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Discussions

Simulated tritium concentrations in river waters of the western Lake Taupo catchment, New Zealand with MODPATH particle tracking

M. A. Gusyev[1], D. Abrams[2], M. W. Toews[1], U. Morgenstern[1], and M. K. Stewart[1,3]

[1]GNS Science, Avalon, Lower Hutt, 5011, New Zealand
[2]Illinois State Water Survey, Champaign, IL, 61820, USA
[3]Aquifer Dynamics & GNS Science, P.O. Box 30368, Lower Hutt, New Zealand

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Correspondence to: M. A. Gusyev (maksymgusyev@gmail.com)

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Abstract

We simulated in a previous study tritium concentrations in the river waters of the western Lake Taupo catchment (WLTC) using MODFLOW/MT3DMS model (Gusyev et al., 2013). The model was calibrated to match simulated tritium to measured tritium in river waters at baseflows of the Waihaha, Whanganui, Whareroa, Kuratau and Omori river catchments of the WLTC. Following from this work we now utilized the same MODFLOW model for the WLTC to calculate the pathways of groundwater particles (and their corresponding tritium concentrations) using steady-state particle tracking with MODPATH. In order to simulate baseflow tritium concentrations with MODPATH, transit time distributions (TTDs) such as cumulative frequency distribution (CFD) and probability density function (PDF) are generated with particle tracking for the river networks of the five WLTC catchment outflows. Then, PDFs are used in the convolution integral with tritium concentration time series obtained in the precipitation. The resulting MODPATH tritium concentrations yield a very good match to measured tritium concentrations and are similar to the MT3DMS simulated tritium concentrations, with the greatest variation occurring around the bomb peak. MODPATH and MT3DMS also yield similar Mean Transit Times (MTT) of groundwater contribution to river baseflows, but the actual shape of the TTDs is strikingly different. While both distributions provide valuable information, the methodologies used to derive the TTDs are fundamentally different and hence must be interpreted differently. With the current models setting, only the methodology used with MODPATH provides the true TTD for use with the convolution integral.

1 Introduction

Particle tracking is a widely applied tool to calibrate aquifer porosity values in groundwater flow models and to characterize water availability and quality at groundwater discharge points such as wells, springs, lakes and streams (Haitjema, 1995; Kaufman et al., 2001; McGuire and McDonnell, 2006; Stichler et al., 2008). For example, particle tracking results are commonly used for mapping recharge contributing area to the pumping wells (US EPA, 1994) and obtaining transit times of groundwater at the discharge point (Haitjema, 1995; McGuire and McDonnell, 2006). The MODPATH generated transit time represents the time taken by a groundwater molecule to travel in a groundwater volume from the starting cell, i.e., groundwater recharge at the aquifer top, to an outlet cell, such as a pumping well or a spring (Pollock, 1994; Boronina et al., 2005; McGuire and McDonnell, 2006; Sanford, 2010). Integrating over all flow paths in an area, a transit time distribution (TTD) can be constructed from MODPATH transit times at a discharge point. The TTD provides the fraction of water that had a certain transit time through the aquifer and can vary both in shape and in scale, usually defined as a central tendency such as mean transit time (MTT) or mean residence times (MRT) (McDonnell et al., 2010; Stewart et al., 2012). The TTDs can then be an input to the convolution integral to obtain tracer concentrations at discharge points. While many lumped parameter models (LPMs) exist to derive these TTDs, using MODPATH/MODFLOW allows one to simulate age groundwater tracer directly relying on the actual groundwater flow dynamics and hence eliminates the need to compare between different alternative LPMs, i.e., exponential, piston-exponential, gamma, dispersion, etc. (McGuire and McDonnell, 2006; Sanford, 2010). For example, Eberts et al. (2012) evaluated tracer concentrations obtained with particle tracking model and several LPMs in wells of four aquifers using an Excel workbook, which uses TTDs both from LPMs and MODPATH as an input to the convolution integral to obtain tracer concentrations at wells (Jurgens et al., 2012).

Groundwater flow and particle tracking models have also been used to simulated isotope tracers at wells, springs and lakes as groundwater discharge points. McMahon et al. (2010) calibrated transient finite-difference MODFLOW and MODPATH models to apparent groundwater ages from isotopes at seven multi-screen monitoring wells. Weissman et al. (2003) modelled chlorofluorocarbons (CFCs) groundwater ages at monitoring wells using cumulative frequency curves obtained with particle tracking

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simulations. Troldbord et al. (2007) constructed probability density curves using particle tracking and obtained isotope concentrations using the convolution integral. Starn et al. (2010) distributed particles with assigned isotope concentrations and estimated groundwater recharge by backwards particle tracking from the well to the model surface. Szabo et al. (1996) presented tritium measurements and other tracers in wells and conducted one dimensional cross-sectional modelling of travel times. Boronina et al. (2005) discussed modelling tritium in an aquifer and a groundwater driven spring with groundwater flow MODFLOW and particle tracking PMPATH model, which is an alternative to USGS particle tracking model MODPATH. Several studies compared MTTs from tritium and CFCs to MTTs obtained with MODPATH particle tracking in the Trout Lake, Wisconsin (Pint et al., 2003; Hunt et al., 2006; Walker et al., 2007). In the Trout Lake watershed, Fienen et al. (2009) used measured stable oxygen isotopes and tritium concentrations in wells to refine groundwater pathways between the Big Muskellunge and Crystal Lakes in a cross-sectional model.

