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Review Papers

A review of methods for modelling environmental tracers in groundwater: Advantages of tracer concentration simulation

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SUMMARY

Mathematical models of varying complexity have been developed since the 1960s to interpret environmental tracer concentrations in groundwater flow systems. This review examines published studies of model-based environmental tracer interpretation, the progress of different modelling approaches, and also considers the value of modelling tracer concentrations directly rather than estimations of groundwater age. Based on citation metrics generated using the Web of Science and Google Scholar reference databases, the most highly utilised interpretation approaches are lumped parameter models (421 citations), followed closely by direct age models (220 citations). A third approach is the use of mixing cell models (99 citations). Although lumped parameter models are conceptually simple and require limited data, they are unsuitable for characterising the internal dynamics of a hydrogeological system and/or under conditions where large scale anthropogenic stresses occur within a groundwater basin. Groundwater age modelling, and in particular, the simulation of environmental tracer transport that explicitly accounts for the accumulation and decay of tracer mass, has proven to be highly beneficial in constraining numerical models. Recent improvements in computing power have made numerical simulation of tracer transport feasible. We argue that, unlike directly simulated ages, the results of tracer mass transport simulation can be compared directly to observations, without needing to correct for apparent age bias or other confounding factors.

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1. Introduction

Mathematical models of varying complexity have been developed since the 1960s to interpret temporal changes of environmental tracer concentrations in groundwater flow systems. These models typically provide a statistical description of groundwater age (i.e. residence, transit or travel time), the mean of which can be combined with a flow path length to estimate a lateral groundwater flow velocity and flux across an interface (such as groundwater recharge or discharge) (Cook and Böhlke, 2000). As mathematical models have evolved, the more complex methods have advanced to a state where hydraulic simulation of a groundwater flow system is combined with solution of an advection–dispersion equation describing tracer movement (e.g. Park et al., 2002; Bethke and Johnson, 2008; Leray et al., 2012). For these more complex models, environmental tracer observations offer an ability to constrain estimates of aquifer properties through calibration of a numerical groundwater flow model.

Environmental tracers provide an ability to assess the internal dynamics of a groundwater system and to quantify timescales associated with groundwater flow (Cook and Böhlke, 2000; Kazemi et al., 2006). The inherent value of environmental tracers is that they can be interpreted to provide an integrated estimate of the flow velocity between two given locations; for example, between a recharge zone and a discharge zone, or between a contaminant source and potential receptors. This is valuable for water resource management, since it represents an appropriate scale of interest and can account implicitly for aquifer heterogeneity at a range of scales (Larocque et al., 2009), which is often impossible (or at best, extremely complicated) to measure directly.

Selecting an appropriate modelling approach depends on the purpose or objective of modelling. The motivation for this review was to evaluate progress in modelling approaches to interpret environmental tracers within a groundwater basin. For this reason, despite related research in catchment hydrology (e.g. McGuire and McDonnell, 2006; Hrachowitz et al., 2013) and ocean and climate sciences (e.g. Deleersnijder et al., 2001; Delhez et al., 1999; Hall and Plumb, 1994; Hall and Haine, 2002) these fields were not included in the review. This review focuses on approaches that, in addition to characterising a natural groundwater flow regime, would assist in estimating the response of a system to anthropogenic stresses. This review explores published studies in which environmental tracer observations have been interpreted using quantitative tools (i.e. models). Three main modelling approaches are described: (1) lumped parameter models; (2) mixing cell models; and (3) direct age models. Equivalences between each of the methods are explored and recent trends are discussed, including the modelling of direct age as well as simulations of tracer transport that account explicitly for the accumulation and decay of tracer mass. We consider the advantages of the latter approach, the results of which can be verified by comparison to environmental tracer observations. However, we concede that the conceptual simplicity of direct age simulation makes it a useful tool for stakeholder engagement and public communication.

1.1. Quantifying groundwater fluxes

Globally, there is an increasing demand for groundwater resources to support Earth's population, and in turn, there is an increasing reliance on groundwater and the need to understand regional scale flow systems (Gleeson et al., 2012). Groundwater basins present great potential for water resource development in undeveloped regions and in areas with over-allocated surface water systems. However, extraction from multi-layered aquifer systems can significantly alter the natural flow regime of such areas, including the reversal of flow directions and the enhancement of inter-aquifer leakage (Konikow and Kendy, 2005). In many regions, regional scale groundwater basins encompass both freshwater resources and hydrocarbon resources (such as unconventional gas, i.e. coal seam gas and shale gas). Mutual development of these resources requires an understanding of both large and small scale flow systems (Tóth, 1962, 1963), which comes with a relatively high cost and technical challenges during characterization (Alley et al., 2013). One key scientific challenge in characterization is the quantification of rates of water movement (i.e. fluxes) within a complex three dimensional geologic setting. Due to data paucity, assessments of groundwater flow systems often require multiple lines of evidence (including environmental tracers) in order to account for variations in flow path lengths and groundwater ages, from which fluxes may be estimated.

Accurate prediction of the response of a groundwater system often relies on numerical models. It is well known that the calibration of such models to hydraulic head observations alone provides an estimate of the ratio of hydraulic conductivity (or transmissivity) to recharge under steady state conditions or an estimate of aquifer diffusivity (i.e. K/S or T/S) under transient conditions (Haitjema, 2006). The inclusion of environmental tracer observations in model calibration provides an independent estimate of groundwater fluxes and can be used to estimate rates of recharge and lateral flow (Larocque et al., 2009). Recent research involving the estimation of statistical distributions of groundwater age (i.e. residence time) has begun to integrate the concepts of groundwater age simulation and tracer-based measurement (Janssen, 2008; Ginn et al., 2009). Whilst theoretical relationships are generally known, methodological challenges remain when attempting to use environmental tracer measurements in a quantitative groundwater model (Sanford, 2011).

1.2. Environmental tracers

Environmental tracers may be classified into one of three categories: (1) those that have an estimable initial concentration (or activity) and a known rate of decay or fractionation (e.g. ^{39}Ar, ^{14}C, ^{36}Cl, ^{2}H, ^{3}H, ^{81}Kr, ^{85}Kr, ^{18}O); (2) those that have a known initial concentration and are non-reactive while in the subsurface (e.g. noble gas isotopes, CFCs, SF_6, and, more recently, trifluoromethyl sulphur pentafluoride and Halon, 1211); and (3) those that accumulate over the time spent in the subsurface (e.g. ^{36}Cl, ^{3}He, ^{4}He). For any environmental tracer with a known or approximate initial concentration, and a measurable outflow concentration, the rate of movement in the subsurface will follow physical processes (e.g. advection, dispersion, diffusion, radioactive decay, and transformations such as biodegradation), meaning that the time spent in the subsurface (i.e. the age) can be estimated. The age interpreted from tracer observations is known as the apparent age (Kazemi et al., 2006). The 'apparent age' name infers that tracer ages may not always correspond directly with water ages. For example, where interaction with immobile zones (e.g. stagnant zones or aquitard units) occurs along a groundwater flow path, diffusive processes may result in tracer ages that are older than the actual water age. Utilising multiple tracers with different mass transport characteristics may help address the interaction with immobile zones, but only qualitatively. Many other definitions of groundwater age also exist; these are described subsequently in Section 1.3. Alternatively, observations of different environmental tracer types may help to define the frequency distribution of water molecules of different ages in a given sample of groundwater. Simple analytical expressions describing horizontal and vertical flow velocities, age profiles and distributions, mean age for simple aquifer conceptualisations, and estimating fluxes such as recharge are given in Vogel (1967) and Cook and Böhlke (2000). The range of environmental tracers that can be used to infer groundwater ages or residence times are reviewed in Geyh (2005), Plummer (2005), Newman et al. (2010), Herczeg and Leaney (2011), and Suckow et al. (2013).

1.3. Groundwater mixing: the crux of environmental tracer interpretation

Groundwater sampled at a given location will be a mixture of waters that have been transported via various flow paths. For the purposes of discussion, it is useful to consider how mixing can occur under idealised conceptions of flow. For the simplest possible conceptualisation of groundwater flow, Dupuit–Forchheimer conditions (i.e. horizontal flow only; Dupuit, 1863; Forchheimer, 1886), the degree of mixing will generally be proportional to the heterogeneity of the aquifer sampled. Similarly, under a slightly more complex (but still idealised) conceptualisation, such as a nested Tóthian flow system that includes vertical flow (Tóth, 1962, 1963), the degree of mixing will also be proportional to the screen extent of the observation well sampled. In practice however, due to the inherent complexity of subsurface flow systems, the frequency distribution a of groundwater sample will generally be more complex than calculated by simple linear combination of horizontal and vertical mixing. Additional mixing can be attributed to processes such as mechanical dispersion, chemical diffusion, and preferential flow, each of which has the potential to complicate environmental tracer interpretation.

