

Spring 1-1-2014

Solute Age and Groundwater Well Contamination

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Solute Age and Groundwater Well Contamination

by

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A thesis submitted to the
Faculty of the Graduate School of the
University of Colorado in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
Department of Civil, Environmental and Architectural Engineering

2014

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Solute Age and Groundwater Well Contamination
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Larbkich, Warangkana (Ph.D., Hydrology, Water Resources and Environmental Fluid Mechanics)

Solute Age and Groundwater Well Contamination

Thesis directed by Prof. Roseanna M. Neupauer

Solute age is a measure of the amount of time that a solute has been in an aquifer. A water sample that contains solute will represent a distribution of solute ages, accounting for the different travel times and paths from recharge points to the sampling location. This research introduces the concept of solute age as a tool to assess groundwater well contamination. We show that solute age for a sorbing solute is older than groundwater age because sorbing solutes move more slowly than groundwater. This implies that a pumping well contaminated by a sorbing solute would remain contaminated for longer after source removal than what would be expected based on groundwater age. In this work, we develop the adjoint equation of solute age. Using forward equations to calculate solute age under transient flow conditions, a separate forward simulation is needed for each possible release time. This is computationally burdensome and the results are limited to only the preselected set of release times. We show that an adjoint equation of solute age, however, can be used to solve for the solute age distribution at a particular observation location and time with a single simulation to account for all possible release times. This more efficient adjoint equation provides comparable results to those found using the forward equation. In addition, in this work we use solute age to evaluate the effectiveness of a riverbank filtration (RBF) system. We use the adjoint equation of solute age to calculate the spatial and temporal distribution of travel times between a river and an RBF well (equivalent to solute age) where the river water level fluctuates. Successful filtration in an RBF system will require that the travel time is long enough to achieve sufficient contaminant degradation, so the distribution of travel times can be used to evaluate the effectiveness of an RBF system.

Acknowledgements

First of all, I wish to express my special appreciation and thanks to my Adviser, Professor Roseanna Neupauer. Her mentorship about groundwater, academic writing and research presentation was invaluable. Her advice and contributions of time have been priceless, and I am extremely grateful.

Secondly, I wish to express my sincere gratitude to Professor Harihar Rajaram for his advising during the first two years of my doctoral program. Additionally, I especially thank Professor Janet S. Herman, Professor Shemin Ge, Professor Diane M. McKnight, and Professor Joseph Ryan for serving as my committee members and for their brilliant comments and suggestions. Also, special thanks go to Mr. Dave Colvin and Mr. Jacob Bauer from Leonard Rice Engineers, Inc. for providing the model files for the case study.

Finally, I wish to thank my family. Words cannot express how grateful I am to my parents, grandmother, and great-aunt for all their love and encouragement. My study was funded by the Royal Thai Government Scholarship and the CEAE Department of Ph.D Completion Fellowship, University of Colorado at Boulder.

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Chapter 1

Introduction

1.1 Problem statement

Groundwater withdrawal for public supply in the U.S. has increased steadily since 1950 [31]. Groundwater is susceptible to contamination, and is very difficult to remediate if it is contaminated [34]. Land use activities such as using pesticides and fertilizers, mining, or accidental release of chemicals into the aquifer can cause contamination in groundwater. Furthermore, if the contaminated groundwater reaches drinking water wells, which are located in the aquifers, the contaminated drinking water can cause serious effects on human health. Thus, it is necessary to protect the aquifer and groundwater wells from contamination. To protect the groundwater wells, the approaches include to determine the expected time a contaminant will take to reach the well, and the timing the wells remain contaminated or the contaminant at the well will decrease to an acceptable level after source removal [20, 29, 36, 47, 50].

A useful tool for assessing the likelihood of contamination of groundwater wells is groundwater age. Groundwater age is a measurement of the amount of time that water particles have been in the aquifer. It also represents the amount of time an aqueous chemical tracer has been in the aquifer because a tracer travels through the aquifer at the same rate as a water particle. This similarity in behavior of water and tracer movement has led to the application of groundwater age as a tool to assess the groundwater well contamination. An older groundwater represents a longer amount of time that an aqueous contaminant takes to reach the well. This affects the groundwater well contamination in two competing ways. First, wells at the locations with older groundwater

are more distant from the source of contamination than at the locations with younger groundwater. Contaminant concentrations at the more distant locations are lower because of dispersion. Thus, wells at the locations with older groundwater should represent lower levels of contamination. However, in some situations, an older groundwater can lead to increased groundwater well contamination. For example, if the wells are contaminated and the source is removed to prevent further contamination, these wells will remain contaminated until all of the contaminated water that has already recharged the aquifer passes them. In wells with older groundwater, contamination will persist for a longer time.

Although groundwater age is an appropriate tool for assessing groundwater well contamination by chemical tracers, it is not appropriate for addressing groundwater well contamination by sorbing solutes which travel more slowly than groundwater because they periodically attach to the soil surface and then detach from the soil surface as they move through the aquifer. In the context of groundwater well contamination, if the well is contaminated with a sorbing solute and the source of contamination is eliminated, the contamination will persist for a longer time than would be expected based on groundwater age.

Reactive solutes also behave differently than chemical tracers. Although decaying solutes travel at the same rate as groundwater, the amount of solute decreases over time. Thus, in the case of decaying contaminants, a well is less susceptible to reaching an unacceptable level of contamination compared to the case of a chemical tracer. Furthermore, the contaminant may decay to concentrations that are below levels of concern.

For these reasons, groundwater age is not an appropriate tool for assessing groundwater well contamination for sorbing and reactive solutes. Instead, my research introduces a new concept, called “solute age”, that represents the amount of time that a solute particle has been in the aquifer.

1.2 Overview of this work

The goal of my research is to develop and test the concept of solute age for quantifying groundwater well contamination. The first objective of this study is to develop the standard governing equations for solute age based on the principle of conservation of mass following the approach used by others to develop the governing equations for groundwater age. The solute age equations are more complex because I add the appropriate terms to account for reactions (e.g. linear equilibrium sorption and first-order decay) in the governing equations. The second objective of this study is to develop the adjoint equation of solute age and to demonstrate that the adjoint equations provide the same information as the standard governing equations of solute age that I developed in the first objective but are more computationally efficient. The last objective of this study is to apply the solute age approach to riverbank filtration (RBF) at an actual site, and to demonstrate how solute age developed from the adjoint equation can be used efficiently in the design and analysis of RBF systems.

1.3 Background

1.3.1 Groundwater age

Groundwater age is defined as the amount of time it takes a groundwater parcel to travel from its point of recharge (either land surface or water table) to a given location in the aquifer [9, 24, 30, 54]. The simple perspective of groundwater age is based on the movement of water particles by advection along a flow path. In a one-dimensional domain, for example, groundwater age is the ratio of distance along the flow path to velocity [5, 6]. Groundwater age from this perspective is generally determined by isotope dating method which is related to using concentrations of single isotopes [5, 10, 33], and gives an estimate of mean age [19]. Since groundwater age in this perspective is straightforwardly calculated from the flow information, it has been widely used to evaluate groundwater velocities and hydraulic properties, and to calibrate parameter flow models [8, 15, 30, 33, 48, 59].

The second perspective of groundwater age which is more realistic is that the movement of water particles is controlled by not only advection but also dispersion and diffusion due to mixing between different flow paths. The groundwater sampled at the location of observation contains a mixture of groundwater ages (i.e. a mixture of water particles each of which has its own unique age) [7, 19, 57, 59]. Thus, age is a distributed quantity, not a single absolute value, and can be represented by probability density function [17, 18, 19]. In this perspective, the transport of age-mass is also defined as age carried with water molecules and continuously transported over time by advection and dispersion along the flow regime [5, 6, 22, 23, 24, 56] where age mass is defined such as the product of water mass and age [23, 24]. However, since the distributions of age are affected by the transport processes of advection and dispersion [22], shapes of age distributions can be used to estimate transport model parameters and reflect the heterogeneities in the aquifer [17, 19, 59]. Also, groundwater age is used to assess the vulnerability of a groundwater system to the contaminant and to evaluate groundwater contamination such as representing timing that the groundwater quality will be improved after stopping polluting activities [30, 36, 59].

To determine the distribution of groundwater age, different governing equations of groundwater age have been developed based on the advection-dispersion equation. Goode [24] developed a governing equation of mean groundwater age for calculating the spatial distribution of mean groundwater age. However, since mean age does not represent the entire distribution of groundwater age, this equation is limited in its application. To address this limitation, Varni and Carrera [56] developed a governing equation for calculating the cumulative distribution function (CDF) of recharge time under steady or transient flow conditions, which can be used to calculate the probability density function (PDF) of groundwater age. Although solution to this governing equation provides the entire distribution of groundwater age, solving this equation under transient flow conditions requires multiple simulations, one for each recharge time, which is inefficient. Ginn [22] developed a governing equation for the PDF of groundwater age which eliminates the need for solving the equation multiple times by including an age dimension. However, because this equation has an additional dimension, it cannot be solved with a conventional groundwater simulator except

under simple conditions [60]. Other methods that have been suggested for simulating groundwater age are calculating the discrete distribution of groundwater age from multiple tracers [57], integrating Darcy's law and the fundamental rules of probability theory [35], and using random walks in five dimensions including three spatial coordinates, one time coordinate, and one age coordinate with the probability theory [17].

The groundwater age distribution, however, has some challenges in estimations and applications under heterogeneity which is common in natural groundwater systems. Since the distributions of age are affected by both advection and dispersion, an age distribution is possibly effected by non-Fickian dispersion which exists in the natural system (e.g. non-Fickian dispersion caused by a wide range of velocities [18]). However, the governing equations of groundwater age (e.g. [22], [56]) have been developed only by the conditions under Fickian dispersion [17, 22, 23, 61]; therefore, the application of the groundwater age equation in real groundwater systems is limited [19]. Weissmann et al. [59] present groundwater age distributions that account for non-Fickian dispersion. They also show that the contaminated water observed at a monitoring well in a heterogeneous aquifer has a broad distribution of ages and that the mean of simulated groundwater age distribution does not correspond to mean age calculated from tracer concentrations. In a heterogeneous aquifer, the groundwater age distribution can also be significantly affected by a strong pumping well that causes transient leakage of much older water from confining layer to mix with young water in the aquifer, and results in increasing mean age around the well [63].

1.3.2 Adjoint approach

The adjoint approach is a useful tool for quantifying solute transport in a situation in which a solute is observed at one or a few locations and times of interest, and information about the position of the solute at multiple times in the past is desired. In the adjoint approach, information is propagated backward in time from the observation point to the recharge locations. The adjoint approach is useful for solute age simulations because the solute age distribution is a representation of the multiple times in the past that the solute entered the aquifer. Neupauer and Wilson [37, 38]

developed an adjoint equation of solute transport to calculate a PDF of backward travel time that was used to identify the release time of a contaminant in an aquifer. These adjoint equations of solute transport have been developed for transient flow conditions and chemical reactions [39, 40, 41, 43]. The adjoint approach has also been used to assess the effectiveness of waste repositories by determining the remaining time before a toxic contaminant from the repository locations reaches the biosphere [11], to calculate the capture zone of a pumping well [42], and to assess the vulnerability of water supply well to an unknown source within the capture zone by determining the expected time to reach maximum concentration at the well and the exposure time to concentration at the well above threshold [36].

1.3.3 Riverbank filtration

Riverbank filtration (RBF) is a surface water treatment technology that uses an aquifer adjacent to a river as a natural filter [16, 32]. A production well, or RBF well, in the aquifer near the river draws water from both the aquifer and the river, and contaminants in the river water undergo biological and chemical reactions while traveling through the subsurface materials. RBF has been widely used to remove suspended particles, natural organic matter, organic contaminants, nutrients, pathogens and viruses [1, 12, 13, 14, 27, 44, 45, 58]. Because the contaminated water is naturally filtered in this method, RBF requires less additional chemical treatment and is considered as a cost-effective technology [4, 45].

A key parameter in siting the RBF well is the travel time of the contaminants from the river to the RBF well [2, 12, 32, 44], which must be sufficiently long to allow adequate time for biological and chemical reactions to occur in order to produce higher quality water. For example, in North America, the RBF is commonly used as a primary treatment for pathogens, and RBF wells are designed with travel times from hours to weeks [25]. Another example is that Sprenger et al. [53] study the effectiveness of RBF well by determining travel times between the RBF well and the river, and compare to the travel times required for contaminant removal recommended by the typical groundwater protection regulations or presented by different literature reviews (e.g.

the range of travel times required for removal of bacteria and viruses are 11-63 days and 13-43 days, respectively). The travel time of the contaminant depends on the sorption properties of the contaminant, groundwater velocity along the flow path, the distance between RBF well and the river, the pumping rate, fluctuating river levels and flood events [2, 12, 46, 53]. For example, there are slight variations in travel times due to the river stage fluctuations [44]. Also, Sprenger et al. [53] and Eckert and Irmischer [16] found that flood event not only increases transport of contaminant but also shortens travel time between the river and the RBF well. This is because during flood events the hydraulic gradient between the river and the adjacent aquifer increases significantly. Tracer-based approach, Darcy's law and particle tracking simulations are used to estimate travel time for the assessment of RBF [2, 12, 44].

1.4 Organization of this thesis

Chapter 2 of the thesis addresses the first objective of developing the standard governing equations for solute age. I develop the governing equation of mean solute age based on the approach that Goode [24] used for mean groundwater age, and I illustrate the limitations of the equation. I also develop the governing equation for solute age distribution based on the approach of Varni and Carrera [56] for the groundwater age distribution. In addition, through a hypothetical one-dimensional example, I illustrate the means of using solute age to assess the persistence of contamination at a groundwater well.

Chapter 3 addresses the second objective of developing the adjoint equation of solute age. I develop the adjoint equation for a contaminant that exhibits both sorption and decay under transient flow conditions. My adjoint equation is developed to determine a distribution of solute age of a contaminant that was sampled at an observation point. This is different from the adjoint equations developed by Neupauer and coworkers [37, 38, 39, 40, 41, 43] who developed the adjoint equation for an instantaneous point source of contaminant, instead of a distributed continuous source that I use. I also demonstrate the accuracy of our adjoint equation through a hypothetical two-dimensional example by comparing the results with solute age derived from standard governing

equation that I developed in Chapter 2.

Chapter 4 addresses the third objective of applying the solute age approach to design of an RBF system. The study site is downstream of a major metropolitan area where the river water level fluctuates, and the contaminant of concern is assumed a sorbing and decaying contaminant. I use solute age to determine travel time between the the river and the RBF well. In addition, I demonstrate how solute age developed from the adjoint equation can be used to evaluate the effectiveness of the RBF well. Chapter 5 addresses conclusion and recommendations for future work.

Chapter 2

Introduction of solute age to assess groundwater well contamination

Groundwater withdrawal for public supply in the U.S. has increased steadily since 1950 [31]. Groundwater is susceptible to contamination, and is very difficult to remediate if it is contaminated [34]. Land use activities such as using pesticides and fertilizers, mining, or accidental release of chemicals into the aquifer can cause contamination in groundwater. Furthermore, if the contaminated groundwater reaches drinking water wells, which are located in the aquifers, the contaminated drinking water can cause serious effects on human health. Thus, it is necessary to protect groundwater supply from contamination. To protect the groundwater wells, the approaches include to determine the expected time a contaminant will take to reach the well, and the timing the wells remain contaminated or the contaminant at the well will decrease to an acceptable level after source removal [20, 29, 36, 47, 50].

A useful tool for assessing the likelihood of contamination of groundwater wells is groundwater age, which is defined as the amount of time since a groundwater parcel has recharged the aquifer [9, 24, 54]. Groundwater age has been used to evaluate the contamination at a groundwater well in a few key ways: First, on the basis of the assumption that most contaminants have entered the aquifer recently, groundwater that is older than 100 years sampled at a pumping well, for example, is clean because contamination was not present when water entered the aquifer. It also has been used as a tool to evaluate how much the pumping well is replenished by natural or artificial recharge; young groundwater sampled at a pumping well implies that the water at the well is well replenished by recharge [9, 30, 60]. In addition, groundwater age represents timing that the groundwater quality

at a well will be improved after stopping polluting activities [30].

Any groundwater sample contains a mixture of parcels that recharge the aquifer at different times; thus, a groundwater sample contains a distribution of ages [56]. Several mathematical models for calculating groundwater age distributions have been created by many researchers, each with different assumptions. For example, Goode [24], Varni and Carrera [56] and Ginn [22] developed approaches for calculating groundwater age by considering age as a mass that is transported in the aquifer. The equations are based on the advection-dispersion equation (ADE) for a conservative and non-reactive tracer.

Goode [24] presents an equation for calculating the mean groundwater age in a steady flow field, given by

$$\frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial A}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\theta v_i A) + \theta(1) = 0 \quad (2.1)$$

$$\left[D_{ij} \frac{\partial A}{\partial x_j} - v_i A \right] \cdot \mathbf{n}_i = 0 \text{ on } \Gamma_1 \quad (2.2)$$

$$\left[D_{ij} \frac{\partial A}{\partial x_j} \right] \cdot \mathbf{n}_i = 0 \text{ on } \Gamma_2 \quad (2.3)$$

where $A(\mathbf{x})$ is mean groundwater age, x_i are the spatial directions ($i = 1, 2, 3$), v_i is groundwater velocity in the x_i direction, θ is porosity, D_{ij} is the i, j^{th} component of dispersion tensor, Γ_1 is a no-flow or inflow/recharge boundary, Γ_2 is the outflow boundary, and \mathbf{n}_i is the component of the outward unit normal vector in x_i direction. A mean groundwater age of zero or flux of mean groundwater age of zero is specified at the recharge boundary because water entering the aquifer has an age of zero. Mass flux occurring only by advection is specified at the outflow boundary. The last term on the left hand side of (2.1) represents the aging of water, at a rate of 1 year per year, for example. The solution of (2.1) is the spatial distribution of mean groundwater age assuming steady flow conditions, and assuming that the mass flux across the boundary is proportional to the water flux [24].

