have a suite of age tracers to better constrain the range of the age distribution in a water sample. However, having a suite of age tracer results for a single sample often results in incongruent results.

We collected groundwater and surface water samples around a longwall coal mine in NSW, Australia for general hydro-chemical parameters and multiple age tracers including stable (δ^2H and $\delta^{18}O$) and radioactive isotopes (^{14}C, ^3H, SF_6, CFCs) aiming to identify surface water-groundwater interactions. Sampling was undertaken during two events at each location. Age tracers were analyzed in a limited number of selected samples.

In the preliminary interpretation of the results, single dispersion models were used for each tracer and where there is considerable variation between young and old tracer MRTs, binary mixing models with two dispersion model segments were used for multiple age tracers. For the samples that have multiple age tracers, LPM results for each tracer indicated contradictory MRT estimates. The presence of both young (^3H) and old tracer (^{14}C) indicate a considerable proportion of each type of water in the sample. This paper focuses on interpreting apparently contradictory age tracer results for samples collected from the mine goaf and deep and shallow groundwater bores.

Keywords: Surface water-groundwater interactions, Mean residence time, Isotopes, tracers, Lumped parameter models

Background

Idealized groundwater age or residence time is defined as the time passed since water entered the saturated zone until reaching the sampling point (International Atomic Energy Agency 2013). Naturally, due to changes in fluid potential and entropy of the groundwater system, individual water molecules may follow different paths to reach the sampling point since recharge. Therefore, a groundwater sample is characterized by a frequency distribution of groundwater ages, not a single value of 'age'. In a mining context, due to mining operations, more hydrogeological factors such as dispersive flow and dual domain effects resulting in preferential flow paths add complexity, widening the range of groundwater ages in a sample. This has resulted in an increased emphasis on the use of multiple age tracers for groundwater dating in hydrogeological studies. Additionally, considering factors such as screen lengths of the monitoring bores s relative to aquifer thickness, and sampling techniques, the use of multiple age tracers minimizes uncertainty and improves sensitivity analysis. The application of multiple age tracers further provides clarification of processes that may misguide the interpretations based on a single tracer.

LPMs are commonly used to interpret age tracer results of groundwater samples with mixed components of young and old water. Mean residence time (MRT) and the young water fraction present in a groundwater sample can be estimated using a mixing LPM. Understanding the degree of interactions based on the fraction of young water that reaches the tracer-free deep aquifers may help manage risks of depletion or other adverse effects on connected aquifers and surface water. It is important to note the geochemical interaction that may take place in the deep groundwater systems, that may change the tracer concentration in groundwater. In some situations, groundwater can appear to be much older. Inverse modelling approaches using tools such as PHREEQC (Parkhurst and Appelo, 1999) and Netpath (Plummer *et al*., 1991) can be used to make corrections for this apparent old groundwater age.

Lumped Parameter Models

Maloszewski and Zuber (1996) derived weighted functions for age distributions in different aquifers and recharge settings, and a MRT can be estimated for water samples. However, this is not always equal to the mean age of the flow lines contributing to the sample as the tracer concentrations are not a linear function of age (Cook & Böhlke 2000). These LPMs have been introduced since the 1950s. Turnadge and Smerdon (2014) characterises LPMs as an approach most appropriate for data-poor groundwater systems and is aimed to provide a preliminary understanding of the groundwater system under study.

The piston-flow model (PFM), exponential mixing model (EMM), exponential piston-flow model (EPM), partial exponential model (PEM) and dispersion model (DM) are the five key LPMs. Piston flow models assume the flow lines of water have the same transit time, while diffusion and dispersion are considered negligible. Exponential models mathematically correspond to a response function of a well-mixed reservoir. Binary mixing models (BMM) are applied when there are two mixed groundwater components that follow any one of the five LPMs. Application of these models are comprehensively discussed in Zuber and Maloszewski (2008). Tracer LPM by (Jurgens, Böhlke & Eberts 2012) was used for lumped parameter modelling of the age tracers.

Estimating young groundwater fractions

Groundwater flow patterns and mixing patterns identified by the aquifer properties, and well construction details, must be considered when choosing the appropriate lumped parameter model for tracer data. Shevenell and Goff (1995) and Apollaro *et al.* (2015); (2016) used two models: a piston flow model with no mixing and an exponential model with complete mixing to obtain lower and upper limits for the MRT of a given sample. This approach resulted in a wide distribution of mean ages. The application of more than one age tracer has been found to better constrain the distribution of the MRT of a groundwater sample by Gardner *et al.* (2011) and Kashiwaya *et al.* (2014). Another approach is the use of time series tracer data where the LPMs have reproduced the predicted variation of tracer concentrations over time (McGuire & McDonnell 2006). Bexfield *et al.* (2012) identified mixed groundwater based on tracer concentrations and calculated the mixing fractions of young water in mixed groundwater samples using BMM (DM+DM).