Corresponding to the range of mixing that can occur, a broad range of definitions for groundwater age exist; these have been summarised previously by Cook and Böhlke (2000), Kazemi et al. (2006) and most recently by McCallum et al. (2014a), among others. The simplest method by which to estimate the age of a groundwater sample is to use Darcy's Law while assuming lateral flow only; this is known as the hydraulic age (Kazemi et al., 2006). Vogel (1967) presented a solution based on Darcy's Law for the vertical distribution of hydraulic age in an unconfined aquifer with uniform recharge and constant thickness. A range of similar analytical solutions for hydraulic age were summarised by Cook and Böhlke (2000). However, these are only appropriate for highly homogeneous flow systems or short well screen intervals; otherwise, the type and extent of mixing needs to be characterised. A slightly more complex conceptualisation is to assume no mixing of groundwater moving along a flow path by advective transport alone; this is known as an advective, piston flow, or streamtube age (Kazemi et al., 2006) or a kinematic age (Varni and Carrera, 1998). For complex conceptualisations, advanced mathematical models are often invoked to interpret the spatial variability in tracer concentrations. For example, Ginn et al. (2009) demonstrated that, even in homogeneous flow systems, the statistical distribution of groundwater age will be an inverse Gaussian distribution (indicating mixing and a bias toward younger ages), rather than a Dirac or Gaussian distribution (indicating zero or minimal mixing respectively). A third conceptualisation of groundwater age relates to ages derived from environmental tracers, known as apparent ages (Cook and Böhlke, 2000) or tracer ages (Purtschert, 2008). These ages provide an integrated estimate of various groundwater mixing processes. Following similar work in oceanographic modelling (Waugh et al., 2003), McCallum et al. (2014a, 2014b) recently demonstrated the potential for bias in apparent ages due to nonlinear variations in atmospheric concentrations and aquifer heterogeneity. The authors demonstrated that the use of additional tracers with coincident timescales may be used to correct for apparent age bias.

1.4. Other sources of uncertainty in environmental tracer interpretation

The range of confounding factors involved in the interpretation of 'ages' from tracer concentrations have been summarised by Purtschert (2008) and Newman et al. (2010). A variety of factors uniquely affects each of the groundwater age tracers. Such factors may include uncertainties associated with: initial concentrations (e.g. $^{14}C_0$ variation = ±15 years); the additive or dilutive effects of radioactive decay, hydrochemical reactions and sorption (e.g. ^{14}C A_0 uncertainty: Ingerson and Pearson, Tamers, Mook, Fontes and Garnier, and Eichinger models); mixing effects due to interaction with rock matrices (Zuber and Motyka, 1994; Sanford, 1997; Zuber et al., 2011) or low hydraulic conductivity units (Bethke and Johnson, 2002; Zinn and Konikow, 2007); recharge temperatures; excess air entrapment (Heaton and Vogel, 1981); unsaturated zone thickness (Cook and Solomon, 1995); reducing conditions; sorption; hydrodynamic dispersion and diffusion (Sudicky and Frind, 1981; Schlosser et al., 1989; Ekwurzel et al., 1994; Sanford, 1997); and air contamination, degassing and fractionation of gas tracers during sampling (Stute and Schlosser, 2000).

The interpretation of groundwater ages from radioactively decaying isotopes is subject to uncertainty, since the input concentrations (or activities) used in such calculations are often poorly constrained. Old age environmental tracers featuring relatively poorly-constrained input functions include ^{14}C and ^{36}Cl. A range of analytical models exist for estimating the appropriate input activity for ^{14}C-derived ages (e.g. Ingerson and Pearson, 1964; Tamers, 1967; Fontes and Garnier, 1979; Mook, 1980; Eichinger, 1983). Similarly, the initial activity of ^{36}Cl is dependent upon spatial location, while the initial concentration of stable chloride is both spatially and temporally variable. Uncertainty in the initial activity of ^{36}Cl was discussed extensively by Davis et al. (1998) and has also been considered in studies such as Bentley et al. (1986), Purdy et al. (1996), Davis et al. (2000) and Park et al. (2002). Young age environmental tracers such as tritium, CFCs, SF_6, and ^{85}Kr feature initial input concentrations that are variable over time and dependent upon location in space, particularly latitudinal location. Temporal variations in ambient atmospheric concentrations of ^{85}Kr are also complicated by the concentration increases due to the atomic bomb pulse and, more recently, the reprocessing of nuclear fuel rods. Similarly, the interpretation of stable isotope ratios may be confounded by the effects of evaporation and transpiration. Such processes may result in the isotopic signature of recharged water being significantly different from that of precipitation (Stumpp et al., 2009). Uncertainty relating to time-variant input functions can also be attributed to thick unsaturated zones, which can result in significant time lags between the time of precipitation and the time of infiltration to groundwater (Cook and Solomon, 1995).

A key assumption when using environmental tracers to derive groundwater ages is that the system is closed with respect to the addition or removal of tracer mass. The presence of additional subsurface sources or sinks is therefore a significant confounding factor when interpreting groundwater ages from concentrations of radioactively decaying or other types of environmental tracers. The influence of additional sources is often dependent upon the geology encountered by groundwater as it moves along a flow path. The confounding effects of a range of subsurface sources were examined extensively by Lehmann et al. (1993). The effects of subsurface sources on groundwater age estimation have also been discussed specifically for SF_6 (Busenberg and Plummer, 2000), ^{39}Ar (Andrews et al., 1991) and ^{36}Cl (Andrews et al., 1986). Ages based on ^{14}C activities may be erroneously large if processes which dilute the activity of ^{14}C as a fraction of total carbon are present; these include the oxidation of organic matter and the dissolution of carbonate minerals (Lehmann et al., 1993; Wood et al., 2014). The existence of terrigenic sources is the basis for groundwater dating using ^{4}He, which is produced by the radioactive decay of Uranium and Thorium isotopes. Concentrations of these elements vary between geological facies. Helium also features a high diffusion coefficient and may easily migrate into aquifers from adjacent aquitards or from the deeper crust. Therefore, ^{4}He is recognised as a semi-quantitative tool only (Torgerson and Stute, 2013). The reduction of CFC concentrations by microbial degradation and sorption was discussed by Plummer and Busenberg (2000) and Bauer et al. (2001). If not accounted for, such reductions in concentration can lead to estimation of erroneously young groundwater ages from CFC observations. Zones of stagnant water (e.g. rock matrices or aquitards) can act as sinks for tracers. Diffusive exchange between aquifers and such sinks can result in the removal of up to all observable tracer concentrations from an aquifer. Estimates of apparent age under such conditions may feature a bias toward older ages (Maloszewski and Zuber, 1991, 1993). For this reason, it is commonly accepted that a multi-tracer approach should be used to assess the effects of diffusive exchange.

When interpreting environmental tracer concentrations in the context of groundwater flow system characterisation, an additional complication is introduced when large scale anthropogenic stresses alter the flow regime (e.g. Massoudieh, 2013). For example, Bourke et al. (2014) recently investigated changes to groundwater-surface water connectivity in the Pilbara region of Western Australia. Here the ambient hydrologic regime had been altered by mine dewatering activities, causing a disconnected ephemeral system to convert to a connected perennial stream system. For this recently stressed system, and due to the recycled nature of disposed mine discharge, stable isotopes of water and chloride were found to be unsuitable tracers for the characterisation of groundwater-surface water connectivity. Similarly, lumped parameter models were judged unsuitable to represent the complexity of the hydrologic system, due the recent imposition of large scale anthropogenic stresses.

2. Method of review

For this review, the theoretical development and application of each approach identified above for the interpretation of environmental tracer concentrations was examined. This review was constrained to peer-reviewed publications and citation metrics were generated for each interpretation approach using the Web of Science and Google Scholar databases. For each interpretation approach, three seminal and highly cited publications were identified that either introduced the method to the groundwater literature or formed the basis for subsequent citations (Table 1).

The most highly-utilised tracer concentration interpretation tools are lumped parameter models (LPMs; Maloszewski and Zuber, 1982, 1996) and direct age models (DAMs; Goode, 1996; Ginn, 1999). A third approach is the use of mixing cell models (MCMs; Campana, 1975; Simpson and Duckstein, 1975). In addition to these three approaches, advective particle tracking has also been used to interpret environmental tracer observations. However, many applications using this approach have focused wellhead capture zone identification and conceptualising groundwater flow paths. For these reasons, this review is focused on the development and application of LPMs, MCMs, and DAMs, and only briefly discusses advective particle tracking models.