Equation (2.1) is limited because it can be applied for calculating the mean groundwater

age only in a steady flow field, and it assumes that mass flux across the domain boundaries is proportional to water flux. Also, mean groundwater age does not represent the entire distribution of groundwater age. To address this limitation, Varni and Carrera [56] developed a governing equation for the cumulative distribution function (CDF) of recharge time, $F(t_R; t, \mathbf{x})$, describing the probability that water particles at location \mathbf{x} at time t entered the aquifer at or after time t_R . The governing equation is given by [56]

$$\frac{\partial(\theta F)}{\partial t} = \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial F}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\theta v_i F) \quad (2.4)$$

$$F(t_R; t, \mathbf{x}) = 0 \quad t \leq t_R \quad (2.5)$$

$$F(t_R; t, \mathbf{x}) = H(t - t_R) \text{ on } \Gamma_1 \quad (2.6)$$

$$\left[D_{ij} \frac{\partial F}{\partial x_j} - v_i F \right] \cdot \mathbf{n}_i = -v_{2i} F_2 \cdot \mathbf{n}_i \text{ on } \Gamma_2 \quad (2.7)$$

where H is Heaviside's function, Γ_1 is the recharge surface, Γ_2 is the boundary with prescribed mass flux, v_{2i} is velocity of fluid flowing across the boundary in the i direction, F_2 is the distribution of water particles entering or leaving the aquifer through the prescribed mass flux boundary, and t_R is the recharge time. The solution of (2.4) gives $F(t_R; t, \mathbf{x})$ for a single t_R and all \mathbf{x} and t in the domain. To obtain the full CDF, (2.4) must be solved repeatedly for many different values of t_R . The probability density function (PDF) of recharge time, $f_{t_R}(t_R; t, \mathbf{x})$, is calculated from the CDF using

$$f_{t_R}(t_R; t, \mathbf{x}) = \frac{\partial}{\partial t_R} F(t_R; t, \mathbf{x}) . \quad (2.8)$$

Groundwater age, a , is defined as $a = t - t_R$. From the CDF of recharge times, $F(t_R; t, \mathbf{x})$ and PDF of recharge times, $f_{t_R}(t_R; t, \mathbf{x})$, we can define a CDF of groundwater age, $F_a(a; t, \mathbf{x})$ and PDF of groundwater age, $f_a(a; t, \mathbf{x})$, given by

$$f_a(a; t, \mathbf{x}) = \frac{\partial}{\partial a} F_a(a; t, \mathbf{x}) . \quad (2.9)$$

Under steady flow conditions, $F_a(a; t, \mathbf{x})$ is independent of t_R so solving (2.4) for a single recharge time is sufficient. However, under transient conditions, (2.4) must be solved for multiple recharge times. If the number of potential recharge times is large, this approach is not practical. In contrast, Ginn [22] developed a governing equation for groundwater age that includes an age dimension; thus the PDF of groundwater age over multiple recharge times can be obtained by only one simulation. This governing equation for groundwater age is given by [22, 60].

$$\frac{\partial(\theta\rho)}{\partial t} = \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial \rho}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\theta v_i \rho) - \frac{\partial}{\partial a} (\theta \rho) \quad (2.10)$$

$$\rho(\mathbf{x}, a, t) = \rho \text{ on } \Gamma_1 \quad (2.11)$$

$$\left[D_{ij} \frac{\partial \rho}{\partial x_j} - v_i \rho \right] \cdot \mathbf{n}_i = -v_{2i} \rho_2 \cdot \mathbf{n}_i \text{ on } \Gamma_2 \quad (2.12)$$

where a is the age dimension and $\rho = \rho(\mathbf{x}, a, t)$ is the mass density of water at time t and a point \mathbf{x} with an age of a , and ρ_2 is the mass density of water crossing Γ_2 . The term containing the derivative with respect to age, a , represents the aging of the water mass at a unit rate, e.g., 1 year per year. It has a similar form as the advection term, and can therefore be simulated as advective transport in the age dimension at a unit velocity [60]. Although (2.10) can be solved to obtain a groundwater age distribution, it cannot be solved by conventional groundwater flow and transport simulators, except under special situations.

Groundwater age is a measurement of the amount of time that water particles have been in the aquifer. It also represents the amount of time an aqueous chemical tracer has been in the aquifer because a tracer travels through the aquifer at the same rate as a water particle. This similarity in behavior of water and tracer movement has led to the application of groundwater age as a tool to assess the groundwater well contamination.

An older groundwater represents a longer amount of time that an aqueous contaminant takes to reach the well. This affects the groundwater well contamination in two competing ways. First, wells at the locations with older groundwater are more distant from the source of contamination than at the locations with younger groundwater. Contaminant concentrations at the more distant

locations are lower because of dispersion. Thus, wells at the locations with older groundwater should represent lower levels of contamination. However, in some situations, an older groundwater can lead to increased groundwater well contamination. For example, if the wells are contaminated and the source is removed to prevent further contamination, these wells will remain contaminated until all of the contaminated water that has already recharged the aquifer passes them. In wells with older groundwater, contamination will persist for a longer time.

For sorbing solutes, the solute does not travel through the aquifer at the same rate as a water particle; thus, groundwater age is not an appropriate tool for assessing groundwater well contamination for these chemicals. Instead, my research introduces a new concept, called “solute age”, that represents the amount of time that a solute particle has been in the aquifer. For non-sorbing solutes, solute age in a water sample is equivalent to groundwater age. However, for sorbing solutes, which travel at a slower rate than water particles, solute age in a water sample is greater than the groundwater age. In the context of groundwater well contamination, if a well is contaminated with a sorbing solute and the source of contamination is eliminated, the contamination will persist for a longer time than would be expected based on groundwater age.

For a reactive solutes, specifically for decaying solutes, the amount of contamination may decrease over time. Thus, in the case of solute age for decaying contaminants, a given point in the aquifer is less susceptible to becoming contaminated or reaching an unacceptable level of contamination compared to the case of groundwater age. Furthermore, the contaminants may decrease to concentrations that are below levels of concern.

The goal of this study is to introduce solute age as a tool for assessing the contamination at a groundwater well. In the next section, we derive the governing equations for solute age. Next, we investigate the effects of sorption and decay on solute age and the persistence of contamination at a groundwater well under steady state conditions. In this work, we focus on linear equilibrium sorption and first-order decay; however, the approach could potentially be applied to other sorption and reaction models.

2.1 Governing equations of solute age

We derive the governing equations of mean solute age and the solute age distribution based on the approaches used to derive the governing equation of groundwater age [24, 56]. In order to obtain the governing equation and the boundary conditions of mean solute age, we use the same basic approach as Goode [24], and define two new quantities, and apply them to the ADE and the boundary conditions. An assumption used to derive the governing equation of mean groundwater age at a point in the domain is that the temporal integral of concentration is uniform throughout the domain. For decaying solutes, however, the temporal integral of concentration is not uniform so we cannot derive the governing equation of mean solute age for a decaying solute based on the approach of Goode [24]. Thus, we derive the governing equation of mean solute age only for a sorbing solute.

In order to obtain the equation for solute age distribution, we use the similar concept to that Varni and Carrera [56] used to derive the governing equation for groundwater age distribution, which is valid for both sorbing and decaying solutes (2.32). The methods used to derive the governing equation for mean solute age and solute age distribution are shown in Section 2.1.1 and 2.1.2, respectively.

2.1.1 Mean solute age

Following Goode [24], we define two quantities, E and M , as

$$E = \int_0^{\infty} tc \, dt \quad (2.13)$$

$$M = \int_0^{\infty} c \, dt \quad (2.14)$$

where c is flux concentration, E represents a time-weighted average concentration, and M is related to the total mass of contaminant. Under steady flow conditions and when the mass flux across the

boundary is proportional to water flux, M is uniform [24, 52]. Using these quantities, the mean groundwater age is given by Goode [24],

$$A = \frac{E}{M} = \frac{\int_0^\infty tc \, dt}{\int_0^\infty c \, dt} \quad (2.15)$$

where A is the mean groundwater age.

Goode [24] developed the governing equation for mean solute age by multiplying each term in the ADE for a conservative solute by t , integrating each term over the time domain, using the definitions from (2.13) to (2.15), and rearranging to obtain the governing equation for mean groundwater age. We follow the same approach as Goode [24] to obtain the governing equation for mean solute age. We also require the mass flux across the boundary is proportional to the water flux, and we require steady flow conditions. To obtain the governing equation for mean solute age, we start with the ADE. Since in the case of decay, M in (2.14) is not uniform, we cannot use the approach of Goode [24] to obtain a mean solute age equation for a decaying solute. Therefore, we start with the ADE for a solute that exhibits only linear kinetic sorption which is given by

$$\theta \frac{\partial c}{\partial t} + \rho_b \frac{\partial c_s}{\partial t} = \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial c}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\theta v_i c) \quad (2.16)$$

$$\rho_b \frac{\partial c_s}{\partial t} = \rho_b \alpha_s (K_d c - c_s) \quad (2.17)$$

$$\left[D_{ij} \frac{\partial c}{\partial x_j} - v_i c \right] \cdot \mathbf{n}_i = 0 \text{ on } \Gamma_1 \quad (2.18)$$

$$\left[D_{ij} \frac{\partial c}{\partial x_j} \right] \cdot \mathbf{n}_i = 0 \text{ on } \Gamma_2 \quad (2.19)$$

where c_s is sorbed phase concentration (mass of solute per mass of solid), ρ_b is bulk density, α_s is the sorption rate constant, and K_d is partition coefficient.

We define two new quantities as $E_s = \int_0^\infty tc_s \, dt$ and $M_s = \int_0^\infty c_s \, dt$. With these definitions, we apply the approach of Goode [24] to (2.16) to (2.19) by multiplying each term by time, t , and integrating over the time domain, to obtain the governing equation of solute age with the boundary

conditions which are given by (see Appendix A)

$$\frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial A}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\theta v_i A) + \theta + \rho_b K_d = 0 \quad (2.20)$$

$$\rho_b \alpha_s (K_d A - A_s) + \rho_b K_d = 0 \quad (2.21)$$

$$\left[D_{ij} \frac{\partial A}{\partial x_j} - v_i A \right] \cdot \mathbf{n}_i = 0 \text{ on } \Gamma_1 \quad (2.22)$$

$$\left[D_{ij} \frac{\partial A}{\partial x_j} \right] \cdot \mathbf{n}_i = 0 \text{ on } \Gamma_2 \quad (2.23)$$

where $A_s = E_s/M$.

If the solute follows a linear equilibrium sorption model, $\alpha_s \rightarrow \infty$, so $A_s = K_d A$. With this condition, (2.20) and (2.21) simplify to

$$\frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial A}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\theta v_i A) + \theta R = 0 \quad (2.24)$$

where $R = 1 + \rho_b K_d / \theta$ is the retardation coefficient.

Equation (2.24) is similar to the governing equation for mean groundwater age, (2.1), except that the aging term is multiplied by R . The R in the aging term accounts for the fact that the sorbing solute travels at a rate of $1/R$ relative to a non-sorbing solute (or relative to groundwater), thus the travel time of the sorbing solute is a factor of R longer than the travel time of a non-sorbing solute or groundwater particle. Consequently, the sorbing solute has an age of R times older than a non-sorbing solute or groundwater.

2.1.2 Solute age distribution

Varni and Carrera [56] developed an expression for the CDF of recharge time in order to obtain an expression for the groundwater age distribution. They defined $F(t_R; t, \mathbf{x})$ to represent the portion of water particles at \mathbf{x} at time t that entered the aquifer at or after time t_R . The quantity, F , is equivalent to the concentration of a tracer that started entering the aquifer at time t_R with unit concentration, and therefore F is governed by the ADE [56].

To obtain the equation for solute age distribution, we use a similar concept in the context of solute age. We define $F(t_R; t, \mathbf{x})$ to present the portion of water particles at \mathbf{x} that contain dissolved solute that entered the aquifer at or before time t_R . Then, the quantity F is equivalent to the concentration of a reactive chemical that started entering the aquifer at or after time t_R with unit concentration, and that is undergoing the same reaction processes as the solute.

In this case, F is governed by the ADE for a solute that exhibits linear kinetic sorption with first-order decay, given by

$$\theta \frac{\partial F}{\partial t} + \rho_b \frac{\partial F_s}{\partial t} = \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial F}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\theta v_i F) - \lambda_a \theta F - \lambda_s \rho_b F_s \quad (2.25)$$

$$\rho_b \frac{\partial F_s}{\partial t} = \rho_b \alpha_s (K_d F - F_s) - \lambda_s \rho_b F_s \quad (2.26)$$

$$F(t_R; t, \mathbf{x}) = 0 \quad t \leq t_R \quad (2.27)$$

$$F_s(t_R; t, \mathbf{x}) = 0 \quad t \leq t_R \quad (2.28)$$

$$F(t_R; t, \mathbf{x}) = H(t - t_R) \text{ on } \Gamma_1 \quad (2.29)$$

$$\left[D_{ij} \frac{\partial F}{\partial x_j} - v_i F \right] \cdot \mathbf{n}_i = -v_{2i} F_2 \cdot \mathbf{n}_i \text{ on } \Gamma_2 \quad (2.30)$$

where λ_a is the first-order decay rate in aqueous phase, and λ_s is the first-order decay rate in sorbed phase. The solute is assumed to be entirely in the aqueous phase as it enters the aquifer because the solute that enters the aquifer through natural or artificial recharge will necessarily be in the aqueous phase. For the equation of solute age distribution, we define F_s as the ratio of sorbed phase concentration (units of mass of solute per mass of solid) to the unit source concentration in the aqueous phase (units of mass of solute per volume of water). Note that F_s is not a CDF.

If the solute follows a linear equilibrium sorption model, $\alpha_s \rightarrow \infty$, $F_s = K_d F$ and $\lambda_a = \lambda_s$, (2.25) and (2.26) simplify to

$$R\theta \frac{\partial F}{\partial t} = \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial F}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\theta v_i F) - \lambda_a \theta R F \quad (2.31)$$

Equation (2.31) is similar to the governing equation for the groundwater age distribution (2.4),

except for the addition of the retardation coefficient and the decay term in (2.31).

Under steady flow conditions, solute age, $a = t - t_R$, is independent of t_R , so we can define the CDF of solute age as

$$F_a(a; \mathbf{x}) = F(a; t, \mathbf{x} | t_R = 0) \quad (2.32)$$

and the PDF of solute age is given by

$$f_a(a; \mathbf{x}) = \frac{\partial F_a(a; \mathbf{x})}{\partial a}. \quad (2.33)$$

2.2 Examples

In this section, we present a hypothetical example to demonstrate the differences between solute age and groundwater age. We use a one-dimensional, homogeneous, confined aquifer (Figure 2.1), with specified head at the east boundary, specified flux at the west boundary, and a weak pumping well in the center of the domain. We assume steady flow conditions. We simulate solute age for four different conditions: (1) tracer (i.e., groundwater age), (2) linear equilibrium sorption, (3) first-order decay, (4) linear equilibrium sorption and first-order decay. We use MODFLOW-2000 [26] to simulate groundwater flow, and we use MT3DMS [62] to simulate solute age. Parameter values used in the simulations are shown in Table 2.2.

2.2.1 Mean solute age

To calculate mean solute age, we solve (2.24) using MT3DMS. We simulate the aging term as a zero-order growth term. Figure 2.2 shows the mean solute age as a function of position, and Table 2.2 shows the mean solute age at the pumping well (at $x = 500$ m). Figure 2.2 shows that mean solute age increases with distance from the recharge boundary. The solute enters the aquifer at the boundary at $x = 0$ m, so all solutes (tracer or reactive) have a mean solute age of $A = 0$ yr

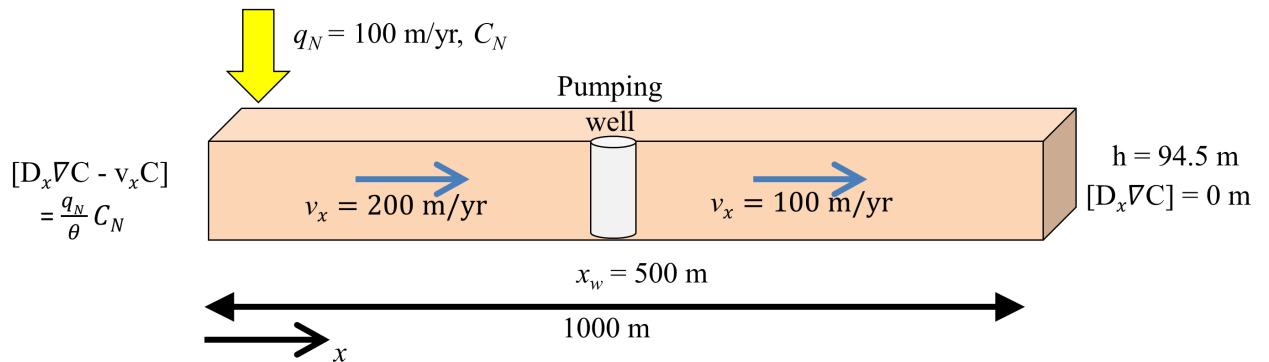


Figure 2.1: One-dimensional aquifer and boundary conditions used in the example problem.

Table 2.1: Flow and transport parameters for the example problem.

Parameter	Value
Length	1000 m
Spatial discretization, Δx	0.5 m
Transmissivity	1000 m ² /yr
Pumping well location, x_w	500 m
Pumping rate	50 m ³ /yr/ m ²
Source location	at $x = 0$ m (recharge boundary)
Recharge rate, q_N at the recharge boundary*	100 m/yr
Source concentration, C_N^\dagger	1 kg/m ³
Longitudinal dispersivity, α_L (where dispersion coefficient, $D_{11} = \alpha_L v_1$)	10 m
Porosity, θ	0.25
Retardation coefficient, R	2
Decay rate in aqueous phase, λ_a	0.25 yr ⁻¹

* q_N/θ represents v_{2i} in (2.30).

† C_N represents F_2 in (2.30).