Methodology

In this study, we undertook a multi-tracer approach to understand surface water-groundwater interaction around an underground longwall coal mine in Australia. Twenty one groundwater samples were collected from shallow (50m), deep (400m) groundwater bores, and dewatering bores The samples were collected for cations, anions, stable isotopes of oxygen, hydrogen, and carbon, trace elements, radiocarbon (^{14}C), tritium (^{3}H), Chlorofluorocarbons (CFCs), and Sulphur Hexafluoride (SF_6).

Monthly rainfall data for tritium was used and is from a ANSTO sampling site located at Sydney airport monitoring station (2006-2014). Data before 2006 were obtained by using monthly averages from Melbourne and Brisbane, which were the closest and most comprehensive data collection sites. Missing data within a given year were replaced by the monthly average concentrations of available data in each year. In cases where data were missing for the entire year, the concentration was set to the average value of the years before and after. Annual CFC and SF6 concentrations are available for the years 1935 to 2015 from Bullister (2015).

The choice of lumped parameter model suitable for the given bore is determined based on the confined/unconfined nature of the aquifer and the construction of the bore (Jurgens, Böhlke & Eberts 2012). None of the bores monitored can be categorized as having short screens (less than 10m). Additionally, the 3H results were used to identify the water samples with possible mixing of old and young water. The unsaturated travel time is assumed to be zero for the analysis purposes.

Tracer Results and Discussion

Table 1 presents the tracer concentrations and activities for shallow and deep groundwater samples collected from the longwall mine site. Quantification limits and errors of results are presented in Timms *et al.* (2022). The CFC-11 and CFC-12 data were found to be contaminated in many samples indicating higher equilibrium concentrations than the atmospheric concentrations after corrections. Therefore, CFC-113 only was used for the LPMs as it is considered to have the least contamination issues.

Three coal seam samples, one Jurassic and Triassic samples have detected ^{3}H concentrations below the detection limit (0.04TU). Concentrations of 3H in precipitation measured at the Brisbane station peaked during 1962 and reached a plateau with less variation after 1990 with a mean concentration of about 1.9 TU. The lowest concentration recorded during this period is 1.3 TU, in 2005. Similarly, the comparable variations in atmospheric radiocarbon recorded due to the nuclear testing have been addressed by calibration with modern

***Table 1** Multi-tracer data for shallow and deep groundwater samples at and near a coal mine. CFC and SF6 results have been corrected for elevation, temperature, and salinity. 14C data has been normalized for δ13C but not corrected for geochemical interactions (sources and sinks). Quantification limits and errors of tracer results are provided in Timms* et al. *(2022).*

ID	Bore type	Screened Strata	CFC-113 (pptv)	^{3}H (TU)	SF$_6$ (pptv)	^{14}C (pMC)
1	Shallow	Triassic Sandstone	21.95	0.02*	8.35	80.93
2	Shallow	Jurassic Sandstone	0.00		3.01	
3	Shallow	Triassic Sandstone	61.77	0.4	10.40	
4	Deep	Coal seam	0.44	0.06	2.06	5.36
5	Deep	Coal seam	47.98			1.77
6	Shallow	Triassic Sandstone	0.00	0.1	3.35	56.26
7	Deep	Coal seam		0.07		8.51
8	Shallow	Triassic Sandstone		0.47	10.30	82.74
9	Deep	Coal seam		0.42		3.18
10	Deep	Coal seam	0.44	0.04*	0.71	5.45
11	Deep	Coal seam				
12	Deep	Coal seam		0.11		5.09
13	Deep	Coal seam		0.04*		5.06
14	Shallow	Jurassic Sandstone	15.80	0.04*	2.61	33.39
15	Deep	Coal seam				
16	Shallow	Triassic Sandstone	21.95	0.04*		71.6
17	Deep	Coal seam		0.04*		5.73
18	Shallow	Triassic Sandstone				15.86
19	Shallow	Jurassic Sandstone	44.17	0.12	0.30	3.39
20	Shallow	Jurassic Sandstone		0.04*		70.26
21	Shallow	Triassic Sandstone	42.53	0.05*		45.83

pMC – Percent Modern Carbon. pptv - parts per trillion (1012) by volume. TU – Tritium units

* – Results below lower limit of detection and therefore has higher percentage of uncertainty.