In the particle tracking technique, groundwater velocities obtained with a groundwater flow models are used to produce particle pathlines with associated particle travel times. These pathlines and travel times account only for advective transport and do not include chemical parameters that are available in transport models such as MT3DMS (i.e. dispersion, diffusion, decay, sorption, dual porosity). Therefore, a direct comparison of measured and simulated environmental tritium tracer concentrations with particle tracking (MODPATH/MODFLOW) and transport (MT3DMS/MODFLOW) models is needed to provide important insights about the applicability of the particle tracking to simulation of groundwater contaminant movement in the aquifer systems and river waters at baseflows.

This study is a continuation of the western Lake Taupo catchment (WLTC) work, which has two objectives: (1) to simulate tritium concentrations in river waters of the WLTC, and (2) to gain understanding of MODPATH and MT3DMS applicability by comparing river TTDs of both models. In the first phase of this work, detailed in Gusyev et al. (2013), a steady-state MODFLOW model of the region was calibrated to

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observed groundwater elevations and baseflows. This model was the basis for a transient MT3DMS model that had annual inputs of tritium in precipitation and was calibrated to observed tritium values in base flow. To expand on this work, a steady-state particle tracking MODFLOW/MODPATH model has been developed, utilizing the calibrated values from the MODFLOW/MT3DMS model. Next, TTDs are generated for the river waters of the Waihaha, Whanganui, Whareroa, Kuratau and Omori catchments of the WLTC. Then the tritium concentrations in the outlets of the five river catchments are simulated by convoluting the tritium input time series with the MODPATH generated TTD obtained for the river network. These results are compared with measured and MT3DMS simulated tritium concentrations for the Waihaha, Whanganui, Whareroa, Kuratau and Omori river catchments (Gusyev et al., 2013). In addition, we compare the MODPATH and MT3DMS TTDs and discuss the discrepancies between the methodologies and proper interpretation of each distribution. Finally, the current limitations of the MODPATH approach in view of spatially varying groundwater contaminant simulations, such as nitrate, are discussed.

2 Approach

2.1 MODFLOW model

The groundwater flow model MODFLOW of the WLTC was developed by Gusyev et al. (2013) using the Visual MODFLOW (VMOD) graphical user interface (Harbaugh et al., 2000; SWS, 2012). A brief summary of the WLTC model settings and calibration to groundwater levels and river baseflows is presented in this paper. For the detailed description refer to Gusyev et al. (2013). In the MODFLOW model, the WLTC area of 1072 km^2 was represented by the finite-difference grid with a uniform grid cell size of 80 m resulting in 500 rows and 335 columns. The WLTC aquifer system was assumed to be 320 m thick based on the WLTC hydrogeology and was represented with a uniform layer thickness of 20 m for each of 16 layers. The rivers and streams of the WLTC

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were assigned to layer 1 as drain cells with drain bottom elevation 1 m below the top elevation of layer 1. The water level in Lake Taupo was simulated using a constant head boundary of 357 m, which was assigned to relevant model layers using bathymetry data (Gusyev et al., 2013). In the calibrated model, Gusyev et al. (2013) used groundwater recharge values in 10 recharge zones, see Fig. 1a. From the MT3DMS model, the calibrated effective porosity values of the transient MT3DMS model were used as the starting point for the MODPATH particle tracking with the calibrated heads and flows of the steady-state MODFLOW model (Gusyev et al., 2013).

2.2 MODPATH model

MODPATH version 4 (Pollock, 1994) was used to conduct forward particle tracking in the WLTC (Gusyev et al., 2013). In forward particle tracking option, the particles are released at the water source (e.g., point of groundwater recharge) and collected at sink cells such as drains. These sink cells could be either weak, meaning they can only discharge a portion of water entering the cell, or strong, meaning they discharge all groundwater reaching them (Pollock, 1994; Abrams et al., 2013). For the weak sink option, the VMOD value was used to stop particles where discharge to sink cells is greater than a specified total inflow to the cell; we elected to use the 5 % default setting (SWS, 2013). However, this setting is not expected to be important in our case due to relatively thin layers of 20 m and location of all sink cells in layer 1. In cases where the sink cells comprise a larger percentage of the aquifer thickness, other MODPATH settings should be considered (Abrams et al., 2013).

In each grid, one MODPATH particle was assigned at the water table and cell centre using a custom Python script, resulting in 120 585 particles. The location of these grid cells and the vertical position of a particle were identified by interrogating MODFLOW groundwater heads (*.hds) and VMOD grid file (*.vmg). All assigned particles were tracked forward in time with a 30 day time step from starting cell location to the ending cell location, and discharged in the sink cells such as drains. The transit time of each particle was recorded in the MODPATH endpoint file. An R script was used to separate out the transit times from the endpoint file for each of the five river catchments and sorted by their transit times. These selected particles were scaled by their associated groundwater recharge value obtained from a starting cell location to construct cumulative frequency distributions (CFDs) of transit times for river waters at baseflow of the five WLTC river catchments.