The literature review identified key applications of each method, which either (a) resulted in significant improvements in flow system characterisation, or (b) identified flaws in the method or the context in which the method performed poorly. For each key publication, the number of citations per year was calculated for the period 1980–2014 (Fig. 1). The number of citations per year is used as a gross metric and does not distinguish the reasons for citation, which may in some cases be trivial. In addition, and for a given interpretation approach, more than one seminal publication may be referenced by the same citing paper. Nonetheless, trends apparent from gross citation metrics are believed to be consistent with the evolution of the tracer interpretation approaches over time.

3. Review results

3.1. Lumped parameter models

Lumped parameter models are based upon the mathematical operation known as convolution. Convolution-based models treat the groundwater flow system as a single non-distributed ‘black box’ and involve the use of closed form, analytical, parametric solutions; therefore, the method is well-suited to the characterisation of data-poor groundwater systems or for use as a first-order approximation. The LPM method is essentially a model regression approach, in which a convolution function is calibrated to a time series of tracer concentrations observed at a given location. The function is typically parametric, though non-parametric alternatives have recently been developed (Cirpka et al., 2007; Engdahl et al., 2013; Massoudieh et al., 2014; McCallum et al., 2014c). Alternatively, the convolution function is calibrated to a spatial distribution of tracer concentrations along a groundwater flow path, all recorded at the same point in time (e.g. Harrington et al., 2002) to estimate average linear velocity. Mathematically, the LPM approach involves the convolution of a tracer input function with a tracer decay function and a weighting function to produce an output that is then matched (typically through a least squares calibration process) to an observed time series (Maloszewski and Zuber, 1982; Maloszewski et al., 2004):

$$C_{out}(t) = \int_0^t C_{in}(t-\tau)\exp[-\lambda(\tau)]g(\tau)d\tau \quad (1)$$

where t = time of tracer sampling [T], τ = an integration variable, C_{in} = input tracer concentration [M.L^{-3}], C_{out} = outlet tracer concentration [M.L^{-3}], λ = radioactive decay constant (included when appropriate), and g = a weighting function (Cook and Böhlke, 2000). The latter term is commonly known by a multitude of names, including a response or mixing function, or a residence time, transit time or travel time distribution. The weighting function is the frequency distribution of a tracer transported along flow paths of varying lengths. Importantly, this function is also known as a groundwater age distribution and represents the effect of mixing

Table 1
Published applications of the lumped parameter model approach to regional scale groundwater flow characterisation.

References	Location	Tracer(s) used	Mixing model(s) used	Parameter(s) estimated
Herrmann et al. (1986)	Lange Bramke basin, Germany	^{3}H, ^{18}O	DM	Recharge, lateral flows, discharge, storage
Benischke et al. (1988)	Northern Limestone Alps, Austria	^{3}H, ^{18}O	DM	Lateral flows, discharge, storage
Lian (1991)	Xi'an, China	^{2}H, ^{3}H, ^{18}O, ^{14}C	EM, PFM	Lateral flows, recharge
Zuber et al. (2001)	Lublin, Poland	^{3}H	EM, EPFM, DM	Hydraulic conductivity
Maloszewski et al. (2002)	Northern Limestone Alps, Austria	^{2}H, ^{3}H, ^{18}O	DM	Lateral flows, discharge
Einsiedl (2005)	Franconian Alb, Germany	^{3}H	DM	Lateral flows, discharge, storage, porosity

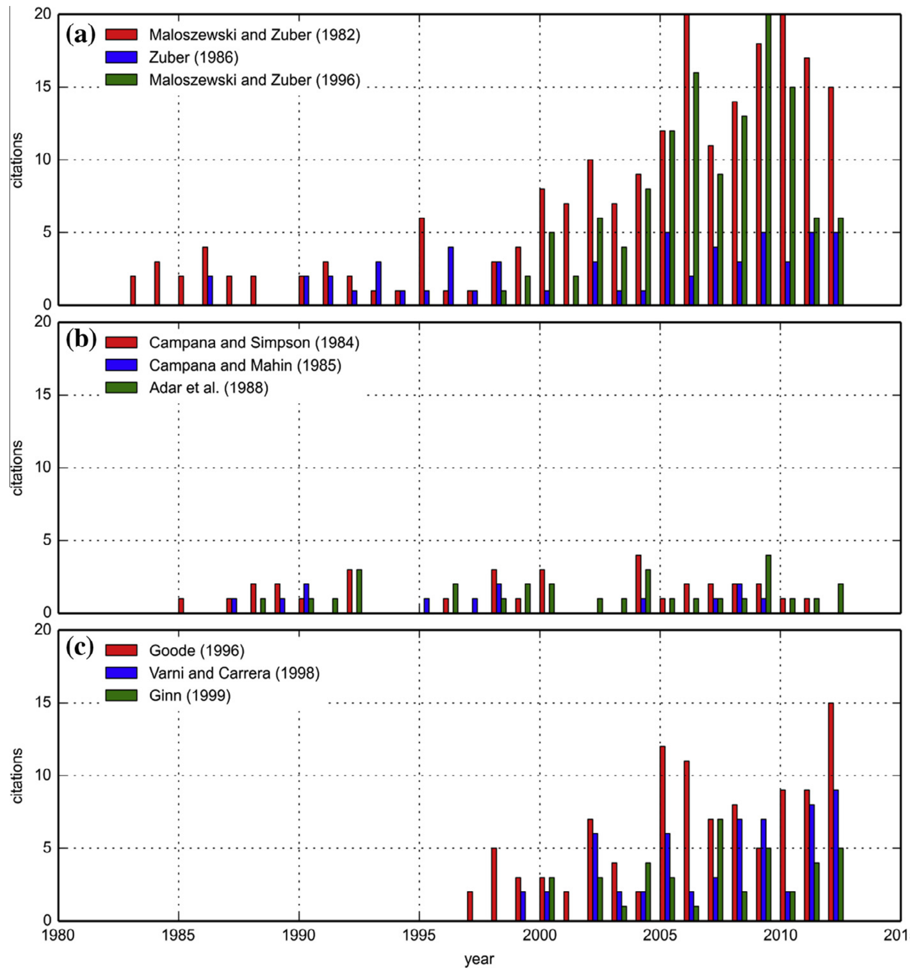

Fig. 1. Citation metrics for environmental tracer interpretation approaches: (a) lumped parameter model; (b) mixing cell model; (c) direct age model.

of flow paths. Indeed, the integral of $g(\tau)$ is unity and therefore can be viewed as a probability density function of groundwater age for a sample of water at a given location. This provides a direct link between the LPM and DAM modelling approaches, which is not often directly recognised in the groundwater age research literature. However, the key difference between the two approaches is that, in the LPM approach, this frequency distribution is (traditionally) parametric and is specified *a priori*. Specification of the weighting function is a crucial step in the LPM approach and should be informed by assumptions of aquifer type, geometry and timescale. In contrast, in the DAM approach, this distribution is derived as a result of numerical simulation.

Time series of atmospheric tracer concentrations, which are generally known, are used as tracer input concentrations. The second term in the integral accounts for the radioactive decay of environmental tracer activities and is omitted for non-radioactively decaying tracers. The third component, weighting functions, represent the degree of mixing resulting from the convergence of flow paths of varying lengths. Importantly, it should be noted that these functions do not represent the effects of mixing occurring along the flowpaths. In this review we discuss three commonly-used weighting functions: the piston flow model (i.e. no mixing), the exponential model (i.e. full mixing), and the dispersion model (i.e. partial mixing). The choice of weighting function is based upon knowledge of the hydrogeological configuration and upon the vertical extent of the aquifer sampled (Maloszewski and Zuber, 1982). For example, if groundwater recharge is limited to the farthest extent from a discharge zone (i.e. the sampling location), and if longitudinal dispersion is assumed to be zero, then mixing will approach zero and can be represented by a piston flow weighting function. Similarly, piston flow conditions are consistent with homogeneous aquifer properties. Conversely, if recharge is applied to the entire spatial extent of a homogeneous unconfined aquifer then the degree of mixing will be greater and is better represented by an exponential weighting function. Exponential mixing is consistent with the lateral transport of environmental tracers through an aquifer featuring highly heterogeneous properties. A commonly employed alternative to these approaches is the dispersion weighting function, which represents partial mixing, the degree of which is specified using a ratio of dispersive to advective forcing (McCallum et al., 2014a). Under certain conditions, the age distribution described by the dispersion model is identical to the inverse-Gaussian distribution described by Ginn et al. (2009). The parametric weighting functions described each feature one or more parameters, the values of which are typically estimated through least squares-based calibration of model outputs to observed tracer concentrations. In addition to other weighting function parameters, which may include dispersion, flow velocity and recharge extent, each mixing model also includes a mean age parameter, which is the primary output of model calibration.