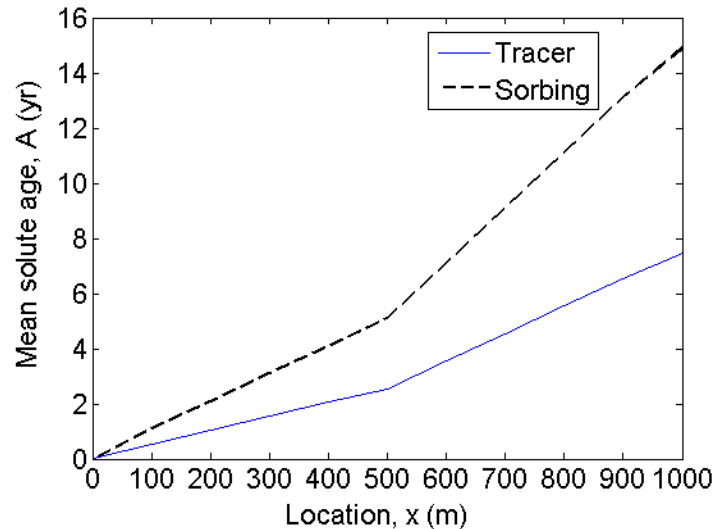


Figure 2.2: Mean solute age as a function of position downstream of the recharge boundary.

there. The advective travel time of a tracer from the recharge boundary to location \mathbf{x} is $t = x/v_1$, so the mean solute age of a tracer at location \mathbf{x} is approximately $A \approx x/v_1$. Note that since solutes are transported by both advection and dispersion, the mean solute age is not exactly equal to the advective travel time. The groundwater velocity upstream of the pumping well at $x_w = 500$ m is $v_1 = 200$ m/yr, so the plot of mean tracer age vs location in Figure 2.2 increases at a rate of 1yr/200 m. Downstream of the pumping well, the groundwater velocity decreases to $v = 100$ m/yr. Thus, a tracer travels more slowly downstream of the well and the mean solute age downstream of the well increases over distance at a higher rate.

Figure 2.2 also shows that mean solute age for a sorbing solute has the same shape as mean solute age for a tracer. However, at any location, mean solute age for a sorbing solute is a factor of R ($R = 2$) higher than the mean solute age for a tracer because sorbing particles travel through the aquifer at a rate of v/R . Mean solute age at the pumping well of sorbing solute is $A = 5.10$ yr, as compared to $A = 2.55$ yr for a tracer (Table 2.2).

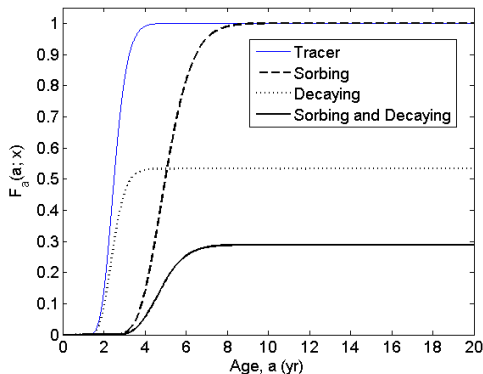


Figure 2.3: CDFs of solute age at the pumping well.

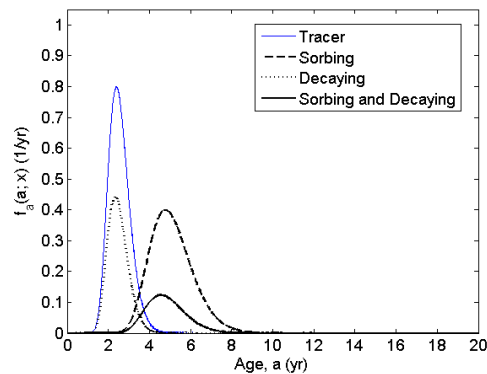


Figure 2.4: PDFs of solute age at the pumping well.

2.2.2 Solute age distribution

To obtain the solute age distribution, we solved (2.31) using MT3DMS, and used the results in (2.32) and (2.33) to obtain the CDFs (Figure 2.3) and PDFs (Figure 2.4) of solute age. Note that since this system has steady flow, solute age is independent of the recharge time, so we used a recharge time of $t_R = 0$ yr. Figure 2.3 shows the CDFs of solute age at the pumping well. The CDF represents the probability that the solute particles at the pumping well have an age of a or less. Figures 2.3 and 2.4 show that the solute age distribution at the pumping well for the tracer ranges from approximately 1 - 4 yr. For the sorbing solute, the distribution is shifted to older ages, approximately 3 - 8 yr. For the decaying solute, the distribution of ages is similar to the distribution of the tracer; however, the CDF reaches a maximum value of 0.53, indicating that 47 % of the solute particles decayed prior to reaching the pumping well. Similarly, for the sorbing and decaying solute, the distribution of ages is similar to the distribution for the sorbing solute; however, the CDF reaches a maximum value of 0.29, indicating that 71 % of the solute particles decay prior to reaching the well. Since the sorbing and decaying moves more slowly than the non-sorbing and decaying solute, a larger portion of it decays prior to reaching the pumping well.

We obtained the PDFs of solute age as in Figure 2.4 for all locations in the domain (see Appendix B), and we used them to calculate the mean solute age at each location. These ages are

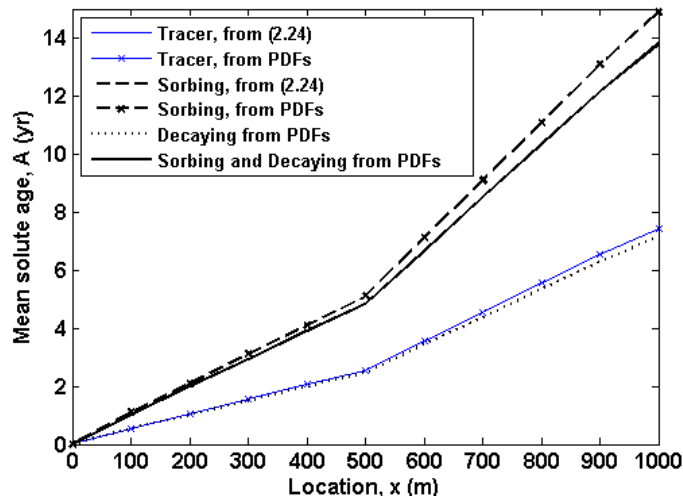


Figure 2.5: Mean solute age as a function of position downstream of the recharge boundary calculated from PDFs.

plotted in Figure 2.5, along with the equivalent mean solute ages calculated using (2.24). Table 2.2 shows the mean solute ages at the pumping well calculated from (2.24) and from PDFs for the four different conditions. Figure 2.5 shows that mean solute age for a tracer and a sorbing solute calculated from PDFs of solute age are consistent with those calculated directly from (2.24). Table 2.2 shows that mean solute age at the pumping well of sorbing solute is $A = 5.10$ yr, as compared to $A = 2.55$ yr for a tracer. For a decaying solute, mean solute age at any location is slightly lower than mean solute age of a tracer because some particles decay before reaching that location. Table 2.2 shows that mean solute age at the pumping well of decaying solute is $A = 2.49$ yr, as compared to $A = 2.55$ yr for the tracer. Mean solute age at any location for a sorbing and decaying solute is older than mean solute age for a tracer because the sorbing solute travels more slowly. In addition, mean solute age at any location for a sorbing and decaying solute is slightly younger than mean solute age for a sorbing and non-decaying solute because some solute particles decay prior to reaching a given point in the aquifer. Table 2.2 shows that mean solute age at the pumping well for the sorbing and decaying solute is $A = 4.85$ yr, as compared to $A = 2.55$ yr for the tracer and $A = 5.10$ yr for the sorbing solute.

Table 2.2: Mean solute age at the pumping well.

Solute Type	Age (yr)	
	From (2.24)	From PDFs
Tracer	2.55	2.55
Sorbing	5.10	5.10
Decaying	NA	2.49
Sorbing and Decaying	NA	4.85

2.3 Discussion

In this section, we discuss the relationship between the results obtained from section 2.2 and groundwater well contamination, and the difference between groundwater well contamination assessed by groundwater age equations and solute age equations. Figure 2.6 shows the relative concentration of solute at the pumping well at $x = 500$ m as a function of time after removal of a source at $x = 0$ m for four different solutes (e.g. (1) tracer, (2) sorbing solute, (3) decaying solute, (4) sorbing and decaying solute). We use this figure and Figure 2.4 to discuss solute age in the context of groundwater well contamination.

Figure 2.4 shows that the distribution of groundwater ages in the pumping well ranges from 1 to 4 years, implying that water or tracer that enters the aquifer at $x = 0$ m will arrive at the well in 1 to 4 years. This also implies that if a source of a tracer at $x = 0$ m were removed, the well would remain contaminated for about 4 years, until all of the solute that entered the aquifer prior to source removal passed the well. This is confirmed in Figure 2.6, which shows the relative concentration of tracer in the well after removal of the source. Suppose an acceptable maximum contaminant level of the tracer is $0.05c_0$, where c_0 is the source concentration. After 3.5 years, the concentration of the tracer at the well is reduced to less than $0.05c_0$.

For a sorbing solute, Figure 2.4 shows that the distribution of solute ages in the pumping well ranges from 3 to 8 years, implying that sorbing solute that enters the aquifer at $x = 0$ m will arrive at the well in 3 to 8 years. This also implies that if a source of a sorbing solute at $x = 0$ m were removed, the well would remain contaminated for about 8 years, until all of the solute

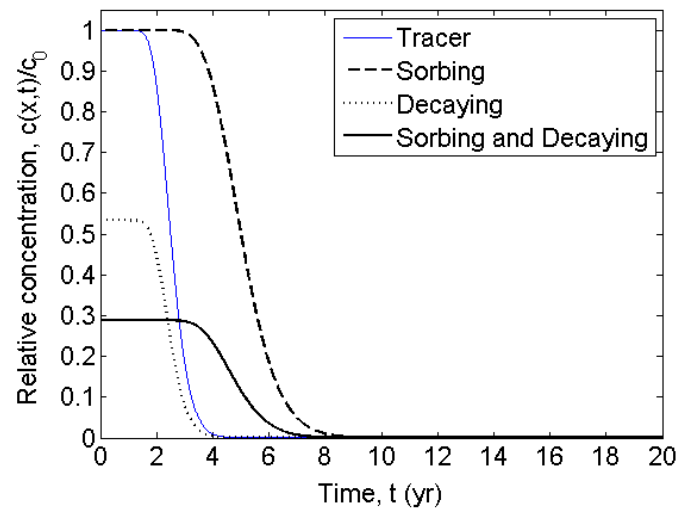


Figure 2.6: Concentration at the pumping well at $x = 500$ m as a function of time after source at $x = 0$ m was removed. c_0 is the source concentration.

that entered the aquifer prior to source removal passed the well. This is confirmed in Figure 2.6, which shows the relative concentration of sorbing solute in the well after removal of the source. Suppose an acceptable maximum contaminant level of the sorbing solute is $0.05c_0$. After 7 years, the concentration of the sorbing solute at the well is reduced to less than $0.05c_0$.

For a decaying solute, the solute age distribution in Figure 2.4 and the relative concentration as a function of time in Figure 2.6 are similar to the distributions for the groundwater age or tracer except that the magnitude is reduced because of decay; at early times, the magnitude is reduced by a smaller amount, while at later time, the magnitude is reduced by a larger amount. This implies that if a source of a decaying solute at $x = 0$ m were removed, the well would remain contaminated for the similar time to a tracer. Suppose an acceptable maximum contaminant level of the sorbing solute is $0.05c_0$. The well will remain contaminated with the decaying solute for a slightly shorter time than with the tracer. This is shown in Figure 2.4 where the distribution of solute age of the decaying solute is slightly narrower than the distribution for the tracer, and in Figure 2.6, where the relative concentration for the decaying solute is achieved in 3.2 years after removal of source, which is earlier than for the tracer.

For a sorbing and decaying solute, the solute age distribution in Figure 2.4 and the relative concentration as a function of time in Figure 2.6 are similar to the distributions for a sorbing solute except that the magnitude is reduced because of decay. Thus, suppose the maximum contaminant level of the sorbing solute is $0.05c_0$, the well would remain contaminated with the sorbing and decaying solute for a longer time than with the tracer but for a shorter time than with the sorbing solute. This is confirmed in Figure 2.6 which shows that the concentration of sorbing and decaying solute at the well is reduced to less than $0.05c_0$ within 6.5 years after source removal, whereas, the concentration of tracer, and sorbing solute are reduced to less than $0.05c_0$ within 3.5 and 7 years of source removal, respectively.

These examples illustrate that the well will remain contaminated with a sorbing solute even after an amount of time equal to the maximum groundwater age has elapsed. On the other hand, a well may remain contaminated by a decaying solute for a slightly shorter time than the maximum

groundwater age. Thus, if groundwater age (which is equivalent to the tracer travel time) were used to assess groundwater well contamination, the persistence of contamination at a well to the sorbing solutes or decaying solute would be misdiagnosed.

2.4 Conclusion

Groundwater age is often used to assess groundwater well contamination. Because tracers travel at the same rate as groundwater, the groundwater age distribution at a location of interest in the aquifer also represents the distribution of travel times of a tracer from a recharge source to the location of interest. For this reason, the groundwater age distribution also represents the length of time that the location of interest will remain contaminated after the source of the tracer is removed. Groundwater age can be obtained through numerical simulations.

Goode [24] presented an approach for obtaining the governing equation of mean groundwater age. Solving the governing equation of mean groundwater age gives mean age as a function of location. Varni and Carrera [56] presented an approach for obtaining the governing equation of groundwater age distribution. Solving the governing equation of groundwater age distribution gives a CDF for the recharge time distribution, and taking the derivative of CDFs over recharge times gives a PDF of recharge time. The CDF and PDF of groundwater age are obtained from the CDF and PDF of recharge time by making a variable substitution of $a = t - t_R$ where a is age and t_R is recharge time.

For a sorbing solute or a decaying solute, the travel time of the solute is not equivalent to the travel time of groundwater. For example, a solute that exhibits linear equilibrium sorption travels more slowly than groundwater because of retardation. For a decaying solute, the solute travels at the same rate as groundwater (or a tracer); however, as a decaying solute travels to an observation point, the contaminant particles decay over time. Thus, upon removal of contaminant source, the concentration of the decaying solute at the observation point would reach an acceptable level of contamination of the decaying solute more rapidly than a tracer. Thus, groundwater age is not an appropriate measure of the persistence of groundwater well contamination to reactive solutes.

Instead, we introduced a new concept called solute age which represents the amount of time since the solutes has recharged the aquifer.

We used the approach of Goode [24] to derive the governing equation of mean solute age for a sorbing solute. Because this approach assumes that the temporal integral of concentration is uniform throughout the aquifer, it is not appropriate for decaying solutes. However, it is appropriate for sorbing solutes. We used the approach of Varni and Carrera [56] to derive the governing equation for solute age distributions for both sorbing and decaying solutes. The CDFs and PDFs of solute age for sorbing solutes are shifted to older ages relative to the distribution of groundwater age because the sorbing particles travel slowly than tracer or groundwater. In view of groundwater well contamination, this implies that a pumping well contaminated by a sorbing solute would remain contaminated for a longer time after source removal than a non-sorbing solute or by what would be expected based on groundwater age. Also, PDF of a decaying solute (non-sorbing) has the same range of age distribution as groundwater age; however, the CDF reaches the maximum value of less than 1. In view of groundwater well contamination, this implies that the pumping well contaminated by a decaying solute would remain contaminated for approximately the same amount of time after source removal as water contaminated with a tracer. However, it will be contaminated with the lower level of contamination than for the case of a tracer. This is because the contaminant particles released at long time ago are already decayed before they reach the pumping well.

The examples presented in this study are based on solutes that exhibit linear equilibrium sorption and first-order decay. The time that an aquifer that is contaminated with a sorbing and decaying solute will take to become uncontaminated, and the level of contamination at the observation point are affected by both sorbing and decaying parameters. Also, these parameters affect the differences between solute age and groundwater age through the applications on the assessment of groundwater well contamination. Therefore, an additional work is need to determine solute age for different sorption models and different reactions.

Chapter 3

Adjoint simulation of solute age

3.1 Introduction

The solute age of a groundwater sample quantifies the amount of time since the solute has entered the aquifer. Any groundwater sample contains a mixture of parcels that recharge the aquifer at different times; thus, a groundwater sample can represent a distribution of solute ages. For a non-sorbing and non-reactive solute, solute age is equivalent to groundwater age. For a sorbing solute, the contaminant moves more slowly than groundwater. As a result, the solute age of a sorbing contaminant will be higher than groundwater age for the same water sample. For the case of a decaying solute, the older solute particles are more likely to have decayed before reaching the observation point so the solute age distribution is shifted toward a younger age relative to a groundwater age distribution.

Solute age has several applications. Chapter 2 demonstrates that solute age is a useful tool for quantifying aquifer vulnerability to a persistent source of contamination. If the source of contamination is removed, a pumping well in the aquifer will remain contaminated until all of the residual contamination has passed the well. The distribution of solute ages at the well is a measure of the amount of time after source removal that a well will remain contaminated. A longer time is needed for a sorbing contaminant than for a non-sorbing contaminant. Also, solute age can be used to prioritize change in land use. For example, different land uses can provide different sources of contamination, and solute age for a different solutes can be used as a tool to determine how long the pumping well will remain contaminated after changing the land use. A possible application

includes prioritizing remediation activities. If a well is contaminated from several different sources, e.g. several different agricultural fields, solute age can be used to determine which of the sources should be remediated first to produce the most rapid improvement to the water quality at the well.

These examples show that solute age is generally applied at a single observation location, such as a pumping well, whereas, the source of solute can be distributed over space and time. Standard groundwater flow and transport simulations can be used to simulate the movement of solute and the distribution of solute age. To obtain a distribution of solute age at a particular location (e.g. a pumping well) and a particular time, it would be necessary to run multiple simulations of a forward transport model, with different solute release times in each simulation [56]. This approach is computationally intensive. Thus, in this chapter, we introduce the adjoint approach as an alternative to calculate solute age distribution.