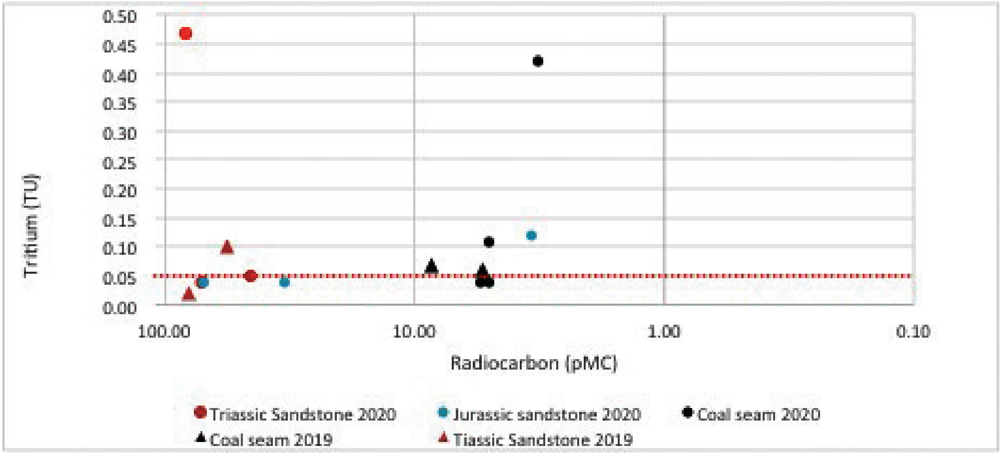

***Figure 2** Tritium versus Radiocarbon plot for identifying mixed samples*

data and international calibration curves in TracerLPM (Jurgens *et al.*, 2012). The radiocarbon results have not been corrected for the possible geochemical interactions that may alter the isotopic composition in water. For this study, the conservative ^{3}H age tracer was used to understand younger groundwaters because CFC and SF$_6$ were prone to contamination.

Groundwaters plotting below 0.15 TUs are considered to be relatively old. Samples with > 0.4 TU are considered to be relatively young water. Coupling two age tracers such as3H with ^{14}C together helps identify recharge timings further. A sample collected from the coal seam had a higher ^{3}H value (0.42 TU) and lower ^{14}C value (3.18 pMC) relative to other coal seam samples indicating a possible mix of old and young water. Most of the other deep-groundwater samples had low ^{3}H contents (<0.15 TU).

Mean transit times calculated for the groundwater samples are provided in Table 2. The Shallow Triassic sample 8 has a younger portion of groundwater with a mean age of 27 years and an older portion with a mean age of 1,500 years. However, as the multiple tracers are combined, for optimization incrementally, an increase in relative squared error is apparent requiring further research to determine the implications on result interpretations.

Lumped Parameter Modelling

Results of individual DM models for the deep coal seam sample show a MRT of 28 years with ^{3}H and 29,401 years with ^{14}C (Table 2). For the combined tracer BMM, a mean age of 28 years was used for the modern component and a mean age of approximately 50,000 years were used for the older component as the 30,000 years result was restricting the BMM model outputs. These results show that 1.7% of the water sample represents young water with a mean age of 28 years. However, the relative squared error is 96%. The three model outputs of the sandstone sample with ^{3}H and ^{14}C combined BMM show relatively lower error ranging between 0.01% and 17.1% with age ranging between 664 and 1519 years. The two tracers are in agreement with 0.25% relative squared error that 30% of 5 year old water is present in the shallow aquifer. The disagreement between the ^{3}H and ^{14}C in the coal seam sample confirms the possibility that groundwater within the coal seam is more susceptible to changes in dissolved carbon concentrations relative to sandstone aquifers. This is due to interactions with coal and other minerals that are old radiocarbon sources. Therefore, further corrections of the radiocarbon results for geochemical interactions are required to confirm the MRT for the coal seam sample.

Sample	LPM name	MRT	Model parameter	Mean age of 1st model component	Model parameter of 1st model component	Mix fraction of 1st model component- %	Mean age of 2nd model component	Model parameter of 2nd model component	Tracers used in optimization	Relative Squared Error (%)
Shallow Triassic sandstone	DM	54	0.03	n/a	n/a	n/a	n/a	n/a	^{3}H	0.00
	DM	6	0.01	n/a	n/a	n/a	n/a	n/a	SF_6	5.2
	DM	1,519	0.01	n/a	n/a	n/a	n/a	n/a	^{14}C	0.00
	BMM-DM-DM	1,397	0	5	0.10	30.20	2,000	0.01	^{3}H ,^{14}C	0.01
	BMM-DM-DM	1,207	0	10	0.10	39.84	2,000	0.01	^{3}H ,^{14}C	0.25
	BMM-DM-DM	664	0	55	0.01	68.72	2,000	0.01	^{3}H ,^{14}C	17.1
	BMM-DM-DM	671	n/a	16	0.01	66.99	2,000	0.01	^{3}H, SF6, ^{14}C	484
Deep coal seam	DM	28	0.03	n/a	n/a	n/a	n/a	n/a	^{3}H	0.00
	DM	29,401	0.01	n/a	n/a	n/a	n/a	n/a	^{14}C	0.00
	BMM-DM-DM	49,175	n/a	28	0.10	1.65	50,000	0.1	^{3}H, ^{14}C	96.5