Many computer software implementations of the LPM approach featuring various aquifer weighting functions have been developed, including RIETHM (Hussein, 1995), FLOWPC (Maloszewski and Zuber, 1996), TRACER (Bayari, 2002), BOXMODEL (Kinzelbach

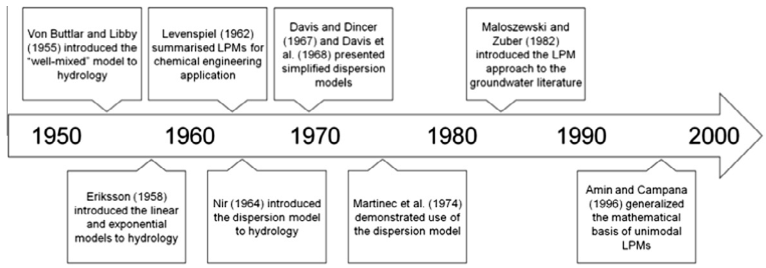

Fig. 2. Timeline of the theoretical development of the lumped parameter model approach to environmental tracer interpretation in hydrology and hydrogeology (1950–2000).

et al., 2002), LUMPED and LUMPEDUS (Ozyurt and Bayari, 2003, 2005), TracerLPM (Jurgens et al., 2012), and Lumpy (Suckow, 2012).

The LPM approach is based on concepts from chemical engineering (Levenspiel, 1962, 1972; Himmelblau and Bischoff, 1968) and was developed in hydrology between the 1950s and 1970s (Kaufman and Libby, 1954; Von Buttlar and Libby, 1955; Begemann and Libby, 1957; Eriksson, 1958; Nir, 1964; Dincer and Davis, 1967; Davis et al., 1968; Martinec et al., 1974). The early evolution of LPM-based approaches has previously been summarised by Raats (1977a) and a timeline of milestone publications over the period 1950–2000 is presented in Fig. 2. Kaufman and Libby (1954) introduced the piston flow model. Von Buttlar and Libby (1955) introduced the 'well-mixed' model. Eriksson (1958) introduced the linear and exponential models, the latter of which was subsequently used by Eriksson (1961, 1963, 1971), Bolin and Rodhe (1973), Peck (1973), Peck and Hurle (1973), and Nir and Lewis (1975). In a 1962 monograph Levenspiel described the use of residence time distributions and convolution-based lumped parameter models for the simulation and understanding of reactor flow in chemical engineering. Nir (1964) introduced the dispersion model. Dincer and Davis (1967) and Davis et al. (1968) subsequently presented a simplification of the Nir (1964) dispersion model. Martinec et al. (1974) demonstrated the use of the dispersion model. The LPM approach was introduced to the groundwater literature in the 1980s by Maloszewski and Zuber (1982). All mixing model types summarised above produce groundwater age distributions that are unimodal. These mixing models can also be used in combination to produce distributions that are bimodal or multimodal. The mathematical basis of the LPM approach was generalised by Amin and Campana (1996), who showed that all unimodal weighting functions can be derived a single basic distribution, the gamma (i.e. Pearson III) distribution.

Calibration of the convolution functions produced by one or more LPMs to observed time series of tracer concentrations at a given well results in the estimation of a statistical distribution (i.e. PDF or CDF) of the range of groundwater ages which in turn represent the range of flow path lengths to the well. A mean groundwater flow velocity based on an assumption of homogeneous hydraulic properties can be calculated by dividing a nominated representative flow path length by the mean of the groundwater age distribution. Further multiplication of the resulting value by a representative (e.g. mean) aquifer porosity value results in a mean Darcian velocity. For steady state flow systems, this velocity is equal to the recharge rate. This approach (i.e. the assumption of horizontal flow only) is appropriate to Dupuit–Forchheimer systems (i.e. located down-gradient of a recharge zone in a regional flow system) unaffected by recharge along the gradient; the LPM approach can also be applied to estimate recharge (e.g. Cartwright and Morgenstern, 2012).

Importantly, it should be recognised that the selection of weighting functions is based on a 2-D cross sectional simplification of what are typically 3-D aquifer systems. The validity of this assumption may be questionable for heterogeneous aquifer systems featuring complex flow systems. The *a priori* choice of aquifer weighting function(s) should be based on a well-informed understanding of groundwater flow paths; otherwise modelling may produce erroneous results, due to incorrect assumptions. In addition, the LPM approach commonly assumes a steady state groundwater flow field rather than transient conditions. In order to accommodate time-variant flow velocities, convolution-based approaches must be expanded (Niemi, 1977, 1990; Ozyurt and Bayari, 2005) and use a time-variant or transformational form of the weighting function (Leray et al., 2014; Massoudieh and Ginn, 2011; Massoudieh, 2013).

To date, published citations of Maloszewski and Zuber (1982), which introduced lumped parameter models to the hydrogeology literature, number in the hundreds, with over 60 citations since 2000. Published applications of the LPM approach to regional scale groundwater flow characterisation are, surprisingly, quite limited. Instead, the approach has primarily been used as to estimate mean ages (rather than fluxes) in the context of pollution susceptibility, or as a qualitative tool to examine the influence of mechanisms including the mixing of different source waters or the effects of dispersion or (matrix) diffusion. The relatively few applications of the LPM approach to regional scale groundwater flow characterisation are summarised in Table 1. Following the 1982 publication, Maloszewski and co-workers have published over 20 papers and reports featuring use of the LPM method, including peer reviewed works by Maloszewski and Zuber (1983, 1985), Maloszewski et al. (1983, 1990, 1992, 1995, 2002, 2006), Herrmann et al. (1986), Stichler et al. (1986, 2008), Benischke et al. (1988), Einsiedl et al. (2009, 2010), Schwientek et al. (2009), Stumpp et al. (2009); and Stumpp and Maloszewski (2010). Other research groups that have published extensively using the LPM include nitrate pollution studies by Buzek et al. (2009, 2012), Osenbrück et al. (2006) and Katz et al. (2001, 2004, 2005, 2009), as well as the estimation of residence times for surface and subsurface flow systems by Kabeya et al. (2007, 2008) and Morgenstern (2004), Morgenstern et al. (2010), Morgenstern and Daughney (2012).

It should be noted that an LPM approach featuring a piston flow-type weighting function is conceptually equivalent to forward advective particle tracking (e.g. Pollock, 1988, 1994). Advective particle tracking is typically applied to the interpretation of non-reactive environmental tracers such as CFCs and SF_6. For example, Reilly et al. (1994) used an advective particle tracking approach to interpret observations of CFC-11 and CFC-12 and thereby estimate recharge rates and hydraulic conductivities of an unconfined sand and gravel aquifer located near Locust Grove, Maryland, USA.

The LPM approach has also shown to be useful for the characterisation of flow in fractured or karst rock groundwater systems (e.g. Long and Putnam, 2004, 2006, 2009). Due to the tremendous complexity of fracture and dissolution features, physically-based simulation is impossible in a direct sense, and is only possible in a probabilistic sense. Instead, the LPM approach provides a means of characterising an effective, or integrated, system response to boundary conditions, such as recharge or surface water–groundwater interaction.

3.2. Mixing cell models

The mixing cell model (MCM, or discrete state compartment model) approach is based on a concept appropriated from chemical engineering (Deans and Lapidus, 1960a, 1960b; Levenspiel, 1962, 1972; Himmelblau and Bischoff, 1968) and was also developed in hydrology during the 1950s through 1970s (Wentworth, 1948; Craig, 1957; Kraijenhoff Van de Leur, 1958; Dooge, 1959, 1960, 1973; Nash, 1959; Eliasson, 1971; Eriksson, 1971; Bolin and Rodhe, 1973; Eliasson et al., 1973; Banks, 1974).