It is noted that the sink cells exaggerate the width of the actual streams. This leads to an error in the MODPATH transit time distribution if the width of the stream cell in MODFLOW is large compared to watershed width (Abrams, 2013). This can be (approximately) corrected by first removing particles with zero transit times from the data set as these particles represent particles assigned on sink cells. Then the remaining transit times are multiplied by the ratio of the particles with non-zero transit times to the total number of particles released. For the five watersheds considered in this study, the ratios of drain cells to total number of cells in the watershed were 0.87 (Waihaha), 0.88 (Whanganui), 0.92 (Whareroa), 0.87 (Kuratau), and 0.88 (Omori).

2.3 Tritium measurements in rain and river waters

Following Gusyev et al. (2013), the same tritium rain and river water measurements were used in this study for the tritium input and calibration targets, respectively. The tritium input to an aquifer was a time series from 1952 to 2011 of annual measured tritium in precipitation. The tritium concentrations measured in river waters at baseflows of the Waihaha, Whanganui, Whareroa, Kuratau and Omori River sub-catchments were used as calibration targets. The tritium data 2001–2002 are from Vant and Smith (2004), 2004–2007 are from Morgenstern (2007), and 1964–1970 are from Morgenstern and Taylor (2009).

2.4 Convolution integral for tritium response

The time-dependent tritium concentration at discharge points, $C(T)$ [TU], can be obtained using the convolution integral (Małoszewski and Zuber, 1982):

$$C(t) = \int_0^\infty C_{\text{in}}(t-T) f(T) e^{-\lambda T} \mathrm{d}T \tag{1}$$

where $C_{\text{in}}(t-T)$ [TU] is the input tritium concentration at time t, $f(T)$ is the probability density function (PDF) of transit times, and $e^{-\lambda T}$ [–] is the subsurface first-order decay; for tritium $\lambda = 0.0562621\,\text{year}^{-1}$. The input tritium concentration, $C_{\text{in}}(t-T)$, varies in time and is a function of the lag time, $(t-T)$, between the current time t and a specific transit time T. In this study, PDFs are obtained for all watersheds using the central finite-difference method on their respective CFDs obtained with MODPATH. Forward and reverse finite-difference methods did not yield appreciably different PDFs; hence numerical error is expected to be small. The convolution integral was evaluated with MATLAB's convolution integral function and an Excel work book using non-parametric version of the convolution integral (Eberts et al., 2012) leading to identical results.

3 Results

3.1 MODPATH transit times

In this study, the tritium calibration with MODPATH for river waters started with porosity values calibrated with MT3DMS. The resulting transit time map obtained with MODPATH particles is shown in Fig. 1b. In Fig. 1b, the colour code represents the starting location and transit time of each particle to the river network. The transit times of MODPATH particles vary from very short (blue) located near surface water features, to relatively long (red) located near groundwater divides. The very short travel times follow the placement of the surface water features in the model and indicate the importance of implementing a detailed river network. In the absence of these detailed surface water features, surface waters would be smeared and discharge zones would be exaggerated, resulting in many particles discharging too soon to the stream (perhaps even with a transit time of zero if they fell directly on the smeared stream network).

As shown in Fig. 1b, the groundwater divides rarely coincide with the surface water divides of the river catchments in the WLTC. Contaminants recharged in one river surface water catchment may be discharged in another river surface water catchment, an important point in view of groundwater quality and pollution management. In other words, ground watersheds do not always coincide with surface watersheds. Therefore, the TTDs in this study are developed from grouped particles based on their respective ground watershed shown in Fig. 1b.

The particle transit times are used to develop CFD curves for the river network in each of five selected catchments, using the adjustment outlined in Abrams (2013) (see Fig. 2a). The CFDs for each catchment differ in both shape and scale, the latter of which is MTT (summarized in Table 1). In order to make a meaningful comparison of shape irrespective of scale, the transit times for the CFD of a catchment were divided by their respective MTT, hence resulting in normalized CFD distribution for each catchment (see Fig. 2b).

In Fig. 2, the normalized CFD curves for all five catchments are roughly similar in shape to the exponential shape CFD. This is consistent with observations made by Haitjema (1995) and Abrams and Haitjema (2013), which state CFDs are generally exponential in shape for larger watersheds. In the WLTC, the entire modelled area receives groundwater recharge and hence is conceptually similar to the exponential flow system described by Małoszewski and Zuber (1982). However, it is also noted that the Omori and Whareroa CFDs are virtually identical in shape, while the Kuratau, Waihaha, and Whanganui CFDs tend to have more short and long transit times. This is consistent with observations made by Abrams and Haitjema (2013) that watersheds with more partially penetrating streams tend to skew toward shorter and longer transit

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times with a smaller frequency of intermediate transit times. This implies that the Kuratau, Waihaha, and Whanganui watersheds have a greater incidence of weak sinks as was also observed by Gusyev et al. (2013).