In the adjoint approach, the flow field is reversed, and information is propagated upgradient in backward time from the observation point to all possible source locations and release times. For a source released at a specific location (e.g. an injection well) and different release times, we can obtain solute age distribution at a particular location and a particular time by running only one simulation. Also, conventional flow and transport simulators can be used to solve the adjoint equation. Thus, the adjoint approach is more efficient for obtaining solute age distribution.

The adjoint approach has been used in a variety of groundwater applications. Neupauer and Wilson [37, 38] developed an adjoint equation of solute transport to identify the release time of contaminant in the aquifer. The adjoint approach also has been used to determine the remaining time before the contaminant at a particular point reached the observation point [11, 21]. Cornaton et al. [11] used the adjoint approach to assess the effectiveness of waste repositories by determining the remaining time before toxic contaminant from the repository locations reaches the biosphere. Neupauer and Wilson [42] used the adjoint approach to calculate the capture zone of a pumping well, which is the region around a pumping well that contributes groundwater to the well within a particular time. Molson et al. [36] used the adjoint approach to assess the vulnerability of a water supply well to the unknown source within the capture zone by determining the expected time to

reach maximum concentration at the well and the exposure time to concentration at the well above threshold.

In the next section, I present the governing equation of solute age for a solute that exhibits linear kinetic sorption and first-order decay. The governing equation of solute age in this chapter includes an internal source and sink terms and the dispersive flux boundary which were not included in the governing equation of solute age presented in Chapter 2. In Section 3.3, I present the adjoint equation of solute age. In Section 3.4, I demonstrate the accuracy of my adjoint equation through a hypothetical two-dimensional aquifer by comparing the results with solute age derived from the adjoint equation shown in Section 3.3 to the governing equation of solute age shown in Section 3.2.

3.2 Forward equations of solute age

The forward governing equation of solute age was developed in Chapter 2 following the approach of Varni and Carrera [56]. The state variable in the equation is $F(t_R; t, \mathbf{x})$ which represents the portion of solute particles arriving at location \mathbf{x} and time t that entered the aquifer at or after time t_R . It represents a cumulative distribution function (CDF) of recharge time t_R . The quantity F is related to the concentration of a reactive chemical that started entering the aquifer at time t_R with unit concentration; thus, the governing equation for $F(t_R; t, \mathbf{x})$ has the same form as the

advection-dispersion equation (ADE), given by

$$\theta \frac{\partial F}{\partial t} + \rho_b \frac{\partial F_s}{\partial t} = \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial F}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\theta v_i F) - \lambda_a \theta F - \lambda_s \rho_b F_s \quad (3.1)$$

$$+ q_I F_v - q_O F$$

$$\rho_b \frac{\partial F_s}{\partial t} = \rho_b \alpha_s (K_d F - F_s) - \lambda_s \rho_b F_s \quad (3.2)$$

$$F(t_R; t = 0, \mathbf{x}) = 0 \quad (3.3)$$

$$F_s(t_R; t = 0, \mathbf{x}) = 0 \quad (3.4)$$

$$F(t_R; t, \mathbf{x}) = g_1(\mathbf{x}, t) \text{ on } \Gamma_1 \quad (3.5)$$

$$\left[D_{ij} \frac{\partial F}{\partial x_j} \right] \cdot \mathbf{n}_i = g_2(\mathbf{x}, t) \text{ on } \Gamma_2 \quad (3.6)$$

$$\left[D_{ij} \frac{\partial F}{\partial x_j} - v_i F \right] \cdot \mathbf{n}_i = g_3(\mathbf{x}, t) \text{ on } \Gamma_3 \quad (3.7)$$

where x_i are the spatial directions ($i = 1, 2, 3$), v_i is groundwater velocity in the x_i direction, θ is porosity, λ_a is the first-order decay rate in aqueous phase, λ_s is the first-order decay rate in sorbed phase, q_I is the volumetric inflow rate per unit volume, q_O is the volumetric outflow rate per unit volume, $g_1(\mathbf{x}, t)$, $g_2(\mathbf{x}, t)$, and $g_3(\mathbf{x}, t)$ are known functions, and Γ_1 , Γ_2 , and Γ_3 are domain boundaries. D_{ij} is the i, j^{th} component of dispersion tensor where $D_{11} = \alpha_L(v_1^2/|v|) + \alpha_{TH}(v_2^2/|v|)$, $D_{22} = \alpha_L(v_2^2/|v|) + \alpha_{TH}(v_1^2/|v|)$, and $D_{12} = D_{21} = (\alpha_L - \alpha_{TH})(v_1 v_2/|v|)$ where $|v| = \sqrt{v_1^2 + v_2^2}$ is the magnitude of the velocity vector. $F_v(t_R; t > t_R, \mathbf{x}) = H(t - t_R)$ represents a unit release of solute and the recharge area for $t > t_R$ where H is the Heavyside function and t_R is the recharge time. $F_s(t_R; t, \mathbf{x})$ is defined as the ratio of sorbed phase concentration (units of mass of solute per mass of solid) to the unit source concentration in the aqueous phase (units of mass of solute per volume of water). Note that $F_s(t_R; t, \mathbf{x})$ is not a CDF. If the solute follows a linear equilibrium sorption model, $\alpha_s \rightarrow \infty$, $F_s(t_R; t, \mathbf{x}) = K_d F(t_R; t, \mathbf{x})$ and $\lambda_a = \lambda_s$, (3.1) and (3.2) simplify to

$$R\theta \frac{\partial F}{\partial t} = \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial F}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\theta v_i F) - \lambda_a \theta R F + q_I F_v - q_O F \quad (3.8)$$

where $R = 1 + \rho_b K_d / \theta$ is the retardation coefficient.

The probability density function (PDF) of recharge time, $f_{t_R}(t, t_R, \mathbf{x})$, is calculated from the CDF using

$$f_{t_R}(t; t, \mathbf{x}) = \frac{\partial}{\partial t_R} F(t; t, \mathbf{x}). \quad (3.9)$$

Groundwater age, a , is defined as $a = t - t_R$. From the CDF of recharge times, $F(t, t_R, \mathbf{x})$ and PDF of recharge times, $f_{t_R}(t, t_R, \mathbf{x})$, we can define a CDF of solute age, $F_a(a, t_R, \mathbf{x})$ and PDF of solute age, $f_a(a, t_R, \mathbf{x})$, given by

$$f_a(a; t, \mathbf{x}) = \frac{\partial}{\partial a} F_a(a; t, \mathbf{x}). \quad (3.10)$$

Under steady flow conditions, solute age, $a = t - t_R$, is independent of t_R , so we can define the CDF of solute age as

$$F_a(a; \mathbf{x}) = F(a; t, \mathbf{x} | t_R = 0) \quad (3.11)$$

and the PDF of solute age is given by

$$f_a(a; \mathbf{x}) = \frac{\partial F_a(a; \mathbf{x})}{\partial a}. \quad (3.12)$$

Equation (3.1) is considered as a forward equation that is solved using forward modeling. With one simulation, we obtain $F(t_R; t, \mathbf{x})$ for all t and \mathbf{x} for a single recharge time t_R . To obtain the full CDF of recharge time, (3.1) must be solved multiple times for different values of t_R , which is inefficient. Alternatively, we introduce the adjoint equation for solute age as shown in the next section, which can produce the full CDF with just one simulation and therefore is computationally more efficient.

3.3 Adjoint equations of solute age

In this section, we derive the adjoint equation of solute age from the ADE for a solute that exhibits linear kinetic sorption with first-order decay, given by

$$\theta \frac{\partial c}{\partial t} + \rho_b \frac{\partial c_s}{\partial t} = \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial c}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\theta v_i c) - \lambda_a \theta c - \lambda_s \rho_b c_s + q_I c_N - q_O c \quad (3.13)$$

$$\rho_b \frac{\partial c_s}{\partial t} = \rho_b \alpha_s (K_d c - c_s) - \lambda_s \rho_b c_s \quad (3.14)$$

$$c(\mathbf{x}, 0) = c_o(\mathbf{x}) \quad (3.15)$$

$$c_s(\mathbf{x}, 0) = c_{so}(\mathbf{x}) \quad (3.16)$$

$$c(\mathbf{x}, t) = g_1(\mathbf{x}, t) \text{ on } \Gamma_1 \quad (3.17)$$

$$\left[D_{ij} \frac{\partial c}{\partial x_j} \right] \cdot \mathbf{n}_i = g_2(\mathbf{x}, t) \text{ on } \Gamma_2 \quad (3.18)$$

$$\left[D_{ij} \frac{\partial c}{\partial x_j} - v_i c \right] \cdot \mathbf{n}_i = g_3(\mathbf{x}, t) \text{ on } \Gamma_3 \quad (3.19)$$

where c is aqueous concentration, c_s is sorbed phase concentration, c_N is inflow concentration, c_o is initial concentration in aqueous phases, and c_{so} is initial concentration in sorbed phase. We apply the sensitivity analysis approach of Sykes et al., [55] to (3.13) to (3.19) to derive the adjoint equation of solute age and the boundary and final conditions. As stated above, the CDF of arrival time between the recharge area and the observation location of interest, \mathbf{x}_w , is equivalent to the concentration at the observation location due to a unit release of concentration from the recharge location, thus, in terms of a sensitivity, the CDF can be expressed as

$$F_t(t; \mathbf{x}, t_R) = \frac{dc(\mathbf{x}_w, t_w)}{dc_N(t_R)}. \quad (3.20)$$

We are actually interested in the CDF of solute age, $a = t - t_R$. Using a change of variables on the previous equation, the CDF of solute age is given by

$$F_a(a; t, \mathbf{x}) = \frac{dc(\mathbf{x}_w, t_w)}{dc_N(t - a)}. \quad (3.21)$$

This CDF is based on the concentration at a specific location and time, for many different ages or, equivalently, for many different values of t_R .

Since (3.13)-(3.19) requires one simulation for each value of t_R , it is inefficient to obtain this CDF from (3.13) - (3.19). Instead, we use sensitivity analysis to obtain the adjoint of (3.13) - (3.19) that more directly solves for this CDF. Using sensitivity analysis, the CDF in (3.21) is rewritten as (Appendix C)

$$\frac{dc(x_w, \tau_w)}{dc_N} = \iint_{\Omega, \tau} q_I \phi(\mathbf{x}, \tau) d\Omega d\tau \quad (3.22)$$

where Ω is model domain. The PDF of solute age is given by

$$f_a(a; \tau, \mathbf{x}) = \frac{\partial F_a(a; \tau, \mathbf{x})}{\partial a} = \int_{\Omega} q_I \phi(\mathbf{x}, \tau) d\Omega \quad (3.23)$$

where ϕ is an adjoint state obtained by solving the adjoint equation given by (see Appendix C)

$$\theta \frac{\partial \phi}{\partial \tau} + \rho_b \frac{\partial \phi_s}{\partial \tau} = \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial \phi}{\partial x_j} \right) + \frac{\partial}{\partial x_i} (\theta v_i \phi) - \lambda_a \theta \phi - \lambda_s \rho_b \phi_s \quad (3.24)$$

$$-q_I \phi + \delta(x_1 - x_{1_w}) \delta(x_2 - x_{2_w}) \delta(x_3 - x_{3_w}) \delta(\tau)$$

$$\rho_b \frac{\partial \phi_s}{\partial \tau} = \rho_b \alpha_s (K_d \phi - \phi_s) - \lambda_s \rho_b \phi_s \quad (3.25)$$

$$\phi(\mathbf{x}, \tau = \tau_w) = 0 \quad (3.26)$$

$$\phi_s(\mathbf{x}, \tau = \tau_w) = 0 \quad (3.27)$$

$$\phi(\mathbf{x}, \tau) = 0 \text{ on } \Gamma_1 \quad (3.28)$$

$$\left[D_{ij} \frac{\partial \phi}{\partial x_j} + v_i \phi \right] \cdot \mathbf{n}_i = 0 \text{ on } \Gamma_2 \quad (3.29)$$

$$\left[D_{ij} \frac{\partial \phi}{\partial x_j} \right] \cdot \mathbf{n}_i = 0 \text{ on } \Gamma_3 \quad (3.30)$$

where ϕ is adjoint state of aqueous phase concentration, ϕ_s is adjoint state of sorbed phase concentration, and τ is backward time. This equation assumes steady flow or negligible specific storage. If the solute follows a linear equilibrium sorption model, $\alpha_s \rightarrow \infty$, so $c_s = K_d c$, and (3.24) and (3.25) simplify to

$$R\theta \frac{\partial \phi}{\partial \tau} = \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial \phi}{\partial x_j} \right) + \frac{\partial}{\partial x_i} (\theta v_i \phi) - \lambda_a \theta R \phi - q_I \phi \quad (3.31)$$

$$+\delta(x_1 - x_{1_w}) \delta(x_2 - x_{2_w}) \delta(x_3 - x_{3_w}) \delta(\tau).$$

The adjoint equation and the initial and boundary conditions are similar to the forward equation of solute age, (3.1) to (3.8), with a few exceptions. The sign on the advection term in the adjoint equation is opposite to the forward equation, and internal sources in the forward equation becomes internal sinks in the adjoint equation. This allows for the upgradient propagation of information. Also, the sink term in the forward equation vanishes because the sink of solute is not a source of adjoint state. There is an additional load term in the adjoint equation that represents the source of adjoint state at the observation location and time. In addition, the second type boundary in

the forward equation becomes a third type boundary in the adjoint equation, and the third type boundary in forward equation becomes a second type boundary in the adjoint equation.

To obtain a distribution of solute ages at an observation point, a source of adjoint state is released at the observation location at the time of interest, and is propagated upgradient and backward in time through the solution of (3.24) - (3.31). The resulting adjoint state is used in (3.23) to obtain the distribution of solute ages for solute that entered at the recharge source.

3.4 Examples

In this section, we demonstrate a hypothetical example to present the consistency between solute age distribution derived from the forward equation of solute age and from the adjoint equation of solute age. The hypothetical aquifer (Figure 3.1) is a two-dimensional, homogeneous, confined aquifer, with specified head at the east and west boundaries. The specified head, h_1 , at the east boundary is constant to 94.5 m. The specified head at the west boundary varies with time,

$$h_1(x_1 = 0 \text{ m}, t) = \begin{cases} 129.475 \text{ m for } t \leq 20 \text{ yr} \\ 258.95 \text{ m for } t > 20 \text{ yr} \end{cases} \quad (3.32)$$

Although this change in head is physically unrealistic, we chose it to emphasize that the results of the adjoint approach are valid, even for substantial temporal changes in velocity. Figure 3.2 shows the head distributions for $t \leq 20$ years and for $t > 20$ years. The solute is released from a recharge area in the western part of the domain. The recharge rate, q_I , is given by

$$q_I = \begin{cases} 0.2 \text{ yr}^{-1} & 102.5 \text{ m} < x_1 < 152.5 \text{ m, and } 127.5 \text{ m} < x_2 < 177.5 \text{ m} \\ 0 & \text{otherwise.} \end{cases} \quad (3.33)$$

A weak pumping well is in the eastern part of the domain. We simulate the solute age distribution at the well using both the forward and adjoint approaches. We use MODFLOW-2000 [26] to simulate groundwater flow, and we use MT3DMS [62] to simulate solute age. Parameter values used in the

simulations are shown in Table 3.1.

3.4.1 Forward simulation

We use forward simulation to obtain the solute age distribution for water samples taken from the pumping well at various observation times (up to $t = 50$ yr). The solute age distribution is equivalent to the probability density function of solute age, $f_a(a; t, \mathbf{x})$, which can be obtained by differentiating the CDF of solute age with respect to age. The CDF of solute age is related to the CDF of recharge time, $F(t_R; t = t_w, \mathbf{x} = \mathbf{x}_w)$. Although this CDF can be obtained by solving (3.8), the solution of (3.8) produces the CDF for all times t for a specific value of the recharge time. Thus, we solve (3.8) multiple times, each for a different recharge time. In this work, we use recharge times of $t_R = 0$ yr, 0.1 yr, 0.2, yr, ... 49.9 yr, for a total of 500 simulations. Figure 3.3 shows the output of a subset of the 500 simulations, representing the CDF of recharge time plotted vs. time t . Each curve represents the output from one simulation, representing on recharge time t_R and many different times t . Note that these are CDFs of recharge time t_R , but are plotted against time t .

The CDF of recharge time for a given time t_w , $F(t_R; t = t_w, \mathbf{x} = \mathbf{x}_w)$, is obtained by extracting the value F at the time t_w from each of the curves in Figure 3.3. These CDFs are plotted in 3.4. Note that what is shown in Figure 3.4 is the probability that the recharge time is greater than t_R , unlike the normal way of presenting a CDF as the probability that the recharge time is less than or equal to t_R . Figure 3.5 shows the CDF of solute age, which is obtained by rescaling the horizontal axis of Figure 3.4 to $a = t - t_R$, and Figure 3.6 shows the PDF of solute age, obtained by numerically differentiating the CDFs in Figure 3.5 with respect to a .