***Table 2** LPM model outputs for samples with young and old water mixing. (n/a - Not applicable)*

Conclusion

The combined tracer BMM outputs provide intermediary mean ages, however with higher relative errors. These incongruent results between young and old tracers may be due to the fact that radiocarbon results used were not corrected for geochemical processes. This would be problematic considering samples were taken from deep coal seams containing old radiocarbon sources such as from carbonate minerals that has the potential to dilute the ^{14}C results observed in the groundwater sample. To account for these geochemical processes ^{14}C results will be corrected via geochemical inverse modelling approaches. The corrected radiocarbon data are expected to provide BMM mean age outputs with lower relative error.

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References

Apollaro, C, Vespasiano, G, De Rosa, R & Marini, L 2015, 'Use of mean residence time and flowrate of thermal waters to evaluate the volume of reservoir water contributing to the natural discharge and the related geothermal reservoir volume. Application to Northern Thailand hot springs', Geothermics, vol. 58, pp. 62-74.

Bexfield, LM, Jurgens, BC, Crilley, DM & Christenson, SC 2012, Hydrogeology, water chemistry, and transport processes in the zone of contribution of a public-supply well in Albuquerque, New Mexico, 2007-9, US Geological Survey Reston, VA.

Bullister, JL 2015, 'Atmospheric Histories (1765-2015) for CFC-11, CFC-12, CFC-113, CCl4, SF6 and N2O', Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee.

Cook, PG & Böhlke, J-K 2000, 'Determining Timescales for Groundwater Flow and Solute Transport', in Environmental Tracers in Subsurface Hydrology, pp. 1-30.

Gardner, WP, Susong, DD, Solomon, DK & Heasler, HP 2011, 'A multitracer approach for characterizing interactions between shallow groundwater and the hydrothermal system in the Norris Geyser Basin area, Yellowstone National Park', Geochemistry, Geophysics, Geosystems, vol. 12, no. 8.

International Atomic Energy Agency 2013, Isotope methods for dating old groundwater, International Atomic Energy Agency.

Jurgens, BC, Böhlke, JK & Eberts, SM 2012, 'TracerLPM (Version 1): An Excel® workbook for interpreting groundwater age distributions from environmental tracer data'.

Kashiwaya, K, Hasegawa, T, Nakata, K, Tomioka, Y & Mizuno, T 2014, 'Multiple tracer study in Horonobe, northern Hokkaido, Japan: 1. Residence time estimation based on multiple environmental tracers and lumped parameter models', Journal of Hydrology, vol. 519, pp. 532-48.

Maloszewski, P & Zuber, A 1996, 'Lumped parameter models for the interpretation of environmental tracer data'(No. 1011–4289). International Atomic Energy Agency (IAEA).

McGuire, K & McDonnell, J 2006, 'A Review and Evaluation of Catchment Transit Time Modeling', Journal of Hydrology, vol. 330.

Jurgens, B., Bohlke, J., Eberts, S., 2012. TracerLPM (Version 1): An Excel® workbook for interpreting groundwater age distributions from environmental tracer data, U.S. Geol. Surv. Tech. Methods Rep. https://doi.org/10.3133/tm4F3

Parkhurst, D.L., Appelo, C., 1999. User's guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water-resources investigations report 99, 312.

Plummer, L.N., Prestemon, E.C., Parkhurst, D.L., 1991. An interactive code (NETPATH) for modeling net geochemical reactions along a flow path. Department of the Interior, US Geological Survey.

Timms, W., Kurukulasuriya, D., Howcroft, W., Meredith, K., 2022. Water tracer tools for optimisation of water management for coal mines - ACARP Project C28024.

Shevenell, L & Goff, F 1995, 'The use of tritium in groundwater to determine fluid mean residence times of Valles caldera hydrothermal fluids, New Mexico, USA', Journal of volcanology and geothermal research, vol. 67, no. 1-3, pp. 187-205.

Turnadge, C & Smerdon, BD 2014, 'A review of methods for modelling environmental tracers in groundwater: Advantages of tracer concentration simulation', Journal of Hydrology, vol. 519, pp. 3674-89.

Zuber, A & Maloszewski, P 2008, Lumped parameter models. No. IAEA-TCS--32/F. 2008.