The original and adjusted (per Abrams, 2013) MTTs for the Waihaha, Whanganui, Whareroa, Kuratau and Omori catchments are presented in Table 1 along with the MTTs obtained with MT3DMS by Gusyev et al. (2013). The adjusted MTT is closest to the MTT obtained with MT3DMS for four of the five river catchments. However, there are confounding factors (i.e. dispersion, dual porosity) that make it difficult to determine whether the adjustment applied to the purely advective MTTs from MODPATH truly bring the MT3DMS and MODPATH MTTs together.

3.2 MODPATH tritium concentrations in river waters

The MODPATH tritium concentrations in river waters of five WLTC catchment outflows are shown in Fig. 3 in tritium units (TU) and are obtained by convoluting PDFs derived from the numerical derivative of the MODPATH CFDs (Fig. 2a) with the tritium input time series (Fig. 4a). The simulated MODPATH tritium concentrations are demonstrated for the sharp tritium rise from 1955 to 1970 due to the bomb-peak in Fig. 3a, for the sharp decline from 1970 to 1990 in Fig. 3b, and for the natural background tritium concentrations from 1990 to 2010 in Fig. 3c. Note that in Fig. 3, the watersheds in the legend are not only listed in order of increasing MTT but also in order of highest tritium peak; hence it appears that the smaller the MTT, the higher the tritium peak will be. For example, the Omori has the smallest MTT (3 year), and as a result tritium will on average remain in the aquifer less time than in the other four watersheds. This reduced transit time of groundwater results in less decay of tritium in the subsurface, see Eq. (1). The resulting tritium maximum output is greater than at the other watersheds (compare the pink curve in Fig. 3a to the other curves).

In the late 1970s/early 1980s, tritium in rain decreased quickly (Fig. 3b). This rapid decrease in tritium can be observed in the Omori output because of its short MTT of 3.15 year and low removal of tritium due to tritium decay of 12.32 year. Conversely,

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the Whareroa, which has a MTT of 16.03 year, removes much more tritium in the subsurface but concurrently is slower to flush out the high concentrations of tritium. As a result, in the early 1980s, the tritium response for the Omori actually dipped below that of the Whareroa during the model simulation (Fig. 3b). As the bomb tritium is decayed and flushed out of the aquifer in the Whareroa, the Omori again returns to the highest tritium concentration due to the shortest transit time (Fig. 3c).

The significance of the above discussion is that sharp changes in an input, be it tritium, nitrate, or some other dissolved constituent in groundwater, can lead to some unexpected responses. In particular, the assumption that the relative magnitude of tritium between two watersheds is a function of the MTT and a constant tritium decay, while true for the peak and present days (at least in this study), was not true in the 1980s. In addition, MTT was an important factor in determining the amplitude of the tritium response curves during the bomb peak in the five river catchments.

3.3 MODPATH and MT3DMS results comparison

MODPATH and MT3DMS simulated tritium concentrations in TU resulting from the tritium input time series (Fig. 4a) are compared in Fig. 4b–f and CFDs in Fig. 4b–f insets for each of the five catchments. The measured tritium concentrations in river waters of each catchment are shown by solid circles. For the tritium calibrated porosity values, the tritium concentrations and CFDs calculated with MT3DMS by Gusyev et al. (2013) are shown by solid lines and calculated with MODPATH are shown by dashed lines. In addition, the MODPATH tritium concentrations were simulated with 25 % lower (MODPATH Low) and 25 % higher (MODPATH High) porosity values than the MT3DMS calibrated porosity (Fig. 4b–f). In these two porosity cases, the MODPATH CFDs have the same shape but are scaled by percentage values and are not shown in the insets of Fig. 4b–f. It is noted that the MODPATH and MT3DMS models yield virtually identical tritium results, with the exception of the peak where there were slight differences in amplitude in all five river catchments. This similarity can be attributed to the fact that WLTC aquifer system is dominated by advective transport and the tritium

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decay process (Gusyev et al., 2013), which reduce influence of the dual porosity mass transfer coefficient and dispersion-diffusion terms in the advection-dispersion equation solved by the MT3DMS (Zheng and Wang, 1999; Zheng, 2006).

While the MODPATH and MT3DMS CFDs are very similar in scale of MTTs, as indicated by Table 1, they are surprisingly different in shape (see Fig. 4b–f insets for a comparison of MODPATH and MT3DMS CFDs). In all five cases, the MT3DMS CFDs have less short transit times compared to MODPATH CFDs. Using the MT3DMS PDFs with the convolution integral in Eq. (1) also produces much smaller tritium concentrations for each of the five river catchments, especially around the peak (these results are not shown). While dispersion could potentially result in similar discrepancies, the tritium response curves were insensitive to dispersion values in the WLTC model. Note that MT3DMS CFDs are not required for generating tritium concentrations with MT3DMS. Gusyev et al. (2013) implemented a method to develop MT3DMS CFDs only after the tritium outputs were developed; hence a calibrated value for porosity could be utilized in developing the MT3DMS CFDs. They were developed to provide a very informative step of how transit times help to shape the tritium output. The shape differences of MT3DMS and MODPATH CFDs are attributed to the limitation of the MT3DMS CFD generation methodology (Zheng, 2009).