For $t \leq 20$ yr, the flow field is steady. Solute that reaches the pumping well during this time entered the aquifer through the recharge area and traveled to the pumping well in approximately 2 to 5 years (solid blue curve in Figure 3.6). For example, consider solute that arrives at the well at $t = 15$ years (red solid line in Figure 3.4). Since the travel time between the recharge area and the well is approximately 2 to 5 years, solute that entered the aquifer at recharges times of 10 to

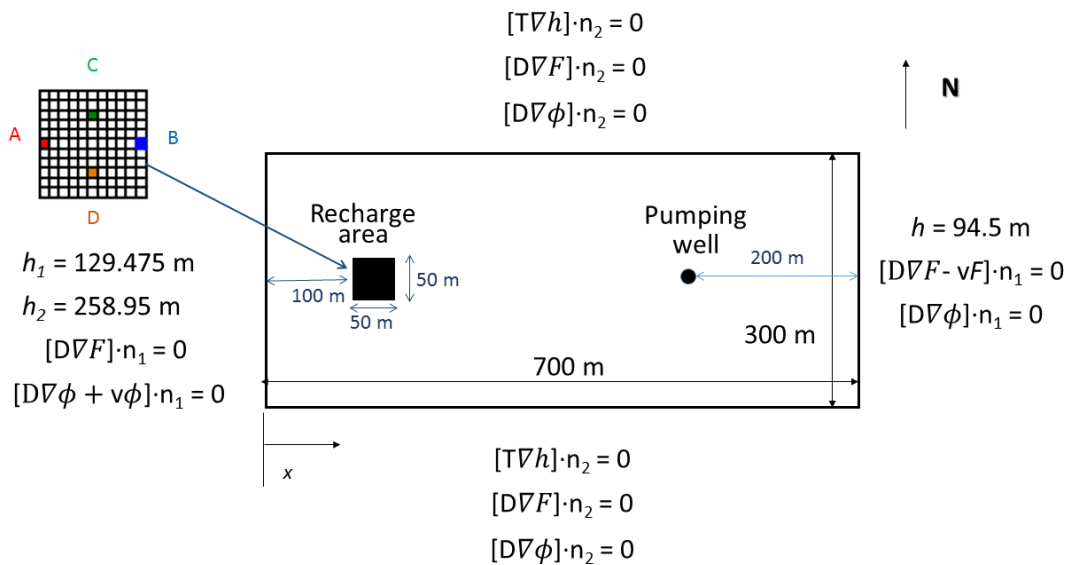


Figure 3.1: Two-dimensional aquifer and boundary conditions used in the example problem. A small box on the upper left hand side of the figure shows grid cells in recharge area used in the simulations, and A, B, C and D are locations where the adjoint distributions are shown in Figure 3.7 and 3.8.

Table 3.1: Flow and transport parameters for the example problem in two-dimensional forward and adjoint simulations.

Parameter	Value
Length	700 m
Width	300 m
Spatial discretization, Δx_1	5 m
Spatial discretization, Δx_2	5 m
Aquifer thickness, B	1 m
Transmissivity	1000 m ² /yr
Pumping well location, (x_{1w}, x_{2w})	(497.5 m, 152.5 m)
Pumping rate, Q_w	3 x 10 ⁵ m ³ /yr
Source location (recharge area)	50 x 50 m ²
Longitudinal dispersivity, α_L	10 m
Transverse dispersivity, α_{TH}	0.2 m
Horizontal dispersivity, α_H	0.2 m
Porosity, θ	0.25
Retardation coefficient, R	2

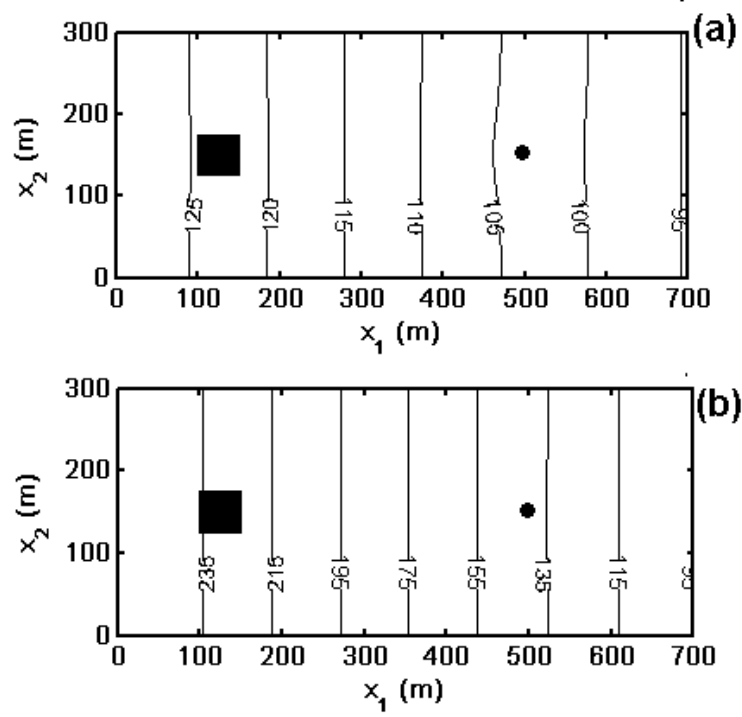


Figure 3.2: Head distribution (in m) for (a) $t \leq 20$ years and (b) $t > 20$ years. The black square denotes the recharge area, and the solid circle denotes the pumping well location.

14 years can arrive at the well at $t = 15$ years. As shown in Figure 3.4, the probability that the recharge time is greater than 13 years for solute that arrives at the well at $t = 15$ years is essentially zero, while the probability reaches a maximum for recharge times less than approximately 10 years. Note that the maximum value is approximately 0.094. This indicates that 9.4% of the solute that enters the aquifer at these recharge times will reach the well, while 91.6% of the solute will bypass the well.

Solute that reaches the pumping well for $t > 22$ years also experienced steady flow conditions, but now with travel times of approximately 0.5 to 1.5 years (cyan curve in Figure 3.6) between the recharge area and the well. Thus, the CDFs in Figure 3.4 show that for recharge times greater than $t - 0.5$ years, the probability of solute arriving at the well by time t is essentially zero; while for recharge times less than $t - 1.5$ years, the probability that solute would have arrived at the well by time t is at its maximum value. In this case, the maximum value is approximately 0.023, indicating that 2.3% of the solute reaches the well, while 97.7% of the solute bypasses the well. Less solute arrives at the well for $t > 22$ years than for $t \leq 20$ years because the total flow rate through the aquifer is higher, and therefore the well extracts a smaller portion of the overall flow. In other words, the capture zone of the pumping well is wider for $t \leq 20$ years and narrow for $t > 22$ years.

Solute that arrives at the well between 20 years $< t < 22$ years experienced transient flow conditions as it traveled from the recharge area to the well. Thus, the travel times fall between the ranges of travel times identified for the steady state conditions for $t \leq 20$ years and $t > 22$ years. Likewise, the distribution of ages varies with t in this range (Figure 3.6). Some of the solute that arrives at the well at $t = 20.5$ years entered the recharge area at $t_R = 20$ years, immediately after the flow field changed, and traveled on the fastest flow path from the recharge area to the well; thus the youngest ages of solute arriving at the well at $t = 20.5$ years are approximately 0.5 years (dashed blue line in Figure 3.6). Also, most of the solute that arrives at $t = 20.5$ years was already in the aquifer prior to the change in the flow field, so it experiences a combination of the fast and slow flow fields, so the PDF of solute ages is shifted toward younger ages, relative to the age distribution for $t \leq 20$ years. As the arrival time increases, the distribution of solute ages shifts

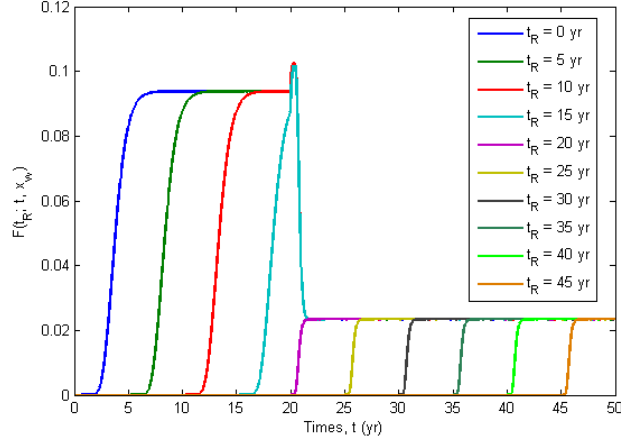


Figure 3.3: CDFs for recharge time at the pumping well under transient flow conditions for recharge time, t_R between 0 and 49.9 years.

towards younger ages (see Figure 3.6) because a larger proportion of the solute experiences the faster flow field. Note also that the maximum values of the CDFs of solute age also change (Figure 3.5). Some of the solute that was in the wider capture zone at $t \leq 20$ years is no longer in the narrower capture zone, so less solute mass arrives at the well, leading to maximum values of the CDF that fall between the two extreme values for $t \leq 20$ years and for $t > 22$ years.

3.4.2 Adjoint simulation

We use the adjoint method to obtain the solute age distribution for water samples taken from the pumping well at four different observations times, $t_w = 20$ yr, 20.5 yr, 21 yr, and 25 yr, or equivalently, $\tau_w = 30$ yr, 29.5 yr, 29 yr, and 25 yr, where backward time τ is defined as $\tau = t_f - t$ and $t_f = 50$ yr. We solved (3.31) by reversing the MODFLOW flow field from the forward simulation to allow upgradient propagation of the adjoint state. The load term in (3.31) was approximated as

$$\delta(x_1 - x_{1_w})\delta(x_2 - x_{2_w})\delta(x_3 - x_{3_w})\delta(\tau) \approx \frac{1}{\Delta x_{1_w} \Delta x_{2_w} B \Delta \tau} \quad (3.34)$$

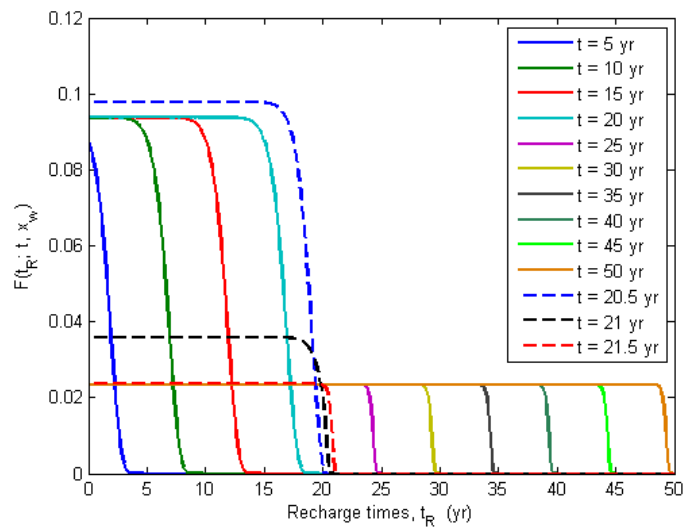


Figure 3.4: CDFs of recharge time at the pumping well under transient flow conditions.

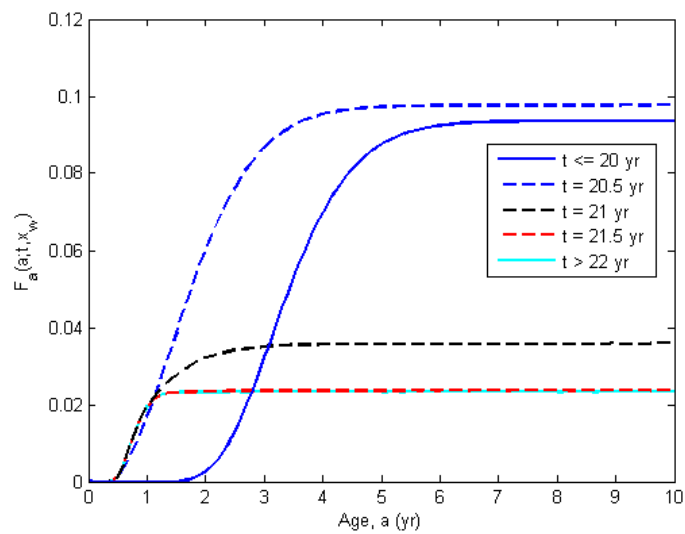


Figure 3.5: CDFs of solute age at the pumping well under transient flow conditions.

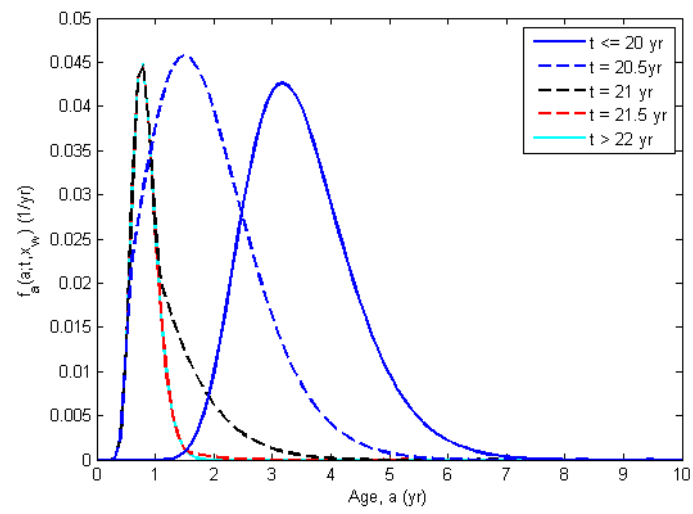


Figure 3.6: PDFs of solute age at the pumping well under transient flow conditions.

where B is the aquifer thickness. Also, it was introduced at the cell containing the well during the time step containing τ_w , where $\Delta\tau$ is the duration of the time step. The boundary conditions are shown in Figure 3.1. The resulting adjoint states are used in (3.23) to obtain the solute age distribution. Note that q_I is non-zero only at the recharge area, so only the adjoint states in the recharge area are used in (3.23).

The temporal distribution of the adjoint state for four grid block in the recharge area (see Figure 3.1 for the locations) for the simulation with $\tau_w = t_w = 25$ yr are shown in Figures 3.7 and 3.8, plotted against backward time τ and solute age $a = \tau - \tau_w$, respectively. Of the four points, point B is closest to the pumping well; therefore, solute that enters the aquifer at this point has the shortest travel time to the well and also the youngest ages. Point A is farthest from the well, so the solute age distribution for solute that entered at this location is shifted to slightly later times. Points C and D are an intermediate distance from the well, and the solute age distribution for solute that entered at either of these locations is shifted to older ages compared to Point B and to younger ages compared to Point A.

The complete solute age distributions for solute that was observed at the pumping well at $t_w = 20, 20.5, 21$ and 25 years, obtained by solving (3.23), are shown in Figure 3.9. The results from the forward simulation are also shown. These results show that the solute age distributions obtained using the adjoint approach match well with those obtained using the forward approach. Some slight discrepancies are apparent for $t_w = 20.5$ yr and $t_w = 21$ yr, due to the adjoint load being released over a finite duration $\Delta\tau$ (see (3.34)) instead of at an instant in time. This discrepancy is not apparent for $t_w = 20$ yr or $t_w = 25$ yr because the solute arriving at the well at these times only experiences a single steady state flow field, so the precise timing of the release is inconsequential. For all $t_w \leq 20$ yr, the solute age distribution would be equivalent to the distribution for $t_w = 20$ years. Also, the solute age distribution for any $t_w > 22$ yr is equivalent to the distribution for $t_w = 25$ yr.

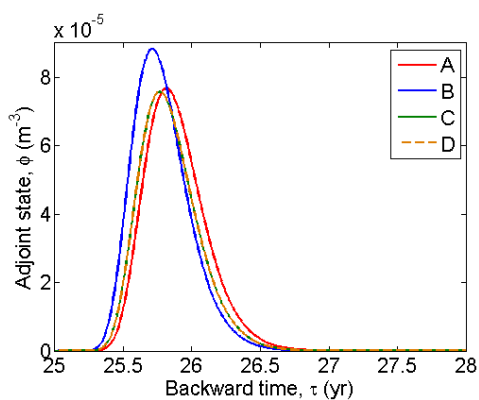


Figure 3.7: Temporal distribution of adjoint state over backward time observed at location A, B, C and D where $t_w = 25$ years and $\tau_w = 25$ years.

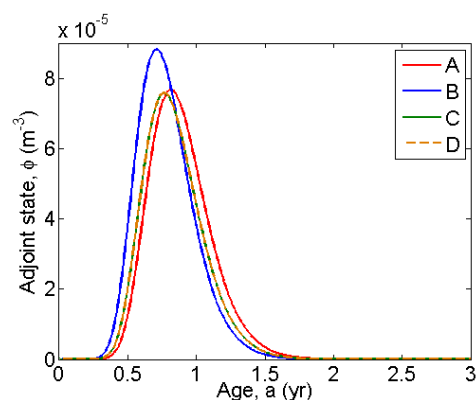


Figure 3.8: Temporal distribution of adjoint state over age observed at location A, B, C and D where $t_w = 25$ years and $\tau_w = 25$ years. Age in x-axis is derived by $\tau - \tau_w$.

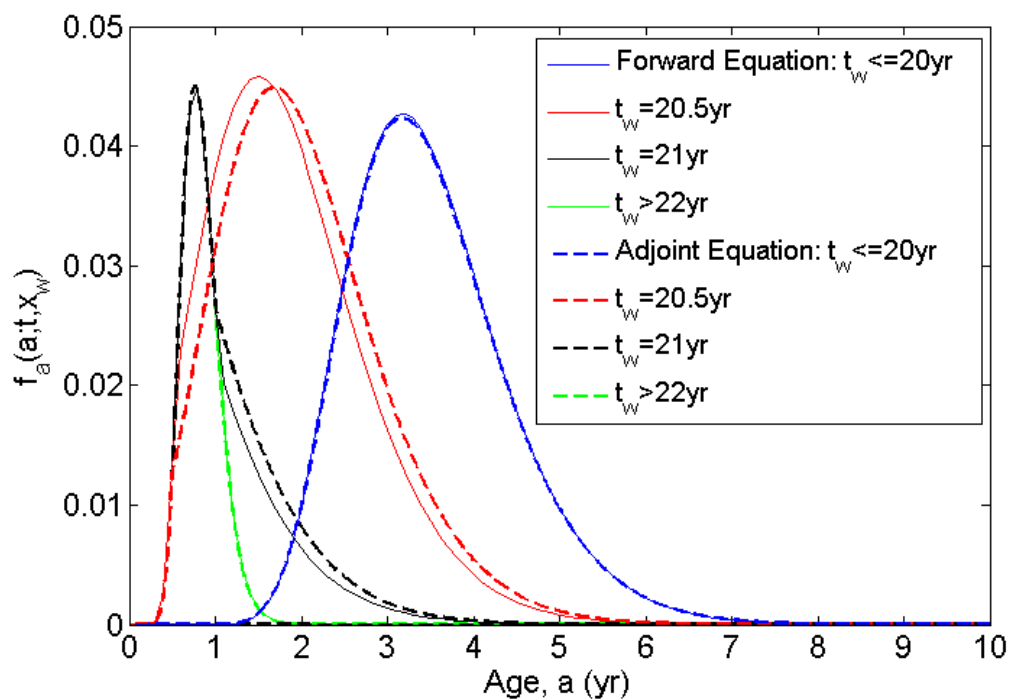


Figure 3.9: Comparison between PDFs of solute age from forward simulation and adjoint simulation at different times.

