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Review Papers

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

Chris Turnadge [a,*], Brian D. Smerdon [b]

[a] CSIRO Land and Water Flagship, Waite Campus, Glen Osmond, South Australia 5064, Australia
[b] Alberta Geological Survey, 402 Twin Atria Building, 4999-98 Avenue, Edmonton, Alberta T6B 2X3, Canada

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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.

Contents

* Corresponding author. Tel.: +61 (8) 8303 8712; fax: +61 (8) 8303 8750.
E-mail address: Chris.Turnadge@csiro.au (C. Turnadge).

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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