3.4 MODPATH and MT3DMS methodology comparison

To generate CFDs for the river networks, uniformly spaced particles were tracked from their release at the top of the aquifers until they reached discharge points such as constant head, river, drain and stream cells in the MODPATH methodology. All particles discharging to a river cell belonging to a particular watershed were sorted from smallest to largest transit time. Particles released directly on a river cell had a transit time of zero; hence never entered the aquifer and were removed before constructing the TTD. Finally, because sink cells comprised an artificially large ($> 8\,\%$) percentage of the watershed surface, the MODPATH transit time correction described in Abrams (2013) was utilized. To construct the CFD, each particle was weighted based on the recharge

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assigned to its cell of origin to the total recharge that was assigned to the watershed. Note that recharge was constant for the entire simulation, so the weight assigned to each particle was constant with time. As a result of the above procedure, the transit time for every particle was accounted for, hence this is a TTD that can be applied in Eq. (1).

For the MT3DMS methodology, the CFD for the river network is generated by simulating groundwater age concentrations. An initial concentration of zero age was assigned ubiquitously at the top of the aquifer and a zero-order decay rate of negative 1 was assigned to MT3DMS to represent ageing of one year per simulation step of one year. All dispersion, diffusion, and sorption parameters were left unchanged from the tritium simulations. The model was then run for 200 year to reach steady-state concentrations in river cells. The simulated concentration found in each river cell is representative of the groundwater age of all particles mixed together in that cell. This methodology was defined by Cornaton (2004) to simulate a spatial map of groundwater *age*, and indeed yields informative cross-sectional images (as shown in Gusyev et al., 2013). The finer the resolution of the model, the better represented is the distribution of groundwater ages throughout the aquifer. To develop the transit time distributions in Fig. 4 insets, the output concentration of each river cell was inferred to represent the mean groundwater transit time of all particles reaching that cell (a result of the assigned zero order degradation rate). The MTT (i.e. output concentration) for each cell was recorded, and these mean transit times were sorted from smallest to largest. A weight was assigned to each time based on the ratio of the influx of groundwater to that cell over the total influx of groundwater to the groundwater watershed.

3.5 Hypothetical examples of MODPATH and MT3DMS CFD methodology

To further illustrate the difference between the two methodologies, we introduce 1-D, 2-D and 3-D cases to construct CFDs for the hypothetical river network in idealized aquifers. For clarity, we will henceforth refer to the CFDs generated using the MODPATH methodology as transit time CFDs. It is noted that the MT3DMS methodology of

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generating CFDs can be replicated in MODPATH and that the MODPATH methodology of generating transit time CFDs can be replicated in MT3DMS. In all three cases, the MODFLOW model was created to have an MTT of 20.5 year by assigning a constant porosity of 0.3, recharge of 0.445 m year^{-1} implemented in layer 1, and saturated thickness of 30.48 m. The model was assigned horizontal hydraulic conductivity of 10 m day^{-1}. For the 1-D model (Fig. 5a), a single layer was utilized, hence the model was a Dupuit–Forchheimer flow model due to the absence of resistance to flow in the vertical direction. The model grid was 30 rows by 5 columns with 10 m cell size. The 1-D case conceptualizes a one dimensional flow aquifer bounded by a no-flow boundary on the left side (dark no-flow cells) representing groundwater divide, a constant head boundary of 30.48 m representing the river network on the right side (blue cells). The MODPATH particles were assigned at each cell centre on the top of the aquifer, see plan view in Fig. 5a, and produced pathlines to the discharge cells, see the cross-sectional view in Fig. 5a. In the 2-D and 3-D models, the model grid had 1000 rows and 1000 columns with cell size of 10 m and five layers of equal thickness and a hypothetical river network implemented in layer 1 (Fig. 5b). As in the 1-D case, the model was surrounded by no-flow cells and the hypothetical river network was represented by the constant head cells of 30.48 m without river bed conductance. Both 2-D and 3-D cases are different in vertical hydraulic conductivity setting in the MODFLOW model. For the 2-D model, a vertical hydraulic conductivity of 1000 m/day was assigned to approximate Dupuit–Forchheimer flow. The simulated groundwater contours range from 30.48 m at the head cells to 31.48 m with contour interval of 0.125 m. In the 3-D model, vertical hydraulic conductivity was set equal to the horizontal hydraulic conductivity and resulted in the same groundwater contour range.

The resulting CFDs of all three cases are demonstrated in Fig. 5c. For the 1-D case simulation, the entire range of transit times (from very short to very long) is represented and the CFD has an exponential shape as expected for the ideal aquifer settings with MTT of 20.5 year, see Haitjema (1995). For the MT3DMS CFD, however, each of the five discharge cells has the exact same groundwater age concentration, which is

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a proxy for MTT of all particles reaching a discharge cell. As a result, the MT3DMS CFD has a pulse shape shown by the orange curve in Fig. 5c with the jump from 0 to 1 occurs at a transit time of 20.5 year, which is indeed the MTT for this aquifer setting. This is indeed significant as it indicates how the MODPATH and MT3DMS methodologies employed for the WLTC model could generate very similar MTTs but very differently shaped CFDs.