3.5 Discussion

The results shown in Figure 3.9 required four adjoint simulations, one for each observation time t_w , and additional post-processing to evaluate the integral shown in (3.23) to obtain the solute age distribution from the distribution of adjoint states. Using the forward approach to obtain the same results required 500 simulations, and additional post-processing to obtain the CDF of solute age, and numerical differentiation to obtain the PDF of solute age, which represent the solute age distribution. Thus, the adjoint approach is computationally more efficient than the forward approach, and leads to equivalent results.

3.6 Conclusion

Solute age is defined as the amount of time since the solute has entered the aquifer. It can be used to determine the travel time that the reactive contaminants such as sorbing or decaying contaminants take to travel from the recharge point to an observation point. In this Chapter, I derive an adjoint equation for calculate solute age under transient flow conditions for a contaminant that is released from a distributed, continuous source. My adjoint equation is derived based on the sensitivity approach where our system parameter of interest is the solute concentration at the recharge source. In addition, we use a two-dimensional hypothetical example to demonstrate the application of adjoint equation for obtaining the solute age distribution. Using adjoint equation to obtain the solute age distribution at a particular location and time, we solve an adjoint equation only one time. This is more efficient than the governing equation for solute age which requires multiple simulations, one simulation for each recharge time. Also, the adjoint equation produce the equivalent results to forward equation.

Chapter 4

The riverbank filtration systems

4.1 Introduction

One application of solute age is to assess the effectiveness of riverbank filtration (RBF). RBF is a surface water treatment technology that uses an aquifer adjacent to a river as a natural filter. The river water is commonly contaminated due to agricultural runoff, effluents from industries and communities [51]. A well in the aquifer near the river draws water from both the aquifer and the river, and contaminants in the river water undergo biological and chemical reactions while traveling through the subsurface materials. The natural processes, including sorption in the riverbed layer and biodegradation and sorption along the flow path, cause a decrease in contaminant levels as river water travels to the RBF well [1, 4, 13]. RBF has been widely used to remove suspended particles, natural organic matter, organic contaminants, nutrients, pathogens and viruses [1, 12, 13, 14, 27, 44, 45, 58]. It also has been demonstrated to remove poorly degradable sulfamethoxazole which is found in effluents from waste water treatment plant [3]. Because the contaminated water is naturally filtered in this method, RBF requires less additional chemical treatment and is considered as a cost-effective technology [4, 45].

Factors that affect the effectiveness of RBF systems include the degree of the hydraulic connection between the riverbed and the aquifer [44], river water fluctuation [49], hydrologic events such as heavy rainfall and runoff [28, 53], river water temperature [16], aquifer properties [53], and redox conditions [3, 25, 53]. For example, the river water fluctuations and the gradual adaptation of the groundwater table in the aquifer adjacent to the river, or heavy rainfall and runoff control

flow and transport in the RBF, and affect water quality of both river water and water at the RBF well by increasing in transport of contaminant to the RBF system [16, 28, 53]. In addition, since the water at the production well is the mixture of both groundwater and river water, the dilution effect becomes an important factor on the contaminant removal in RBF system when the RBF well located farther from the river [2, 53].

A key parameter in siting the the RBF well is the travel time of the contaminants from the river to the RBF well [2, 12, 32, 44], which must be sufficiently long to allow adequate time for biological and chemical reactions to occur in order to produce higher quality water. For example, Grühied et al. [25] review the design and operation of RBF around the world and found that in Europe, RBF is used along with little additional treatment to remove biodegradable dissolved organic carbon, particles and trace pollutants, and RBF wells are designed with travel times from weeks to months. In North America, RBF is commonly used as a primary treatment for pathogens, and RBF wells are designed with travel times from hours to weeks. In Berlin, Germany, the public groundwater supply mainly relies on RBF with travel times at least several months. Another example is Sprenger et al. [53] who study the effectiveness of an RBF well by determining travel times between the RBF well and the river, and compare to the travel times required for contaminant removal recommended by the typical groundwater protection regulations or presented by different literature reviews (e.g. the range of travel times required for removal of bacteria and viruses are 11 – 63 days and 13 – 43 days, respectively). The travel time of the contaminant depends on the sorption properties of the contaminant, groundwater velocity along the flow path, the distance between the RBF well and the river, the pumping rate, fluctuating river levels and flood events [2, 12, 46, 53]. For example, Abdel-Fattah et al. [2] demonstrate that the travel times for a contaminant released at the river location farther from the RBF well is longer than that at the river location closer to the RBF well. They also show that the pumping rate has more effect on river water travel time than location of the pumping well. In addition, according to Partinoudi and Collins [44], there are slight variations in travel times due to the river stage fluctuations. Also, Sprenger et al. [53] and Eckert and Irmscher [16] found that a flood event shortens travel time between the river and the

RBF well. This is because during flood events the hydraulic gradient between the river and the adjacent aquifer increases significantly. Tracer-based approach, Darcy's law and particle tracking simulations are used to estimate travel time for the assessment of RBF [2, 12, 44]. In addition, backward particle tracking simulation has been used to delineate capture zones for the RBF well for a given pumping period, and this can be used to evaluate the effectiveness of RBF well from the view that the capture zone represents the areas around the RBF well which has different travel times and the contaminant concentrations, and the effective RBF well should provide the capture zone which has an acceptable water quality [2].

In this Chapter, I use solute age to evaluate the effectiveness of an RBF well at a site that is downstream of a major metropolitan area where the river water level fluctuates. The contaminant is assumed to sorb and decay as it travels along the flowpath from the river to the RBF well, and this process is expected to reduce the contaminant concentration at RBF well. In this work, we use the adjoint equation developed in Chapter 3 for a sorbing (linear equilibrium sorption) and decaying (first-order decay) solute to calculate solute age of solute that is extracted at the RBF well. In adjoint simulation, the adjoint state is released at the RBF well at a time of interest, and the adjoint state is propagated upgradient in backward time. The breakthrough curve of adjoint states at each model river cell is related to a solute age distribution that represents the time at which solute that arrived at the RBF well at the time of interest entered the aquifer from that river cell. In addition to using the adjoint approach to calculate the distribution of solute travel times, I also demonstrate how solute age developed from the adjoint equation can be used effectively in the design and analysis of a RBF system.

4.2 Site description

The study site is an alluvial aquifer and river system with a river that runs from north to south. The river has average flows of approximately 1,000 cubic feet per second (cfs) with frequent floods of greater than 20,000 cfs, leading to rapid fluctuations in the river stage (See Figure 4.1). The river is frequently dominated by wastewater effluent. RBF was proposed as a treatment method

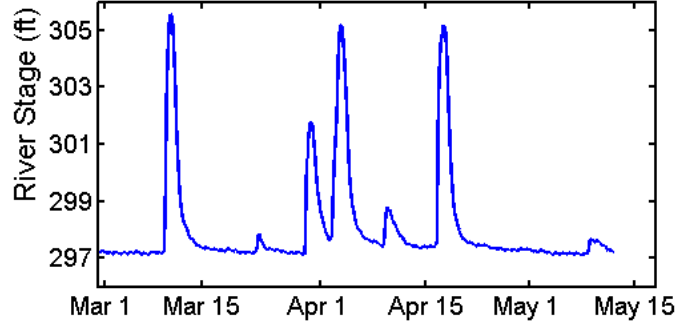


Figure 4.1: River stage as the function of time at year of 2013.

to remove the contaminant from the river water to permit the river water to be used as a drinking water supply. An RBF well was proposed to be placed near a bend in the river, approximately 200 ft from the river.

4.3 Model

To determine solute age, we first obtain the head distribution in the aquifer. Groundwater flow velocities and directions are calculated from Darcy' law using the head distribution. Head, needed for generating groundwater flow velocity in the aquifer, is obtained from

$$S \frac{\partial h}{\partial t} = T \frac{\partial^2 h}{\partial x_i^2} + \frac{K_r}{b_r} (h_r - h) I(\mathbf{x}) - Q_w \delta(\mathbf{x} - \mathbf{x}_w) \quad (4.1)$$

$$h(\mathbf{x}, t = 0) = h_0(\mathbf{x}) \quad (4.2)$$

$$h(\mathbf{x}, t) = h_1(\mathbf{x}, t) \text{ on the boundaries} \quad (4.3)$$

where S is the storage coefficient, h is head, x_i are the spatial directions ($i = 1, 2, 3$), T is transmissivity, K_r and b_r are the hydraulic conductivity and thickness of the river bed, respectively, h_r is head in the river, $I(\mathbf{x})$ is an indicator function that has a value of 1 at the river and a value of 0 everywhere else, Q_w is the pumping rate, and \mathbf{x}_w is the location of the pumping well. Where the

aquifer is directly connected to the river, the flow rate, Q_r , from the river to the aquifer is given by

$$Q_r = \frac{K_r}{b_r} WL(h_r - h) = C_r(h_r - h) \quad (4.4)$$

where W is the river width, L is the river length, and $C_r = (K_r/b_r)WL$ is the river bed conductance.

The adjoint equation of transport, which is used to calculate the solute age distribution, was derived in Appendix C and is given by

$$R\theta \frac{\partial \phi}{\partial \tau} = \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial \phi}{\partial x_j} \right) + \frac{\partial}{\partial x_i} (\theta v_i \phi) - \lambda_a \theta R \phi - q_I \phi \quad (4.5)$$

$$+ \delta(x_1 - x_{1_w}) \delta(x_2 - x_{2_w}) \delta(x_3 - x_{3_w}) \delta(\tau)$$

$$\phi(\mathbf{x}, \tau = \tau_w) = 0 \quad (4.6)$$

$$\left[D_{ij} \frac{\partial \phi}{\partial x_j} \right] \cdot \mathbf{n}_i = 0 \text{ on the boundaries} \quad (4.7)$$

where ϕ is the adjoint state of aqueous phase concentration, τ is backward time, θ is porosity, R is the retardation coefficient, and λ_a is the first-order decay rate. The groundwater velocity in the x_i direction is defined as v_i which is derived from Darcy's law, and is reversed in space and time to allow for upgradient propagation of the adjoint state. D_{ij} is the i, j^{th} component of dispersion tensor where $D_{11} = \alpha_L(v_1^2/|v|) + \alpha_{TH}(v_2^2/|v|)$, $D_{22} = \alpha_L(v_2^2/|v|) + \alpha_{TH}(v_1^2/|v|)$, and $D_{12} = D_{21} = (\alpha_L - \alpha_{TH})(v_1 v_2/|v|)$ where $|v| = \sqrt{v_1^2 + v_2^2}$ is the magnitude of the velocity vector. In this study, we assume that $\partial h/\partial \tau$ is negligible. The volumetric inflow rate per unit volume is defined as q_I which represents the exchange of water from the river to the aquifer, given by

$$q_I = \frac{Q_r(\mathbf{x})I(\mathbf{x})}{WLB} = \frac{C_r(h_r - h)I(\mathbf{x})}{WLB} \quad (4.8)$$

where Q_r is defined in (4.4). The adjoint state from (4.5) is related to the solute age distribution,

$f_a(a; \tau, \mathbf{x}_w)$, according to (Chapter 3)

$$f_a(a; \tau, \mathbf{x}_w) = \int_{\Omega} q_I(\mathbf{x}, \tau) \phi(\mathbf{x}, a; \tau, \mathbf{x}_w) d\Omega, \quad (4.9)$$

where Ω is model domain, and f_a is the distribution of solute ages in the water extracted at the pumping well at \mathbf{x}_w and at time τ .

The modeled aquifer is two-dimensional, homogeneous, and confined. The model of this site was developed by Leonard Rice Engineers, Inc., and was provided to us for use in this investigation. We extended their domain 1,000 m to the east, and modified the boundary conditions and the values used for river bed conductance. The model domain and grid are shown in Figure 4.2, and the boundaries and initial head are shown in Figure 4.3, along with the location of the river and the RBF well.

We redefined the boundaries to be specified head boundaries, with $h_1(x_1 = 0 \text{ ft}, x_2) = h_1(x_1 = 3,600 \text{ ft}, x_2) = 298 \text{ ft}$ on the east and west boundaries, and along the north and south boundaries, head decreases from $h_1 = 298 \text{ ft}$ at $x_1 = 0 \text{ ft}$ and $x_1 = 3,600 \text{ ft}$ to $h_1 = 297.5 \text{ ft}$ at the river grid blocks. With these boundary conditions, groundwater flows toward the river at a very low gradient under natural conditions, except when the river is in flood stage, when water flows out of the river. Then, with pumping, the cone of depression around the pumping well reverses the gradient near the river so that water flows from the river to the well. The original model had constant river bed conductance; however, our model has constant K_r/b_r of 1 day^{-1} , leading to river bed conductance from (4.4) that varies according to the grid block size, where W and L in (4.4) are the width and length, respectively, of the grid block.

We use MODFLOW-2000 [26] to simulate groundwater flow and MT3DMS [62] as the contaminant transport simulator to obtain solute age distributions. We simulate exchange of water between the river and aquifer using the RIV package in MODFLOW, which uses a user-specified river stage. For our simulations, we use the river stages shown in Figure 4.1. The river stage prior to March 1, 2013 is assumed to be constant and equal to the value observed on March 1. Parameter

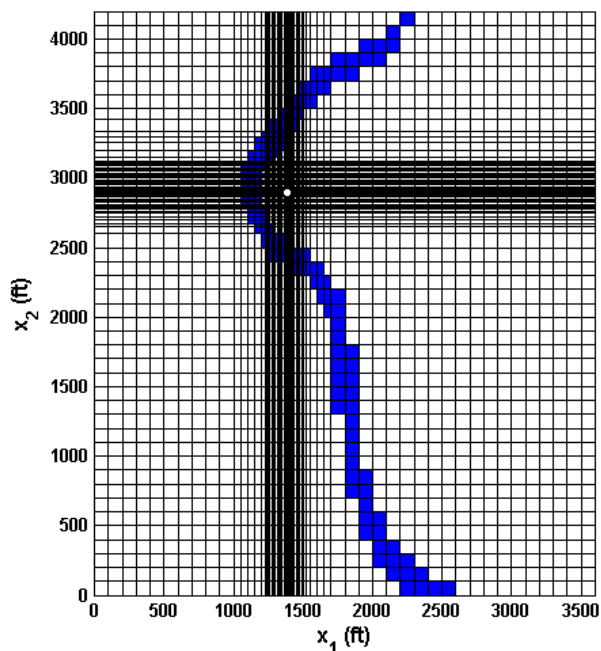


Figure 4.2: Groundwater model domain and finite difference grid. The blue-shaded cells represent river cells, and the white circle at $(x_1, x_2) = (1, 387 \text{ ft}, 2, 899 \text{ ft})$ represents the RBF well.

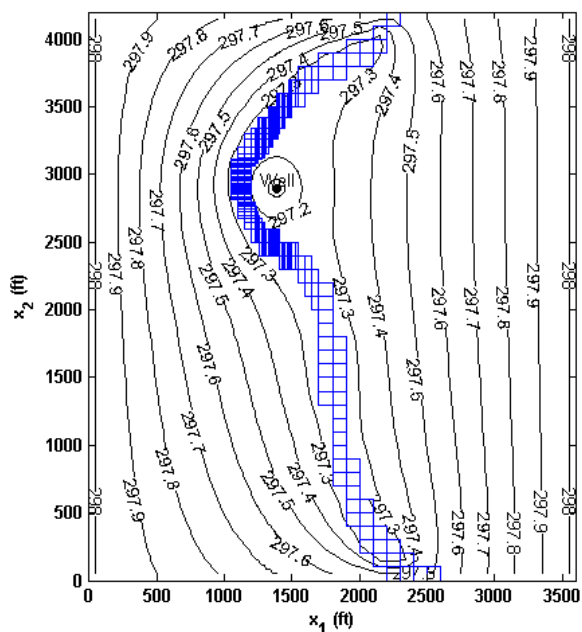


Figure 4.3: Boundaries and initial head. Cells with blue borders represent river cells, and the black circle at $(x_1, x_2) = (1387 \text{ ft}, 2899 \text{ ft})$ represents the RBF well.

values used in the simulations are shown in Table 4.1.

4.4 Results

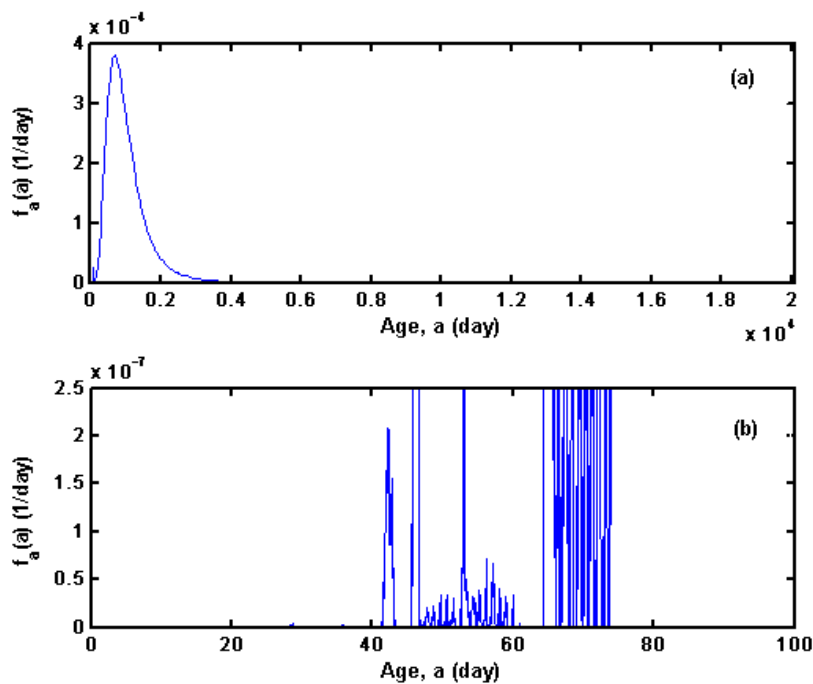
In the adjoint simulation, the RBF well is treated as an instantaneous source of adjoint state. To obtain a distribution of solute ages of the solute that arrived at the RBF well on May 13, 2013 as an example in this study, the adjoint source is released on May 13, 2013, which is defined as backward time, $\tau = 0$ days in the simulation. This adjoint state, ϕ , is propagated upgradient and backward in time from the RBF well. Also, it is used in (4.9) to calculate the distribution of solute ages at the RBF well, which represents the times prior to May 13 when the solute entered the aquifer from the river.