The MCM method was pioneered for groundwater application in the 1970s by Gelhar and Wilson (1974), Przewlocki and Yurtsever (1974), Campana (1975), Simpson and Duckstein (1975), and Diskin and Simpson (1978). The approach was introduced to the peer-reviewed groundwater literature in the 1980s by Llamas et al. (1982) and Campana and Simpson (1984). Numerous applications of the method were subsequently published by postgraduate students of Eugene Duckstein and Michael Campana (Postillion, 1985; Roberts, 1986; Osborn, 1987; Seidemann, 1988; Weaver, 1989; Sadler, 1990; Calhoun, 2000), by Campana (1987), Campana et al. (1997, 2001), Campana and Byer (1996), Campana and Roth (1997), Kirk and Campana (1990), and by Adar and Neuman (1988), Adar et al. (1988, 1992a, 1992b, 2002), Adar and Sorek (1989), Sorek et al. (1992), Adar and Külls (2002).

Mixing cell models are a semi-analytical, semi-distributed Eulerian approach which is well-suited to studies featuring a moderate level of data support. The MCM approach assumes simple instantaneous mixing between discretely defined cells (representing physical areas) at defined temporal intervals. Calibration of the discharge concentration computed by MCM to an observed time series of tracer concentration at a given well results in the estimation of volumetric fluxes between arbitrarily-defined mixing cells over the temporal intervals specified. The mean groundwater age is calculated by applying a unit impulse to an MCM and by calculating the concentration-weighted average of time at a discharge cell over the modelled temporal extent, as described by Eq. (34) of Campana (1975) [and equivalent to Eq. (6) of Campana (1987)]:

$$BDC(N+1) = \frac{S(N) + BRV(N+1) * BRC(N+1)}{VOL + BRV(N+1)} \quad (2)$$

where S = cell concentration [M.L^{-3}], VOL = cell volume [L^3], BRC = cell influx boundary concentration [M.L^{-3}], BRV = cell influx boundary volume [L^3], and BDC = cell discharge boundary concentration [M.L^{-3}]. The two equivalent equations presented by Campana (1975) and Campana (1987) are discrete forms of Eq. (4) of Maloszewski and Zuber (1982). As with the LPM method, the mean groundwater flow velocity along the flow path is then calculated by dividing the mean age by the flow path length and multiplying by a homogeneous (or effective) porosity value. Again, for steady state flow systems, this velocity is equal to the recharge rate.

Subsequent development of the MCM approach included the use of quadratic programming methods by Adar and Neuman (1988). Adar et al. (1992a, 1992b) added rigor to the MCM approach by using cluster analysis to identify discrete hydrochemical zones prior to modelling. Gieske and De Vries (1990) combined the MCM approach with Singular Decomposition methods, while Carroll et al. (2007, 2008) combined the MCM approach with the Shuffled Complex Evolution (Duan et al., 1992) calibration algorithm.

The MCM approach has been applied many times to interpret environmental tracer observations and to thereby estimate rates of groundwater flow, recharge and discharge (Table 2). The majority of published studies focused on semi-arid regions and interpreted spatial variations in observed stable isotope concentrations, while other studies included the use of major ions or radioisotopes (^{3}H, ^{14}C).

The MCM approach to the interpretation of environmental tracer concentrations is relatively simple and, as such, is best suited to in hydrogeological systems that are poorly to moderately well characterised, i.e. in cases where the level of data available is commensurate. However, if the MCM approach is used in a well characterised system then potential for the imposition of structural (i.e. epistemic) error exists, where this refers to the type of prediction uncertainty that results from the use of an overly simple model (Doherty and Welter, 2010).

3.3. Direct age models

The direct age modelling method, which was introduced to hydrogeology in seminal publications in the late 1990s (Goode, 1996; Varni and Carrera, 1998; Ginn, 1999), essentially uses the governing equations for subsurface solute transport to simulate spatial distributions of the statistical distribution of groundwater age (or the moments thereof, including mean age). The theoretical basis for direct age simulation can be traced back to the 1950s. Danckwerts (1953), Spalding (1958), Randolph (1964) and Levenspiel (1962, 1972) derived and described the use of residence time distributions for chemical engineering applications. Raats (1977a,b) derived theoretical solutions for subsurface age transport in steady-state flows but this work was not cited outside of soil solute transport literature. As recently noted by Post et al. (2013), the first simulation of theoretical age featuring zeroth-order accumulation in a hydrogeological model was published by Voss and Wood (1994). Harvey and Gorelick (1995) presented a general framework for the application of temporal moment-generating equations to reactive subsurface solute transport. In a landmark paper, which has since been cited over 30 times, Goode (1996) derived the equation for the transport of the product of mean groundwater age and groundwater mass (generally referred to as age mass). Varni and Carrera (1998) later derived temporal moment equations for the transport of age mass. Ginn (1999) derived equations for generalized non-parametric distributions of groundwater age. Subsequent works by Etcheverry and Perrochet

Table 2
Published applications of the mixing cell model approach to regional scale groundwater flow characterisation.

References	Location	Tracer(s) used	Parameter(s) estimated
Allison and Hughes (1975)	Padthaway, Australia	^{3}H	Lateral flow, recharge
Campana and Simpson (1984)	Arizona, USA	^{14}C	Inter-aquifer leakage, recharge
Campana and Mahin (1985)	Texas, USA	^{3}H	Porosity, recharge, storage
Adar and Neuman (1988)	Arizona, USA	^{2}H, ^{18}O	Inter-aquifer leakage, surface water interaction
Kirk and Campana (1990)	Nevada, USA	^{2}H	Recharge, discharge
Adar et al. (1992)	Arava Valley, Israel	^{2}H, ^{18}O	Lateral flow, inter-aquifer leakage
Harrington et al. (1999)	Otway Basin, Australia	^{14}C	Hydraulic conductivity, inter-aquifer leakage
Dahan et al. (2004)	Nevada, USA	^{2}H, ^{18}O	Interaction with surface water, irrigation sources and sinks
Carroll et al. (2007, 2008)	Nevada, USA	^{2}H	Lateral flow, recharge

(2000), Cornaton (2003), and Cornaton and Perrochet (2006a, 2006b) derived deterministic models of groundwater age by applying residence time theory while considering numerical models of groundwater age. Parallel theoretical development occurred in related geophysical fields such as atmospheric and oceanographic dynamics (e.g. Deleersnijder et al., 2001; Delhez et al., 1999; Hall and Plumb, 1994; Hall and Haine, 2002).

Bethke and Johnson (2002) extended the formulation of Goode (1996) to derive an equation for the contribution of age in an aquifer from an overlying aquitard. More recent extensions of the theory have included Cornaton (2012), who derived a numerical solution to calculate transient distributions of groundwater age, and Engdahl et al. (2012), who derived a numerical solution to calculate non-Fickian distributions of groundwater age. Massoudieh and Ginn (2011) attempted to bridge the gap between directly simulated ages and analytically-derived radiometric ages by deriving a mathematical relationship between the two using Laplace Transforms. Both the DAM and LPM approaches typically assume the existence of a steady state velocity field. The DAM approach has only recently been extended to transient flow regimes (Cornaton, 2012; Gomez and Wilson, 2013; Massoudieh, 2013; Soltani and Cvetkovic, 2013; Leray et al., 2014) and to heterogeneous hydraulic conductivity fields (Engdahl and Maxwell, 2014).

In its most general form, the DAM approach involves computation of the spatial distribution of a statistical description (typically either a probability density or cumulative distribution function, i.e. PDF or CDF) of groundwater age (Ginn, 1999) through solution of what is commonly referred to as the governing equation for groundwater age (Ginn et al., 2009; Gomez and Wilson, 2013; Engdahl et al., 2014):

$$\nabla \cdot (\mathbf{v}\theta\rho) - \nabla \cdot (\mathbf{D}\theta\nabla\rho) + \frac{\partial\theta\rho}{\partial A} = -\frac{\partial\theta\rho}{\partial t} \tag{3}$$

where ρ = groundwater density [M.L^{-3}], A = the groundwater age dimension, θ = aquifer porosity, $\mathbf{v}$ = Darcian groundwater flux (q) [L.T^{-1}] divided by aquifer porosity; and $\mathbf{D}$ = the dispersion–diffusion tensor. Note that in Eq. (3) groundwater density (ρ) varies in time and space as a function of five variables: x, y, z, time and age. An initial condition of zero concentration is applied across the entire model domain. Zeroth-order accumulation of concentrations occurs throughout the model domain. A Dirac delta or Heaviside input boundary condition with a concentration of unity is specified at recharge locations. If a Dirac delta function is used, the breakthrough concentration (BTC) curve observed at any given model cell is equivalent to the PDF of groundwater age at that location. Alternatively, if a continuous input of unity is used then the BTC curve will be equivalent to the CDF of groundwater age at that location.