In the 2-D case, the result yields exactly the same transit time CFD as the 1-D case, which is expected for this idealized (constant recharge, porosity, and saturated thickness) aquifer (Haitjema, 1995) and a very similar MT3DMS CFD (see Fig. 5c). The 2-D MT3DMS CFD is similar to the 1-D case, but it does not have a discrete jump. Rather, there are a few river cells that have a slightly smaller and slightly larger mean transit time (Fig. 5c). This is likely a result of numerical dispersion; a more refined grid would have yielded an even smaller range of mean transit times in each cell. Interestingly, the 3-D case with the isotropic aquifer yields a much different MT3DMS CFD with MTT of 21.86 year than the 1-D and 2-D cases with MTT of 20.5 year (Fig. 5c). This result is due to the resistance to vertical flow, which was absent in the 1-D and 2-D Dupuit–Forchheimer models. This apparent deviation from the other two MT3DMS CFDs does not manifest in the transit time CFD – it is identical on the scale of Fig. 5c.

To further stress aquifer complexities, we investigated two cases of aquifer heterogeneity and sloping river network with the 3-D model. For the aquifer heterogeneity case, we randomly added zones of horizontal hydraulic conductivity with values of 5–30 m day^{-1} throughout the model domain following analysis introduced by Haitjema (1995). Though we repeated this with multiple random hydraulic conductivity zonations, all yielded a similar response in the transit time CFDs of the heterogeneous aquifer, which was consistent with findings by Haitjema (1995). However, the heterogeneous transit time CFD deviated from the prior transit time CFDs, and the MT3DMS CFD deviated further from the homogeneous cases as well (Fig. 5c). The most important observation from this result is that the MT3DMS CFD is becoming less shaped like a pulse and is becoming more similar to the transit time CFD (though for this simple

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case there is still quite a difference between the transit time and MT3DMS CFDs). For the sloping river network case, some headwater stream cells will skim water from only the upper portion of the aquifer (physical weak sinks) and hence will have a concentration (i.e. MTT) in MT3DMS that is younger than the MTT for the entire aquifer (the results of 3-D simulation are not shown). Other stream cells will take up water that has bypassed those headwater streams and hence will have a concentration (i.e. MTT) in MT3DMS that is older than the MTT for the entire aquifer (Abrams and Haitjema, 2013).

To further introduce real world complexities of a 3-D aquifer system, such as the WLTC, saturated thickness, aquifer porosity and groundwater recharge values may have spatial variations resulting in different local groundwater age distributions that will be represented in each of the individual sink cells. Hence, the MT3DMS CFD simulation can, in theory, approach the MODPATH CFD simulation, and this indeed has happened for each of the five WLTC watersheds (compare the CFDs shown in Fig. 4 insets) due to complex WLTC model setting of saturated thickness, recharge and porosity values.

4 Concluding remarks

In this work, we presented an approach to calibrate the steady-state MODFLOW/MODPATH model to measured tritium concentrations in river waters at baseflows of the five river catchments of the WLTC. In the previous study, Gusyev et al. (2013) developed the steady-state groundwater flow MODFLOW model for the WLTC and calibrated the transient MT3DMS model to tritium measurements in river waters. The model had several important features: the uniform 80 m model grid to include small surface water features, 10 zones of groundwater recharge and 5 zones of aquifer porosity. The results of the groundwater flow model indicated variable saturated thickness and groundwater elevations ranging from 357 m above mean sea level at the Lake Taupo lakeshore to over 1000 m in the northern part of the model domain. In this study, the calibrated MODFLOW/MT3DMS model was used with particle tracking MODPATH to produce TTDs and a map of transit times for the WLTC river network. The

MODPATH TTDs were convoluted to obtain tritium concentration in river waters for the five river catchments of the WLTC. The tritium concentrations obtained with MODPATH show a good match to measured tritium time series despite accounting only for the advective transport.

When generating tritium concentrations with MODPATH TTDs, it is important to understand many implicit assumptions of the convolution integral. First, there is no spatial component in the convolution integral, time is the only variable. As a result, input tritium concentrations at each time t are assumed to be spatially uniform over each individual watershed. This is a valid assumption for tritium in precipitation, but it may not be true for other chemicals such as nitrate. Second, λ is assumed to be constant over time and the entire aquifer thickness. Again, this assumption is valid for non-reactive tritium tracer, but may not be for describing zonal reaction processes such as denitrification, which is dependent on organic matter concentrations in the aquifer. Third, the CFDs (and therefore PDFs) are based on steady state model runs with constant recharge and saturated thicknesses. The MODPATH model has the capability of taking into account spatial variations in the vertical and horizontal directions, as well as conducting transient simulations, but the constructing CFDs for this case is non-trivial. Finally, any travel times and resulting reactions of tritium in the unsaturated zone and river beds are not considered. It should be noted that for this particular watershed, these assumptions are reasonable; this is especially true since the tracer is tritium. It is noted that the assumptions underlying the convolution integral may lead to conceptual errors when studying other dissolved constituents in groundwater such as nitrates.