The solute age distribution is presented in Figure 4.4 which shows that solute ages of the solute observed at the RBF well range from 200 days to 2,500 days with mean calculated from this distribution of 1,012 days. This implies that a solute observed at the RBF well on May 13, 2013 entered the aquifer in 200 to 2,500 days ago or on average 1,012 days ago. To evaluate the effectiveness of the RBF well, the RBF well is effective if the travel time between the river and the RBF well is long enough to achieve sufficient contaminant degradation. Thus, in this study, the RBF well will be effective if the travel time required to achieve sufficient contaminant degradation is less than approximately 1,012 days.

Figure 4.4 shows that solute age distribution varies smoothly during the time when the river stage is constant, earlier than March 1, 2013 or $a > 74$ days, and fluctuates considerably when the river stage varies in time, after March 1, 2013 or $a < 74$ days. This result can be explained as follows. The solute age distribution depends on the volumetric flow rate per unit volume between the river and the aquifer, q_I , which depends on river stage and aquifer head (4.8). In this study, since aquifer heads vary with location and time and river stages vary with time, q_I in (4.8) and (4.9) has both spatial and temporal variations. After March 1, 2013, the river stage and the flow rate are higher than usual, the head gradient between the river and the aquifer increases, so more water and consequently more contaminant enters the aquifer. Thus, the probability increases that

Table 4.1: Flow and transport parameters for the study area.

Parameter	Value
Length	3,500 ft
Width	4,200 ft
Spatial discretization, Δx_1	1.5 - 100 ft
Special discretization, Δx_2	1.5 - 100 ft
Aquifer thickness, B	10 ft
Transmissivity	2,540 ft ² /day
Pumping well location, (x_{w1}, x_{w2})	(1, 387 ft, 2, 899 ft)
Pumping rate, Q_w	1,347.5 ft ³ /day
River stage	297 - 306 ft
Hydraulic conductivity of riverbed, K_r	1 ft/day
Thickness of riverbed, b_r	1 ft
Longitudinal dispersivity, α_L	5 ft
Transverse dispersivity, α_{TH}	0.1 ft
Horizontal dispersivity, α_H	0.01 ft
Porosity, θ	0.1
Retardation coefficient, R	2
First-order decay rate, λ_a	$2.5 \times 10^{-4} \text{ day}^{-1}$
Storage coefficient, S	0.015

Figure 4.4: Solute age of the RBF system. (a) Full age range. (b) Enlargement for $a < 100$ day.

the contaminant observed at the RBF well was released when the river water level was higher. As a result, after March 1, 2013 or $a < 74$ days, $f_a(a; \tau, \mathbf{x}_w)$ reflects this behavior.

We evaluated (4.9) for each river grid block to obtain a solute age distribution for each river grid block. Figure 4.5 shows the mean solute age for each river grid block, representing the mean travel time from that block or location to the RBF well. From Figure 4.5, mean solute age for a solute that travels between each location along the river and the RBF well ranges from approximately 60 days to 2,500 days. In addition, the locations along the river nearer to the RBF well have shorter mean solute ages than the locations that are farther from the well. For example, location A which is closer to the well has a mean solute age of 1,000 days, whereas, location C which is farther from the well has a mean solute age of 2,500 days. The other locations including location B which have very young mean age of approximately between 60 - 70 days are the locations where the river gains water from the aquifer for most of times, except during high river stages. For the observation time as May 13, 2013, these river cells contribute water to the aquifer only for times between 60 - 70 days prior to observation which is consistent to mean age approximately between 60 - 70 days.

4.5 Discussion

Since the concentration of solute in river water can be time-dependent due to river stage fluctuations, it may not be sufficient to specify a required travel time. When solute concentration in a river is high, a longer travel time may be needed to achieve sufficient contaminant degradation than when solute concentration in a river is low. To address this issue, we calculate the mean concentration of river water that is extracted at the RBF well. This mean concentration depends on solute age and the concentration in the river water at the time that water recharges the aquifer, and is given by

$$C(t_f, \mathbf{x}_w) = \int f_a(a; t_f, \mathbf{x}_w) C_{riv}(t_f - a) da \quad (4.10)$$

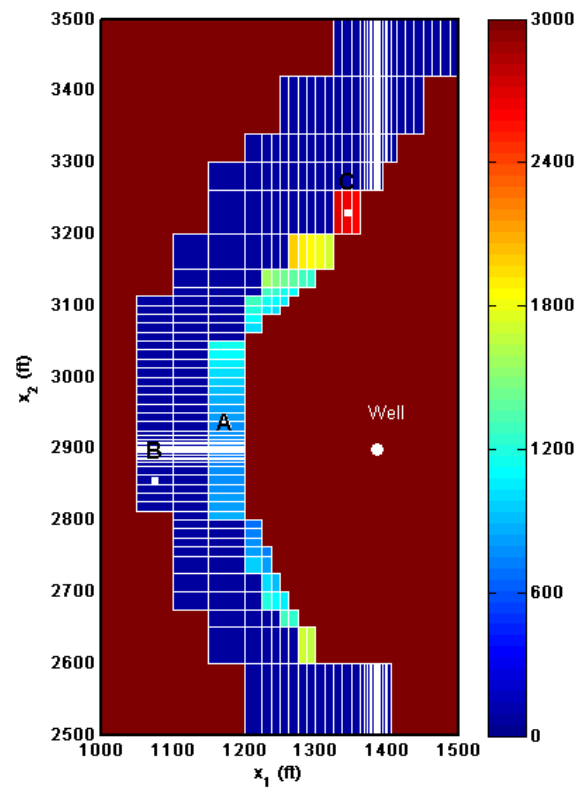


Figure 4.5: Mean solute age (days) for a solute that travels between each location along the river to the RBF well.

where $C(t_f, \mathbf{x}_w)$ is the concentration of a solute when it arrives the well at \mathbf{x}_w and at an observation time t_f , $f_a(a; t_f, \mathbf{x}_w)$ is the distribution of solute ages for a solute from the river that arrives the well at \mathbf{x}_w and at an observation time t_f , and $C_{riv}(t_f - a)$ is the concentration of a solute in the river which varies with time, t , where $C_{riv}(t_f - a) = C_{riv}(t)$ by using the definition of solute age, $a = t_f - t$.

As an example, let the concentration of a solute in the river fluctuate in a sinusoidal pattern as shown in Figure 4.6a. For a given observation time t_f , the integrand in (4.10) is obtained by multiplying the solute age distribution presented in Figure 4.4 by $C_{riv}(t_f - a)$. This integrand is shown in Figure 4.6b for an observation on May 13, 2013. In Figure 4.6b, we also present the integrand for an observation on June 26, 1997 in order to demonstrate the effects of time-dependent concentration in the river on the mean concentration at an RBF well.

Figure 4.6b shows that the integrand for an observation time on June 26, 1997 is higher than May 13, 2013. Using (4.10), we integrate each integrand shown in Figure 4.6b over an age domain, and found that mean solute concentration in the river water that arrives at the RBF well on June 26, 1997 is 4.27 mg/L which is higher than on May 13, 2013 which is 3.25 mg/L. These results can be explained as follows. The ages of the solute particles at the RBF well range from approximately 200 - 2,500 days; thus, the solute was in the river about 200 - 2,500 days prior arriving at the well. We assume solute age distribution at an RBF well on June 26, 2013 is equivalent to the solute age distribution on Figure 4.4a because the river stage on these two observation times are close. For solute that arrives the well on June 26, 1997 which is equivalent to $t_f = t = 14,274$ days, the solute was in the river at t approximately between 11,700 days and 14,000 days, during the time when concentration of solute in the river is high as shown in Figure 4.6a. Then, for solute that arrives on May 13, 2013 which is equivalent to $t_f = t = 20,074$ days, the solute was in the river at t approximately between 17,500 days and 19,800 days, during the time when concentration of solute in the river is low as shown in Figure 4.6a. These results illustrate that since the solute concentration in the river water that arrives at the RBF well are different for different observation times, it is possible that the RBF well is effective only at some observation

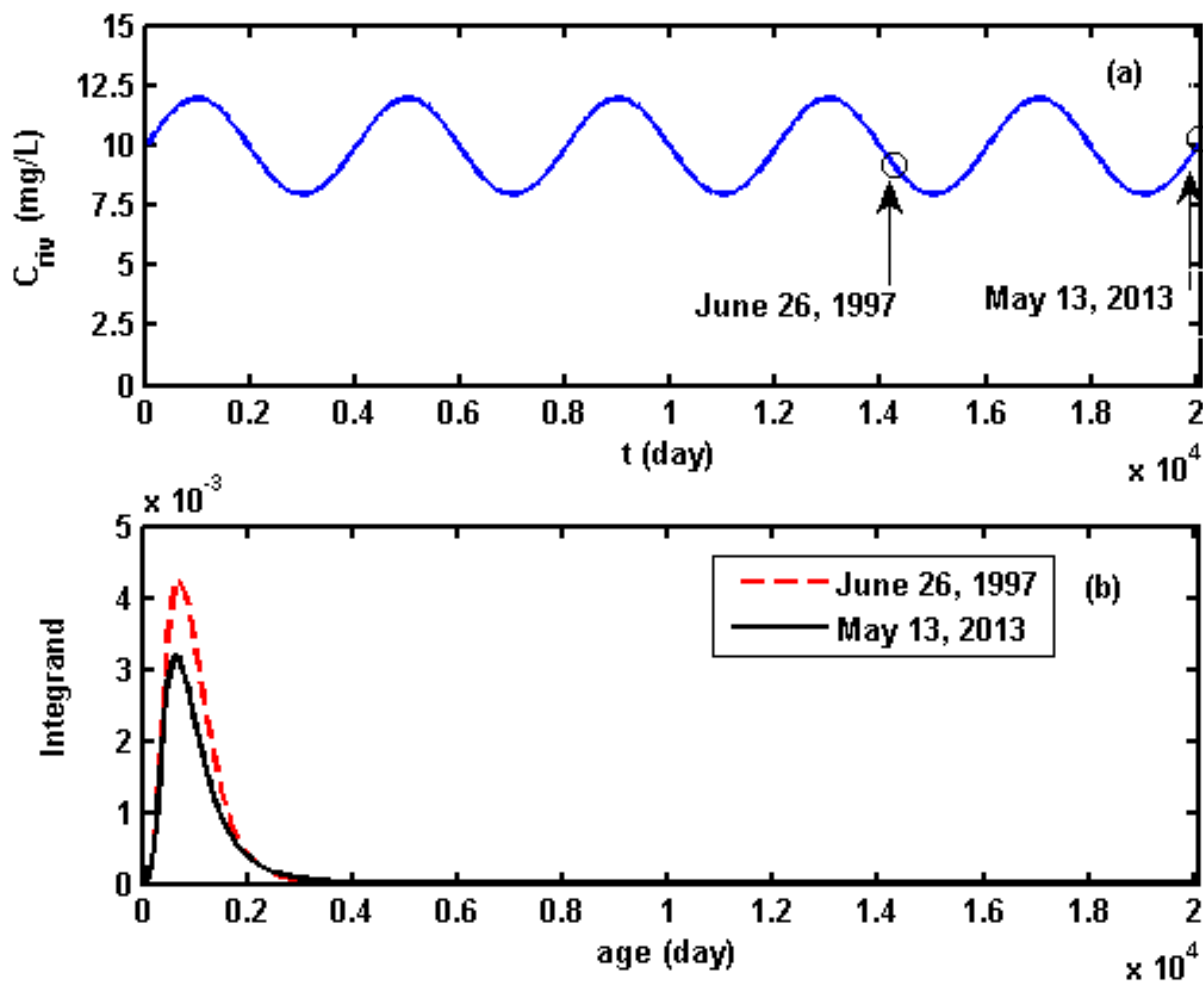


Figure 4.6: Example of calculating the mean concentration in river water at the RBF well. (a) Temporal variation of solute concentration in the river. (b) Integrand of (4.10) for a solute that arrives the well for an observation time on May 13, 2013 ($t = 20,074$ days) and June 27, 2013 ($t = 14,274$ days)

times. For example, if the range of mean concentration at an RBF well for different observation times is between 3.25 mg/L and 4.27 mg/L, and the maximum contaminant level of this chemical allowed in public drinking water systems is 3.5 mg/L, the RBF well is effective only some of the time. However, if the maximum contaminant level allowed is 4.5 mg/L, the RBF well would be effective for all times. Note that mean concentration as of 3.25 mg/L and 4.27 mg/L are higher than the actual concentrations sampled at an RBF well because these mean concentrations do not account for dilution with groundwater that is also extracted at the well.

4.6 Conclusion

A key parameter in siting the the RBF well is the travel time of the contaminants from the river to the RBF well which must be sufficiently long to allow the contaminants to be removed by natural processes. A solute age distribution at an RBF well represents the distribution of travel times from the river to the RBF well, so it can be used to assess the effectiveness of an RBF well. We illustrate the application of solute age to assess an RBF system using a particular study area. For this study area, river flows show frequent increases of short duration. We use the adjoint approach to calculate the solute age distribution for a sorbing and decaying contaminant. This solute age distribution can also be used to calculate the mean solute concentration of a river water that arrives at the RBF well which does not account for dilution with groundwater. The mean solute concentration can vary in time if the river water quality varies in time, and can be compared to the desired concentration to evaluate the effectiveness of the RBF well.

Chapter 5

Conclusion and Future work

5.1 Conclusion

Groundwater age has been used to assess groundwater well contamination. Because tracers travel at the same rate as groundwater, the groundwater age distribution at a particular location in the aquifer also represents the distribution of travel times of a tracer from a recharge source to the location of interest. For this reason, the groundwater age distribution also represents the length of time that the location of interest will remain contaminated after the source of the tracer is removed. For a sorbing solute, the travel time of the solute is not equivalent to the travel time of groundwater. Sorbing solutes travel more slowly than groundwater because of retardation. For decaying solutes, although they travel at the same rate as groundwater (or a tracer), the contaminant particles decay over time as it travels to an observation point. Thus, groundwater age is not an appropriate tool to assess groundwater well contamination to sorbing or decaying contaminants. Instead, we introduce a new concept called solute age. Solute age is a measure of the amount of time that solute has been in the aquifer. I developed the governing equations of solute age by following the approach used by others for deriving groundwater age. The solute age equations are more complex because I add the appropriate terms to account for reactions (e.g. linear equilibrium sorption and first-order decay).

In Chapter 2, to introduce the concept of solute age, I derive the standard governing equations for solute age that exhibits linear equilibrium sorption and first-order decay following the approach used by others to derive the standard governing equations of groundwater age. Through an illustrative example, I demonstrate that solute age should be used to assess groundwater well

contamination to the reactive contaminants instead of groundwater age. In chapter 3, I develop the adjoint equation for determining solute age of the water sample observed at a particular location and time and under transient flow conditions. In an example problem for a two-dimensional hypothetical aquifer and transient flow conditions, I demonstrate that the solute age distribution obtained from my adjoint equation is equivalent to the distribution obtained from the standard governing equation. In chapter 4, to evaluate the effectiveness of a riverbank filtration (RBF) well, I use solute age to evaluate the travel time between a river and an RBF well at a site that is downstream of a major metropolitan area where the river water level fluctuates and the contaminant of concern is assumed a sorbing and decaying contaminant. I use the the adjoint equation developed in Chapter 3 for a sorbing and decaying solute to calculate solute age of solute that is extracted at an RBF well. Also, I demonstrate the approach for using solute age derived from my adjoint equation in the assessment of the effectiveness of an RBF well.

Using my governing equation of solute age for the example problem under steady flow conditions, we find that the CDFs and PDFs of solute age for sorbing solutes are shifted to older ages relative to the distribution of groundwater age because the sorbing particles travel slowly than tracer or groundwater. In view of groundwater well contamination, this implies that a pumping well contaminated by a sorbing solute would remain contaminated for a longer time after source removal than a non-sorbing solute or by what would be expected based on groundwater age. Also, PDF of solute age for a decaying solute (non-sorbing) has approximately the same range of age distribution as groundwater age; however, the CDF reaches the maximum value of less than 1. In view of groundwater well contamination, this implies that the pumping well contaminated by a decaying solute would remain contaminated for approximately the same amount of time after source removal as water contaminated with a tracer. However, it will be contaminated with the lower level of contamination than for the case of a tracer. Thus, if groundwater age were used to assess groundwater well contamination, the persistence of the well to contamination by sorbing solutes or decaying solute would be misdiagnosed.

For transient flow conditions, the forward governing equation for solute age must be solved

once for each recharge time to obtain a distribution of solute ages at a particular water sample. The adjoint equation of solute age that I developed is more efficient than the governing equation of solute age because with one simulation, it can produce the complete solute age distribution for a given observation time. Also, the adjoint equation produce the equivalent results to forward equation. Multiple simulations of the adjoint equation would need to be run to obtain the solute age distribution for multiple observation times.