Under steady state flow conditions, and by integrating Eq. (3) with respect to age, Eq. (3) simplifies to the governing equation for spatially distributed mean groundwater age (Goode, 1996):

$$\nabla \cdot (\mathbf{v}\theta\rho) - \nabla \cdot (\mathbf{D}\theta\nabla\rho) + 1 = 0 \tag{4}$$

Initial and boundary conditions are applied as described for Eq. (3), except that the Dirac delta input function is used exclusively. Using Eq. (4), groundwater density (ρ) is now a function of only four variables (x, y, z, t) and represents the first moment of the PDF of groundwater age. The spatial distribution of variance or other higher statistical moments of the PDF of groundwater age can also be calculated from Eq. (3) (Varni and Carrera, 1998). Although groundwater age distributions may not always be normally distributed (Engdahl et al., 2013), the distribution variance may still serve as a useful metric by which to measure the degree of age mixing in a groundwater sample (McCallum et al., 2014a).

The direct simulation of age is a fully distributed approach and therefore requires a high level of data support. Computation of the spatial distribution of the statistical distribution of groundwater age is difficult, as it is a four or five dimensional problem (x, y, z, t, a) and has been performed using customised solute transport codes (e.g. Woolfenden and Ginn, 2009; McCallum et al., 2014a,b,c,d) based on the Lagrangian random walk particle tracking approach (RWPT, Kinzelbach, 1988; Uffink, 1988; LaBolle et al., 1996). Under certain conditions, the governing equations for random walk particle tracking are analogous to the advection–dispersion equation. This approach accounts for mixing processes at various scales and has been used to identify probability distributions of groundwater age. RWPT approaches to the solution of the advection–dispersion equation for solute transport have been comprehensively reviewed by Delay et al. (2005) and Salamon et al. (2006). Lagrangian approaches such as RWPT feature numerous advantages over their Eulerian counterparts, including zero numerical dispersion, mesh independence, perfect global mass conservation (Delay et al., 2005; Salamon et al., 2006) and minimal assumptions required with regards to mixing. Computation of the spatial distribution of the first statistical moment of the groundwater age distribution (i.e. the mean age) is much simpler and can be performed using standard solute transport software (e.g. MT3DMS, Zheng and Wang, 1999; FEFLOW, Diersch, 2005; COMSOL Multiphysics, COMSOL AB 2006).

Unlike other approaches to the interpretation of environmental tracer observations, the DAM approach has seldom been used in the context of regional scale groundwater flow system characterisation. This is mainly because the numerical requirements of the DAM approach are much greater, especially solutions for statistical distributions of groundwater age, which are functions of five variables (i.e. x, y, z, t, a). In addition, since numerical solutions of the advection dispersion equation must satisfy the Courant criterion, they therefore demand a much higher discretisation resolution than typically used for flow models. For these reasons, published applications of the DAM approach have generally been limited to qualitative studies of local scale (i.e. at scales of tens to hundreds of metres) hydrologic processes (e.g. Wilson and Gardner, 2006; Riedel et al., 2011). The few intermediate to regional scale applications of the DAM are summarised as follows. Engesgaard and Molson (1998) simulated the spatial distribution of mean age using a 2-D vertical cross sectional model of the Rabis Creek aquifer, Denmark. Vertical profiles of directly simulated mean ages compared poorly to observed tritium concentrations. An analytical solution was found to provide a more accurate representation of the tritium profile. This solution also provided an estimate of the recharge rate to the Rabis Creek aquifer. Bethke et al. (1999) modelled spatial distributions of mean age in addition to those of ^{36}Cl and ^{4}He for three vertical cross sections of the Great Artesian Basin, Australia to assist in the interpretation of point tracer observations. Their results included the estimation of spatially variable flow velocities as well as aquitard diffusion coefficients. Tompson et al. (1999) used ^{3}H and ^{3}He data to improve the conceptualization of a groundwater flow system in a recharge area in Orange County, California, USA. In this case, mean groundwater ages were calculated using a Lagrangian approach to tracer transport based on a 3-D numerical flow model. Weissmann et al. (2002) interpreted observations of CFC concentrations using a 3-D model of the Kings River Alluvial Fan aquifer, California, USA. Spatially distributed CFC results were found to compare poorly to directly simulated mean ages and CDFs. This was interpreted to mean that CFC-based ages did not represent the mean age of the aquifer system, thereby implying that an influx of older water may occur. Lemieux and Sudicky (2010) simulated historical spatial distributions of mean age using multiple connected vertical 2-D cross sectional models. Their results informed estimation of the dynamics of subsurface meltwater mixing processes during glacial cycles. Eberts et al. (2012) simulated age PDFs for four contrasting groundwater flow systems in California, Connecticut, Florida, and

Nebraska, USA. Age distributions were compared favourably to those simulated using the direct age approach. Leray et al. (2012) interpreted CFC and SF_6 observations in the Plœmeur fractured rock aquifer located near Lorient, France. Model calibration to CFC concentrations resulted in improved constraint of spatially distributed hydraulic conductivity parameters. Molson and Frind (2012) simulated the spatial distribution of mean age using both an idealised 2-D vertical cross sectional model and a 3-D model of the Waterloo Moraine aquifer complex, Canada. Mean ages were used to inform the definition of capture probability in the context of public wellhead protection.

In contrast to an apparent lack of application to regional scale hydrogeological systems, the DAM approach has been successfully applied in a number of theoretical studies to investigate the significance of groundwater flow and solute transport processes. Using a simplified 2-D vertical cross sectional model of the Eocene Carrizo aquifer, Texas, Castro and Goblet (2005) compared directly simulated mean ages to two other modelled ages: advective ages and ^{14}C ages. The authors concluded that the direct simulation of mean ages may be the most robust approach for complex heterogeneous flow systems, such as those featuring faults. Also examined was the influence of dispersion on modelled mean ages under spatially variable hydraulic conditions. Using an idealised 3-D four layer model, Zinn and Konikow (2007) examined the effects of groundwater extraction on modelled spatial distributions of mean age. The authors concluded that, under certain hydrogeologic conditions, mean age distributions in developed aquifers may be affected by leakage induced from low-permeability units. Woolfenden and Ginn (2009) examined the effect of varying aquifer dispersivity on spatially variable age distributions using a 2-D cross sectional model of the Rialto–Colton Basin, California. Jiang et al. (2010) examined the effects of decreasing hydraulic conductivity and porosity with depth on simulated spatial distributions of mean age using two idealised 2-D vertical cross sectional models. The authors found that depth-dependent variations exerted significant influence over the aging and rejuvenation of groundwater. Jiang et al. (2012) and Gassiat et al. (2013) used the DAM approach to investigate the potential locations and extent of high groundwater age zones in multi-layered aquifer–aquitard systems. Engdahl et al. (2013) derived an analytical solution to the estimation of groundwater age distributions. Using both Fickian and non-Fickian models of solute transport, analytical solutions were compared favourably to numerical DAM simulations in terms of flow velocities and dispersion coefficients. In summary, the DAM approach has proved to be a useful tool in theoretical investigations of a wide range of flow and transport processes and dynamics.

4. Discussion

The following discussion is focused on three key points. First, the interpretation of environmental tracer concentration observations in groundwater has been undertaken using a range of mathematical approaches. Although often developed in isolation, equivalencies between many of these distinct approaches can be shown. Second, mixing models are typically used to interpret tracer observations. The basis of such mixing can be subject to conceptual uncertainty and some age interpretation methods are more able to quantify this uncertainty than others. Third, arguments for the direct numerical simulation of tracer concentrations (in lieu of direct age modelling) are presented.

4.1. Equivalence of approaches

The conceptual and mathematical equivalencies between different approaches for modelling environmental tracers are often not well understood, which can be detrimental when attempting to elucidate system complexity, leading to difficulties when comparing results from different approaches. For example, connections between convolution-based and linear reservoir-based approaches have been highlighted by Dooge (1959, 1960), Nash (1958, 1959), Overton (1970), and Ponce (1989). Equivalence can be shown when interpreting a tracer concentration observed at a given distance along a flowpath down-gradient of a source location. On one hand, a (continuous) convolution-based approach (i.e. using an LPM) could be applied, using an input concentration time series and a predefined aquifer weighting function. Alternatively, an equivalent result may be obtained using a (discrete) linear reservoir-based approach (i.e. using an MCM approach) to discretise a flow path of the same length and using the same input concentration time series to force the model. The equivalence between the LPM and MCM approaches has recently been employed to derive non-parametric aquifer weighting functions using matrix-based deconvolution approaches (Cirpka et al., 2007; Engdahl et al., 2013; Massoudieh et al., 2014; McCallum et al., 2014c). The sum-product operations used by the deconvolution methods presented in such studies are directly equivalent to the linear reservoir basis of the MCM approach. Such operations are also discrete equivalents of the continuous convolution integrals of the LPM approach.