Consequently the MODPATH and MT3DMS CFDs were compared to understand better the model results and assumptions for generating CFDs in river networks. Even though the MT3DMS CFDs for the river network are only yielding approximations of the true transit time CFD, the information they provide is still useful. Most importantly, they still yield the correct MTT for the watershed. Furthermore, the MT3DMS distribution provides insight into the variations from an idealized watershed described in Haitjema (1995) and Abrams and Haitjema (2013). These factors include weak sinks, variations

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in saturated thickness, variations in recharge, etc. It is important to note that the MODPATH and MT3DMS CFDs must be interpreted differently, and that only MODPATH is providing the true CFD that should be used in the convolution integral. This is evident by the match of MODPATH tritium responses using the CFD in conjunction with the convolution integral to the MT3DMS tritium outputs (Fig. 4). Using the MT3DMS CFDs with the convolution integral yields a much different (and inaccurate) tritium response because, even though they have a similar mean transit time, the shape of the MT3DMS CFDs generally have both more short and long transit times than MODPATH. Hence, we promote both CFDs when using MODPATH and/or MT3DMS, as the transit time CFD generated by MODPATH is necessary to generate tritium and nitrate output functions with Eq. (1), but the MT3DMS CFD allows us to understand the variation from idealized conditions. This would be particularly useful in assessing when a lumped parameter model could have been used in place of a distributed parameter model, which would be valuable information for future studies.

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Table 1. MODPATH, adjusted MODPATH, and MT3DMS simulated MTT values, and the percent difference of adjusted MODPATH and MT3DMS MTTs.

Name of the river catchment	MTT, years MODPATH	MODPATH (adjusted)	MT3DMS	% difference of MODPATH (adjusted) and MT3DMS MTTs
Omori	3.57	3.15	3.29	−4.26 %
Whanganui	7.26	6.39	6.1	4.75 %
Kuratau	8.67	7.54	7.05	6.95 %
Waihaha	11.83	10.29	9.48	8.54 %
Whareroa	17.42	16.03	15.1	6.16 %

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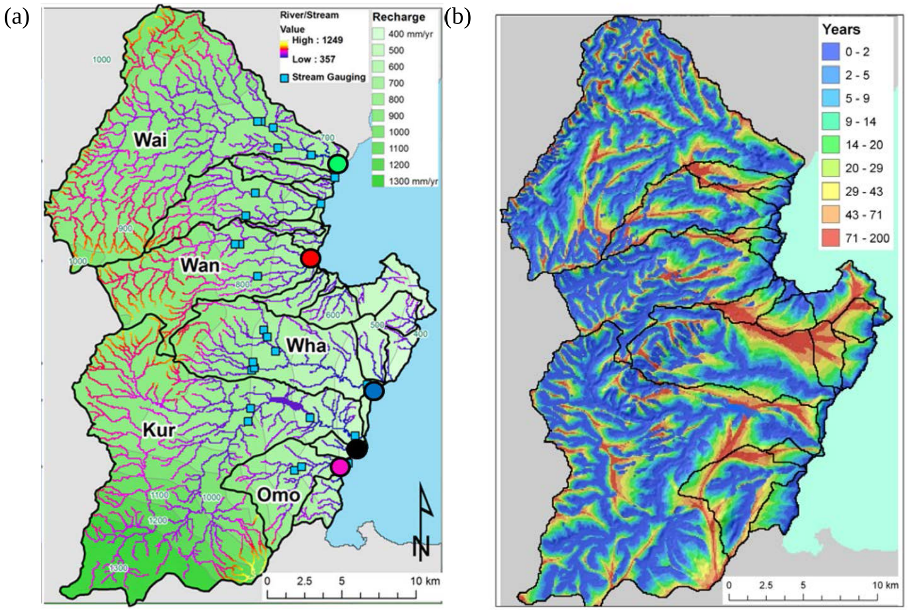

Fig. 1. (a) MODFLOW model setup of the WLTC from Gusyev et al. (2013), and **(b)** the groundwater transit time map for river waters of the WLTC produced with MODPATH/MODFLOW model. The colour coding indicates groundwater age from 0 year (blue) up to 200 year old (red).

(a) (b)

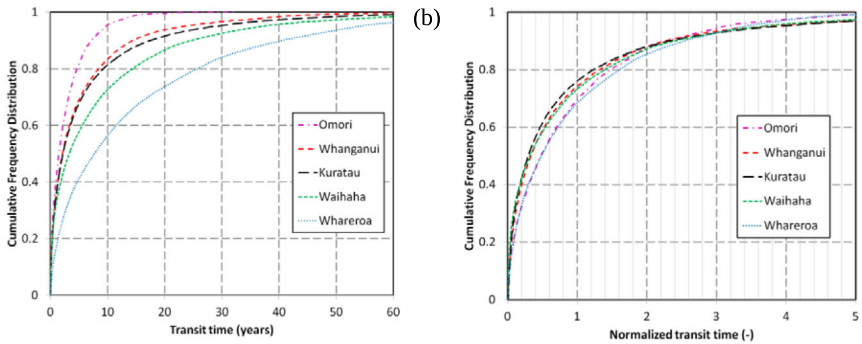

Fig. 2. Cumulative frequency distributions of transit times for five different watersheds in Lake Taupo region **(a)** and CFDs with transit times normalized by MTT from Table 1 **(b)**.