Amin and Campana (1996) showed that unimodal LPM age distributions are special cases of the three parameter gamma distribution (also known as the Pearson type III distribution). The authors state that this distribution is, in turn, equivalent to a time lagged cascade of linear reservoirs described by Nash (1958). It has been suggested that gamma distributions are more appropriate for the characterisation of hydrological age distributions than exponential distributions, since the former allow more flexibility to account for nonlinear effects (Hrachowitz et al., 2010). Ginn et al. (2009) stated that statistical distributions of groundwater age will be "at least inverse Gaussian" in shape. In fact, both the gamma and inverse Gaussian distributions are special cases of the Generalised Inverse Gaussian distribution (Folks and Chikkara, 1978; Chikkara and Folks, 1989):

$$f(x) = \frac{(a/b)^{p/2}}{2K_p\sqrt{ab}} x^{p-1} e^{-(ax+b/x)/2} \tag{5}$$

where a, b and p are function shape parameters and K_p is a modified Bessel function of the second kind. For the gamma distribution, $b = 0$ whereas for the inverse Gaussian distribution, $p = -1/2$. Similarly, it can be shown that the Dispersion mixing model used in many lumped parameter models is a specific solution to the equation for Fickian diffusion in one dimension. For this case, the governing equation is (Levenspiel, 1972):

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} \tag{6}$$

in which C = solute concentration (M.L^{-3}), D_x = coefficient for dispersion in x-direction (L^2.T^{-1}), and v_x = groundwater flow velocity in the x-direction (L.T^{-1}). If a Dirac delta function is used to impose an idealized impulse initial condition then, after algebraic manipulation, the reformulated solution to this equation is equivalent to the Dispersion weighting function (Nir, 1964; Kreft and Zuber, 1978):

$$g(\tau) = \frac{1}{\sqrt{4\pi Pe^{-1}\left(\frac{t-\tau}{\hat{t}}\right)}} \exp\left[-\frac{\left(1-\frac{t-\tau}{\hat{t}}\right)^2}{4Pe^{-1}\left(\frac{t-\tau}{\hat{t}}\right)}\right] \tag{7}$$

in which variables are as described previously for Eqs. (1), (6), (7); Pe^{-1} is the inverse of the Péclet number, i.e. $1/(v_x x/D_x)$; and $\hat{t}$ = mean groundwater age. In summary, it may be observed that direct mathematical equivalencies exist between the results of (a) LPMs, regardless of the mixing model specified (since all are essentially versions of the 1-D solution for solute transport); (b) linear reservoir models (i.e. MCMs), which are effectively a discrete version of the convolution integral; and (c) DAMs, particularly in terms of analytical solutions of the 1-D governing equation for groundwater age.

Recent research by Massoudieh and Ginn (2011) attempted to bridge the gap between directly simulated ages and analytically-derived radiometric ages by deriving a mathematical relationship between the two using Laplace Transforms. Engdahl (2014) subsequently showed that groundwater ages calculated using a Laplace domain solution are equivalent to late-time domain solutions for steady state concentrations of a constant source radiometric tracer. Similarly, Eberts et al. (2012) demonstrated the equivalence of groundwater age distributions calculated using the LPM and DAM methods. The authors concluded that full age distributions are of greater importance than apparent ages (derived from environmental tracer observations) or mean ages (derived from tracer interpretation models) for trend analysis and forecasting.

4.2. Difficulties due to tracer mixing

Identifying, understanding, and accounting for mixing is a primary issue when interpreting environmental tracer observations in groundwater systems. A fundamental step in addressing this issue is developing a conceptual model of the flow system, which could be amended as new information about the system becomes available. For lumped parameter models, the degree of tracer mixing is specified by one or more of the classic mixing models (i.e., piston flow, exponential, dispersion, or combinations thereof) and choosing a weighting function (i.e. $g(\tau)$ in Eq. (1)) that corresponds with the conceptual model of the system. Difficulties can arise when applying the LPM approach to data poor systems for which conceptualisations of flow dynamics are inconclusive. Such data paucity can lead to erroneous assumptions relating to the degree of heterogeneity in hydraulic properties and/or the areal extent of recharge inputs. Similarly, incomplete conceptual models may also lead to incorrect assumptions regarding the range of groundwater ages present in a system, potentially leading to use of a limited suite of environmental tracers. Whilst the LPM approach may provide an adequate first-order understanding of a hydrologic system, evaluation of response to anthropogenic stresses such as large scale groundwater extraction and variations in recharge are difficult to implement. For Direct Age Models, which are implemented using numerical models, the degree of tracer mixing in porous media can be modelled using the classical advective-dispersion equation with the inclusion of a dispersion term (Bear, 1972). In a numerical model, dispersive processes typically represent: (a) hydrodynamic dispersion, caused by variations in pore sizes which result in tortuous flow paths; (b) diffusion, due to solute concentration gradients (Fetter, 2001); and (c) responses to time variant boundary conditions, such as recharge (Frind and Hokkanen, 1987).

Conceptually, mixing due to hydrodynamic dispersion is related to the degree of aquifer heterogeneity, which has been well documented for on groundwater age distributions (Weissmann et al., 2002; Larocque et al., 2009; McCallum et al., 2014b, 2014d). However, the inability to distinguish between the effects of aquifer heterogeneity and distributed recharge can result in conceptual model non-uniqueness (Chavent, 1974; Yeh, 1986; McKenna et al., 2003; Moore and Doherty, 2006). For example, in a well-mixed aquifer, observations consistent with the exponential LPM may indicate a relatively homogeneous aquifer receiving broadly distributed recharge, or may instead indicate piston flow through a vertically heterogeneous aquifer. In comparison, representation of the same groundwater system using a numerical model would enable more specific determination of the mixing cause, and in turn a better understanding of how the system may respond to change.

4.3. Arguments for modelling environmental tracer concentrations directly

The role of interpreted environmental tracer observations in the characterisation of hydrogeological systems is often to develop or refine a conceptual model, or to constrain a numerical model. In turn, a thorough conceptual understanding provides the foundation for developing quantitative groundwater models, assessing water availability, and ultimately providing guidance to water resource management. To achieve these goals requires accurately quantifying groundwater fluxes under a range of scenarios. Modelling the transport of environmental tracer concentrations while accounting for the accumulation and decay of tracer mass offers a robust method to estimate these groundwater fluxes. The simplifying assumptions invoked for LPM and MCM are eliminated when taking a numerical modelling approach, and temporal changes in tracer concentrations can be simulated directly rather than interpreted from groundwater ages calculated analytically or numerically. An advantage of numerically modelling groundwater flow and tracer transport (with accumulation and decay of tracer mass if needed) is the ability to evaluate scenarios involving significant hydraulic stresses that result in transient flow conditions (e.g. significant and time-varying extraction). In these complicated situations, which are becoming more common where development of hydrocarbon resources is intricately linked with non-saline groundwater, the integrated approach of LPM methods may not provide significant insights. Whilst conceptually simple, LPM methods will be unsuitable where the stressor of interest lies somewhere along the flowpath, and under scenarios when the stress results in discrepancies between hydraulic conditions (which respond relatively quickly) and solute concentration conditions (which respond relatively slowly). Mixing cell model approaches, which typically involve significant *a priori* simplifications, may be too coarse to interpret the local or intermediate effects of hydraulic stressors. Advective –only transport approaches may also be inappropriate for stressed groundwater systems due to the potential for induced vertical leakage, particularly from aquitard units. Under such circumstances the potential for leakage from low conductivity units is high and may result in effects that, if not accounted for directly, confound tracer interpretation.

It should also be noted that comparable effects may also occur in groundwater systems featuring stagnant water zones (Maloszewski et al., 2004; Zinn and Konikow, 2007), which can act to bias sampled groundwater age distributions in the same manner as discharge of solutes from aquitards. The implications of groundwater interaction with stagnation zones in a regional scale context were recently discussed by Gassiat et al. (2013). This is of particular relevance to stressed groundwater systems, in which significant development can enhance the existence of stagnation zones. Environmental tracer sampling in the vicinity of such zones may result in the erroneous estimation of apparent ages. This could be assisted by the sampling of multiple tracers, in order to identify potential interactions with stagnation zones.

Suckow (2014) argued that an additional motivation for the direct simulation of tracer concentrations, rather than ages, relates to chemical diffusion constants, which vary between different environmental tracers. Diffusion coefficients are real physical parameters that can be measured in a laboratory or determined from field studies and subsequently included when modelling tracer transport. In comparison, the diffusion coefficient used when directly simulating mean groundwater age represents the mixing of water with itself, due to Brownian motion rather than osmosis. In practice, this coefficient is difficult to parameterise and is instead often treated as a fitting parameter which, along with the dispersion tensor, accounts for an unknown number of mixing processes across a range of scales. More broadly, Hadley and Newell (2014) recently called into question the physical meaning of what the dispersion term in the advection–dispersion equation truly represents. They argued that diffusion is the dominant non-advective process and that the unphysically large dispersion coefficients typically employed in solute and age transport modelling instead represent the diffusion that occurs between geological units of significantly different hydraulic conductivity. This differs considerably from the textbook definition of hydrodynamic dispersion, which is a purely physical process representing the effects of variations in pore scale velocities and flow path tortuosity.

This review found that publications in which numerically modelling groundwater flow and environmental tracer transport (with accumulation and decay of tracer mass) was used to interpret tracer observations have increased in number, but remain fewer than the more popular LPM approach. This may be attributed to the large computational time required by such tracer transport simulations. In addition, such highly parameterized numerical approaches may often be perceived as being complex to implement. Instead, practitioners may rely on simpler, well-established approaches such as LPMs and MCMs. Reilly et al. (1994) simulated the transport of CFCs using the Method of Characteristics (Konikow and Bredehoeft, 1978) in order to interpret field observations and thereby estimate rates of recharge, hydraulic conductivity, streambed conductance and hydrodynamic dispersion for a model of a phreatic aquifer near Locust Grove, Maryland, USA. Castro et al. (1998) used numerical transport modelling of tritium, ^{4}He and ^{40}Ar in order to interpret field observations and thereby estimate horizontal and vertical hydraulic conductivities of a multi-layer model of the Paris Basin, France. Zhao et al. (1998) applied numerical transport simulation to a synthetic model of a confined aquifer in order to estimate the input flux of ^{4}He from underlying crust and mantle and hydrodynamic dispersion parameters. Bethke et al. (2000) simulated the transport of ^{36}Cl in a simple 2-D synthetic model which included advective, dispersive and diffusive processes as well as isotope generation and decay. The authors also simulated the transport of ^{36}Cl in a simplified 2-D model of the Great Artesian Basin, Australia. However, their results were focused on the generation of spatial distributions of mean age rather than hydraulic fluxes. Bauer et al. (2001) simulated the transport of tritium, SF_6, CFC-113 and ^{85}Kr in order to characterise solute retardation processes in a basalt aquifer located near Gambach in Central Germany. Park et al. (2002) simulated the transport of ^{36}Cl and chloride to interpret field observations and thereby estimate aquifer thickness and diffusion coefficient parameters. Zuber et al. (2005) calibrated a transport model to observations of SF_6 in order to estimate a spatial distribution of SF_6. Bethke and Johnson (2008) presented comparisons between spatial distributions of directly simulated mean ages and spatial distributions of ^{36}Cl, ^{4}He (twice), and salinity (TDS) from transport modelling results. Gardner et al. (2013) demonstrated the use of parallel groundwater flow and solute transport software to simulate the time-varying transport of multiple tracers and mean groundwater age. The applicability of the software was demonstrated using a synthetic 3-D model featuring a heterogeneous hydraulic conductivity field. The appropriateness of various tracers was compared in terms of similarity to spatial distributions of mean groundwater age. Argon-39 was found to be the tracer best suited to characterise the hydrogeological system specified. Most recently, McCallum et al. (2014a) proposed arguments in support of the simulation of tracer concentrations rather than "direct" ages. The authors demonstrated the effects of bias on apparent ages derived from a range of young and old environmental tracers. They also highlighted the limitations of various corrections typically applied when calculating apparent ages. As a means of circumventing relating tracer concentrations to apparent ages, the authors advocated the simulation of tracer concentrations using numerical models.

The numerical modelling of groundwater flow and tracer transport (with accumulation and decay of tracer mass) noted above clearly demonstrates the benefit of simulating tracer concentrations to constrain numerical models of groundwater flow systems. As noted by Bethke and Johnson (2008), the calculation of mean groundwater ages is not strictly necessary: instead, groundwater flow velocities and transport rates, as calculated from the matching of numerical model results to environmental tracer observations, can instead be reported directly (i.e. from tracer transport modelling involving accumulation and decay), without reference to the age distribution that they imply. However, calculation of mean groundwater age or residence time from a robustly developed transport modelling (i.e., calibrated to hydraulic conditions and environmental tracer observations) would be a useful by-product for communicating results to a non-scientific audience. Castro and Goblet (2003) provide one of the only documented examples of this workflow (hydraulic and concentration calibration followed by age interpretation), where the final figure (Fig. 12, p. 23) illustrates an interpretation of advective water age constrained by modelling the spatial distribution of ^{4}He.

5. Summary and conclusions

This review examined the progress in modelling approaches to interpret environmental tracers within a groundwater basin. Three approaches have evolved since the 1960s, with a growing number of applications to various hydrogeological problems. lumped parameter models have most commonly been used to estimate mean groundwater ages (i.e. mean residence times), which can be used to estimate fluxes when combined with a flow path length and a representative porosity value. The LPM approach also uses a statistical description of the variability of groundwater age, which is represented by the weighting function used in convolution. However, as this is chosen *a priori*, it is not a model output as such. Generally, only mean ages are typically reported, since flow path lengths in hydrogeological systems are unknown or poorly constrained. More recently, the parameters of the weighting functions used in LPMs have also been estimated (Massoudieh et al., 2012). The LPM approach is unsuitable for the characterisation of the internal dynamics of a hydrogeological system. The approach is also inappropriate for transient groundwater flow fields, and is therefore unsuitable for investigation of the effects of large scale anthropogenic stresses within a groundwater basin. Instead, the LPM approach is well-suited to groundwater systems for which the flow dynamics are not well characterized and feature a dearth of observational (i.e. hydraulic head) data. For these reasons, the approach is often applied to data-poor groundwater systems and has been widely used in similar fields such as catchment and stream hydrology, where flow paths are more easily defined. In addition, first order approximations of groundwater ages and flow rates estimated using the LPM approach are also valuable as they may subsequently be used in the calibration and/or validation of numerical flow and transport models.

The mixing cell model approach employs a simplified discretisation of a groundwater flow system to represent spatial variations in tracer concentrations. Flow velocities are estimated through the matching of cell concentrations to environmental tracer observations. This approach has seen limited use in hydrogeology outside of a handful of research groups, partly owing to improvements in the tractability of alternative methods (i.e. numerical modelling approaches) since the 1980s.

The Direct Age Modelling approach involves the solution of a modified form of the advection–dispersion equation to simulate spatial (and more recently, temporal) distributions of theoretical groundwater ages. This approach has been the focus of much interest by a range of research groups since the mid-1990s (including fields other than hydrogeology), resulting in considerable theoretical development. Applications of this approach to real-world case studies remain limited, in part due to the high spatio-temporal resolution of environmental tracer data required to characterise statistical distributions of groundwater age, as well as the complexities involved in relating tracer concentrations to directly simulated ages. Difficulties in relating ages obtained from environmental tracers to directly simulated ages have recently been discussed (McCallum et al., 2014b). The use of highly parameterized, physically based numerical models confers the additional benefit of quantitatively addressing model uncertainty. The uncertainty associated with model parameters can be explored using formal sensitivity and uncertainty analyses. Typically such analyses quantify parameter uncertainty by evaluating the effect of varying model state properties (such as hydraulic conductivity) on modelled results. These analyses can also investigate the potential for structural error (Doherty and Welter, 2010) by varying boundary condition values. This latter benefit is not possible with the use of analytical, parametric approaches such as LPM and MCM methods.

This review explored published studies of environmental tracers that have been applied in a quantitative manner, and also considered the value of modelling tracer concentrations rather than groundwater ages. The latter approach may be used to directly infer rates of groundwater recharge and discharge, as well as lateral and vertical fluxes, which may be used directly to constrain and develop conceptual and numerical models. Conversely, and although conceptually straightforward, the interpretation and use of groundwater ages is often subject to confounding factors and/or requires considerable simplifying assumptions. Instead, it is suggested that the primary benefit of groundwater ages may lie in their use when communicating conceptual understandings to non-technical audiences. The modelling of groundwater ages is of significant benefit in furthering the conceptual understanding of groundwater flow and transport systems and processes through hypothesis testing using synthetic models.

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