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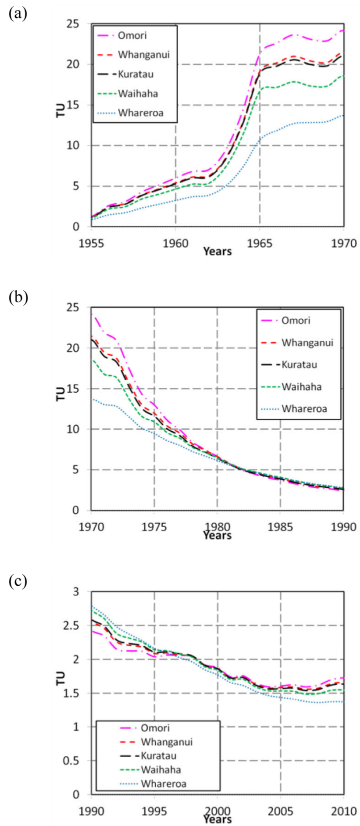

Fig. 3. The baseflow tritium concentrations calculated by MODPATH for five watersheds over three different time spans: 1955–1970 **(a)**, 1970–1990 **(b)**, and 1990–2010 **(c)**. Watersheds are ordered in order of increasing transit time.

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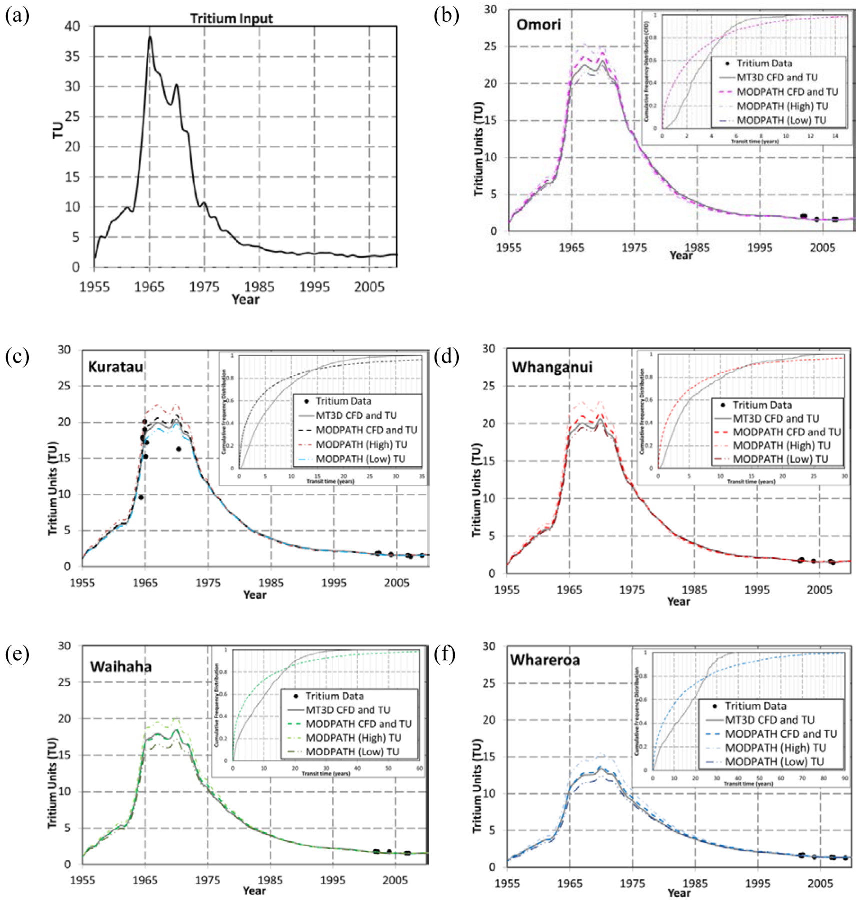

Fig. 4. Annual tritium input concentrations **(a)**. The baseflow tritium concentration and CFD (shown by insets) calculated by MODPATH and MT3DMS (Gusyev et al., 2013) for five watersheds **(b–f)**.

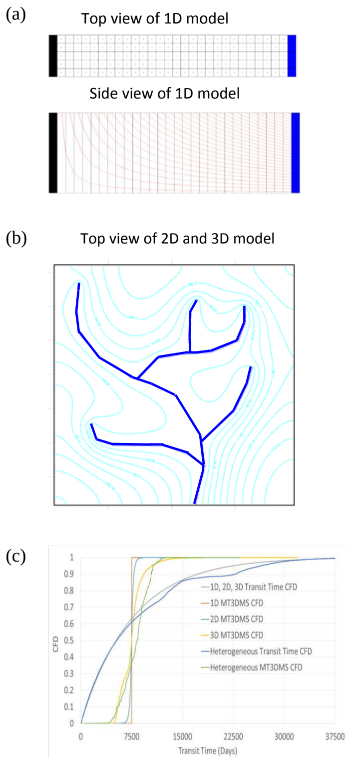

Fig. 5. (a) 1-D conceptual model, **(b)** 2-D conceptual model, and **(c)** MODPATH transit time and MT3DMS CFDs developed for a 1-D, 2-D, and 3-D conceptual model (dispersion and diffusion transport was disabled in the MT3DMS).

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