Solute age is useful in designing RBF systems to ensure sufficient time for reaction along the flowpaths between a river and an RBF well. In addition, if a certain contaminant concentration at an RBF well is required to be achieved, solute age can be used to calculate the concentration at an RBF well by relating the magnitude of solute age and the contaminant concentration at a river. This calculated concentration does not account for the effects of dilution with groundwater so it is higher than the contaminant concentration that would be sampled at an RBF well. Since river stage fluctuates and the contaminant concentration at an RBF well is time-dependent, the results show that the concentration at an RBF well can fluctuate over time as well.

5.2 Future work

The governing equations of solute age and the adjoint equations developed in this study are based on solutes that exhibit linear equilibrium sorption and first-order decay. However, the chemical reactions in groundwater may be more complicated. Therefore, additional work is needed to develop the governing equation for solute age or the adjoint equation for solute age for different chemical reactions.

In addition, I apply my adjoint equation in the example problem by assuming that the specific storage, S_s is negligible, which cause the term containing $S_s(\partial h/\partial t)$ to vanish as shown in Appendix C. Thus, in order to complete the transient simulation, an approach to solve the adjoint equation with this term should be developed.

Using solute age derived from the adjoint equation, although the simulation is run long enough for contaminant from only a part of river closer to the RBF well reaches the RBF well, this

sometimes requires simulation that run for long duration. It is possible that only some locations along that river that provide a significant amount of contaminant should be account in calculation of solute age. Thus, an additional work should be designing a method to select only some parts of river for solute age calculation. In addition, since in this study the simulation is run for contaminant from only a part of river reaching to the RBF well although the contaminant was released from all parts of the river, the results of my study should be compared to forward equations to verify if solute age distribution is accurate and if the solute age is an appropriate measure of the effectiveness of RBF.

Bibliography

- [1] F. A. Abdalla and M. Shamrukh. Riverbank filtration as an alternative treatment technology: Abutieg case study, egypt. NATO Science for Peace and Security Series C: Environmental Security, pages 255–268, 2011.
- [2] A. Abdel-Fattah, R. Langford, and D. Schulze-Makuch. Applications of particle-tracking techniques to bank infiltration: a case study from el paso, texas, usa. Environ. Geol., 55(3):505–515, 2008.
- [3] B. Baumgartena, J. Jähriga, T. Reemtsmab, and M. Jekela. Long term laboratory column experiments to simulate bank filtration: Factors controlling removal of sulfamethoxazole. Water Res., 45(1):211–220, 2011.
- [4] C. Bertelkamp, J. Reungoat, E.R. Cornelissen, N. Singhal, J. Reynisson, A.J. Cabo, J.P. van der Hoek, and Verliefe A.R.D. Sorption and biodegradation of organic micropollutants during river bank filtration: A laboratory column study. Water Res., 52:231–241, 2014.
- [5] C.M. Bethke and T.M. Johnson. Paradox of groundwater age. Geology, 30(2):107–110, 2002.
- [6] C.M. Bethke and T.M. Johnson. Groundwater age and groundwater age dating. Annual Review of Earth and Planetary Sciences., 36:121–152, 2008.
- [7] M.C. Castro and P. Goblet. Calculation of ground water ages—a comparative analysis. Ground Water, 43(3):368–380, 2005.
- [8] P.G. Cook and J.K. Böhlke. Determining timescales for groundwater flow and solute transport. In: Cook PG, Herczeg A, editors. Environmental tracers in subsurface hydrology. Springer US, 2000.
- [9] F. Cornaton and P. Perrochet. Groundwater age, life expectancy and transit time distributions in advective-dispersive systems: 1. generalized reservoir theory. Adv. Water Resour., 29(9):1267–1291, 2006.
- [10] F.J. Cornaton. Transient water age distributions in environmental flow systems: the time-marching laplace transform solution technique. Water Resour. Res., 48(3):1–17, 2012.
- [11] F.J. Cornaton, Y. J. Park, S. D. Normani, E.A. Sudicky, and J.F. Sykes. Use of groundwater lifetime expectancy for the performance assessment of a deep geologic waste repository: 1. theory, illustrations, and implications. Water Resour. Res., 44:W04406, 2008.

- [12] M. Dawe and K. Macquarrie. Assessing water travel times during river bank filtration. International Association of Hydrological Sciences Publication, 297:97–102, 2005.
- [13] W. W. J. M. de Vet, C. C. A. van Genuchten, M. C. M. van Loosdrecht, and J. C. van Dijk. Water quality and treatment of river bank filtrate. Drink. Water Eng. Sci., 3:79–90, 2010.
- [14] J.E. Drewes, C. Hoppe, G. Oldham, J. McCray, and K. Thompson. Evaluation of riverbank filtration systems to optimize removal of bulk organic matter, emerging organic micropollutants, and nutrients. download from vendor site, 2009. Final Report Water Research Foundation, Denver, Colorado.
- [15] S.M. Eberts, J.K. Bohlke, L.J. Kauffman, and B.C. Jurgens. Comparison of particle-tracking and lumped-parameter age-distribution models for evaluating vulnerability of production wells to contamination. Hydrogeol. J., 20(2):263–282, 2012.
- [16] P. Eckert and R. Irmscher. Over 130 years of experience with riverbank filtration in dü sseldorf, germany. J. Water Supply Res. T., 55(4):283–291, 2006.
- [17] N.B. Engdahl, T.R. Ginn, and G.E. Fogg. Non-fickian dispersion of groundwater age. Water Resour. Res., 48(7):1–13, 2012.
- [18] N.B. Engdahl, T.R. Ginn, and G.E. Fogg. Using groundwater age distributions to estimate the effective parameters of fickian and non-fickian models of solute transport. Adv. Water Resour., 54:11–21, 2013.
- [19] N.B. Engdahl and R.M. Maxwell. Approximating groundwater age distributions using simple streamtube models and multiple tracers. Advances in Water Resources, 66:19–31, 2014.
- [20] R. Enzenhöfer, W. Nowak, and R. Helmig. Probabilistic exposure risk assessment with advective-dispersive well vulnerability criteria. Adv. Water Resour., 36:121–132, 2012.
- [21] E.O. Frind, J.W. Molson, and D.L. Rudolph. Well vulnerability: a quantitative approach for source water protection. Ground Water, 44(5):732–742, 2006.
- [22] T.R. Ginn. On the distribution of multicomponent mixtures over generalized exposure time in subsurface flow and reactive transport: Foundations, and formulations for groundwater age, chemical heterogeneity, and biodegradation. Water Resour. Res., 35(5):1395–1407, 1999.
- [23] T.R. Ginn, H. Haeri, A. Massoudieh, and L. Foglia. Notes on groundwater age in forward and inverse modeling. Transp. Porous Med., 79(1):117–134, 2009.
- [24] D.J. Goode. Direct simulation of groundwater age. Water Resour. Res., 32(2):289–296, 1996.
- [25] S. Grünheid, G. Amy, and M. Jekel. Removal of bulk dissolved organic carbon (DOC) and trace organic compounds by bank filtration and artificial recharge. Water Res., 29:3219–3228, 2005.
- [26] A.W. Harbaugh, E.R. Banta, M.C. Hill, and M.G. McDonald. MODFLOW–2000, the U.S. Geological Survey modular ground-water model: User guide to modularization concepts and the Ground-Water Flow Process. U.S. Geological Survey Open-File Report 00-92, 2000.

- [27] C. Hoppe-Jones, G. Oldham, and J.E. Drewes. Attenuation of total organic carbon and unregulated trace organic chemicals in u.s. riverbank filtration systems. Water Res., 44(15):4643–4659, 2010.
- [28] S.A. (Ed.) Hubbs. Riverbank Filtration Hydrology: Impacts on system capacity and water quality. Springer, 2006.
- [29] B.G. Katz, M.P. Berndt, and C.A. Crandall. Factors affecting the movement and persistence of nitrate and pesticides in the surficial and upper floridan aquifers in two agricultural areas in the southeastern united states. Environ. Earth Sci., 71:2779–2795, 2014.
- [30] G.A. Kazemi, J.H. Lehr, and P. Perrochet. Groundwater age. John Wiley, 2006.
- [31] J.F. Kenny, N.L. Barber, S.S. Hutson, K.S. Linsey, J.K. Lovelace, and M.A. Maupin. Tech. Rep. Circular 1334. U.S. Department of the Interior; U.S. Geological Survey, 2009.
- [32] W. Kuehn and U. Mueller. Riverbank filtration—an overview. J. AWWA, 92(12):60–69, 200.
- [33] S. Leray, J-R de Dreuzy, O. Bour, T. Labasque, and L. Aquilina. Contribution of age data to the characterization of complex aquifers. J. Hydrol., 464–465:54–68, 2012.
- [34] J.E. Liggett and S. Talwar. Groundwater vulnerability assessments and integrated water resource management. Streamline Watershed Manage. Bull., 13(1):18–29, 2009.
- [35] H.A. Loaiciga. Residence time, groundwater age, and solute output in steady-state groundwater systems. Adv. Water Resour., 27(7):681–8, 2004.
- [36] J.W. Molson and E.O. Frind. On the use of mean groundwater age, life expectancy and capture probability for defining aquifer vulnerability and time-of-travel zones for source water protection. J. Contam. Hydrol., 127(1-4):76–87, 2012.
- [37] R.M. Neupauer and J.L. Wilson. Adjoint method for obtaining backward-in-time location and travel time probability on a conservative groundwater contaminant. Water Resour. Res., 35(11):3389–33988, 1999.
- [38] R.M. Neupauer and J.L. Wilson. Adjoint-derived location and travel time probabilities for a multidimensional groundwater system. Water Resour. Res., 37(6):1657–1668, 2001.
- [39] R.M. Neupauer and J.L. Wilson. Backward probabilistic model of groundwater contamination in non-uniform and transient flow. Adv. Water Resour., 25(7):733–746, 2002.
- [40] R.M. Neupauer and J.L. Wilson. Backward location and travel time probabilities for a decaying contaminant in an aquifer. J. Contam. Hydrol., 66:39–58, 2003.
- [41] R.M. Neupauer and J.L. Wilson. Forward and backward location probabilities for sorbing solutes in groundwater. Adv. Water Resour., 27:689–750, 2004a.
- [42] R.M. Neupauer and J.L. Wilson. Numerical implementation of a backward probabilistic model of ground water contamination. Ground Water, 42(2):175–189, 2004b.
- [43] R.M. Neupauer, J.L. Wilson, and A. Bhaskar. Forward and backward temporal probability distributions of sorbing solutes in groundwater. Water Resour. Res., 45:W1420, 2009.

- [44] V. Partinoudi and M.R. Collins. Assessing RBF reduction/removal mechanisms for microbial and organic DBP precursors. Jour. AWWA, 99:12:61–72, 2007.
- [45] C. Ray, G. Melin, and R.B. (Eds.) Linsky. Riverbank filtration improving source-Water quality. Water Science and Technology Library, 2003.
- [46] C. Ray, T.W. Soong, Y.Q. Lian, and G.S. Roadcap. Effect of flood-induced chemical load on filtrate quality at bank filtration sites. J. Hydrol., 266:235–258, 2002.
- [47] W.M. Robertson and J.M. Jr. Sharp. Variability of groundwater nitrate concentrations over time in arid basin aquifers: sources, mechanisms of transport, and implications for conceptual models. Environ. Earth Sci., 69:2415–2426, 2013.
- [48] W. Sanford. Calibration of models using groundwater age. Hydrogeol. J., 19(1):13–6, 2011.
- [49] Jürgen Schubert. Hydraulic aspects of riverbank filtration-field studies. J. hydrol., 266:145–161, 2002.
- [50] B. Selle, K. Rink, and O. Kolditz. Recharge and discharge controls on groundwater travel times and flow paths to production wells for the ammer catchment in southwestern germany. Environ. Earth Sci., 69:443–452, 2013.
- [51] L. Sharma, J. Greskowiak, Ch. Ray, P. Eckert, and H. Prommer. Elucidating temperature effects on seasonal variations of biogeochemical turnover rates during riverbank filtration. J. Contam. Hydrol., 428-429:104–114, 2012.
- [52] D.B. Spalding. A note on mean residence-times in steady flows of arbitrary complexity. Chem. Eng. Sci., 9:74–77, 1958.
- [53] C. Sprenger, G. Lorenzen, I. Hülshoff, G. Grützmacher, M. Ronghang, and A. Pekdeger. Vulnerability of bank filtration systems to climate change. Sci. Total Environ., 409(4):655–663, 2011.
- [54] J.D. Stoner, T.K. Cowdery, and L.J. Puckett. Ground–water age dating and other tools used to asses land–use effects on water quality. download from vendor site, 1997. U.S. Department of the Interior, U.S. Geol. Surv. Water Resour. Invest. Rep., 97–4150.
- [55] J.F. Sykes, J.L. Wilson, and R.W. Andrews. Sensitivity analysis for steady state groundwater flow using adjoint operators. Water Resour. Res., 21(3):359–371, 1985.
- [56] M. Varni and J. Carrera. Simulation of groundwater age distributions. Water Resour. Res., 34(12):3271–3281, 1998.
- [57] A. Visser, H.P. Broers, R. Purtschert, J. Sültenfuß, and M. de Jonge. Groundwater age distributions at a public drinking water supply well field derived from multiple age tracers (85Kr, 3H/3He, and 39Ar). Water Resour. Res., 49:7778–7796, 2013.
- [58] W.J. Weiss, E.J. Bouwer, W.P. Ball, C.R. O’Melia, M.W. LeChevallier, H. Arora, R. Aboytes, and T.F. Speth. Study of water quality improvements during riverbank filtration at three midwestern united states drinking water utilities. Geophys. Res. Abstr., 5:04297 (European Geophysical Society), 2003.

- [59] G.S. Weissman, Y. Zhang, E.M. LaBolle, and G.E. Fogg. Dispersion of groundwater age in an alluvial aquifer system. Water Resour. Res., 38(10):1198, 2002.
- [60] L.R. Woolfenden and T.R. Ginn. Modeled ground water age distributions. Ground Water, 47(4):547–557, 2009.
- [61] Y. Zhang, D.A. Benson, and D.M. Reeves. Time and space nonlocalities underlying fractional-derivative models: Distinction and literature review of field applications. Adv. Water Resour., 32:561–581, 2009.
- [62] C. Zheng and G.D. Bennett. Applied Contaminant Transport Modeling, Second Edition. John Wiley & Sons, 2002.
- [63] B.A. Zinn and L.F. Konikow. Potential effects of regional pumpage on groundwater age distribution. Water Resour. Res., 43(6):W06418, 2007.

Appendix A

Derivation of the governing equation for mean solute age

In this appendix, we show the details for obtaining (2.20) to (2.23) from (2.16) to (2.19). Firstly, we multiply each term in (2.16) to (2.19) by t , and integrate over the time domain. The time derivative term in aqueous phases of (2.16) is modified as

$$\begin{aligned} \int_0^{\infty} t\theta \frac{\partial c}{\partial t} dt &= \int_0^{\infty} \theta \frac{\partial(tc)}{\partial t} dt - \int_0^{\infty} \theta c dt \\ &= \theta tc \Big|_{t=0}^{\infty} - \theta \int_0^{\infty} c dt \\ &= -\theta M . \end{aligned} \tag{A.1}$$

The expression on the right hand side of the first line is obtained by using the product rule on the integrand in the expression on the left hand side. The second line is obtained by carrying out the integration. Since θ is independent of t , we can take it outside the integral. The first term in the second line vanishes because $c \rightarrow 0$ as $t \rightarrow \infty$. The third line is obtained by using (2.14).

Following the same approach, the time derivative term in sorbed phases of (2.16) and (2.17)

is modified as

$$\begin{aligned}
\int_0^\infty t \rho_b \frac{\partial c_s}{\partial t} dt &= \int_0^\infty \rho_b \frac{\partial(tc_s)}{\partial t} dt - \int_0^\infty \rho_b c_s dt \\
&= \rho_b t c_s \Big|_{t=0}^{t=\infty} - \rho_b \int_0^\infty c_s dt \\
&= -\rho_b M_s
\end{aligned} \tag{A.2}$$

where we use the definition that $M_s = \int_0^\infty c_s dt$, the fact that ρ_b is independent of t , and $c_s \rightarrow 0$ as $t \rightarrow \infty$.

The dispersion term on the right hand side of (2.16) is modified as

$$\begin{aligned}
\int_0^\infty t \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial c}{\partial x_j} \right) dt &= \frac{\partial}{\partial x_i} \left[\theta D_{ij} \frac{\partial}{\partial x_j} \left(\int_0^\infty ct dt \right) \right] \\
&= \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial E}{\partial x_j} \right) .
\end{aligned} \tag{A.3}$$

Since θ and D are independent of t , we move the time integral inside the derivatives to obtain the second expression. The last expression is obtained by substituting E for the integral term using the definition in (2.13).

The advection term on the right hand side of (2.16) is modified as

$$\int_0^\infty t \frac{\partial}{\partial x_i} (\theta v_i c) dt = \frac{\partial}{\partial x_i} \left(\theta v_i \int_0^\infty ct dt \right) = \frac{\partial}{\partial x_i} (\theta v_i E) . \tag{A.4}$$

Similar to (A.3), since θ and v are independent of t , we move the time integral inside the derivative to obtain the second expression. Also, the last expression is obtained by substituting E for the integral term using the definition in (2.13).

The first term on the right hand side of (2.17) is modified as

$$\int_0^\infty t \rho_b \alpha_s (K_d c - c_s) dt = \rho_b \alpha_s \left(K_d \int_0^\infty tc dt - \int_0^\infty tc_s dt \right) = \rho_b \alpha_s (K_d E - E_s) . \tag{A.5}$$

Since ρ_b , α_s and K_d are independent of t , we can take them outside the integral. The last expression is obtained by using the definitions in (2.13) and $E_s = \int_0^\infty t c_s dt$.

The boundary condition on Γ_1 , (2.18), is modified as

$$\int_0^\infty t \left[D_{ij} \frac{\partial c}{\partial x_j} - v_i c \right] \cdot n_i dt = \left[D_{ij} \frac{\partial}{\partial x_j} \left(\int_0^\infty c t dt \right) - v \int_0^\infty c t dt \right] \cdot n_i = \left[D_{ij} \frac{\partial E}{\partial x_j} - v E \right] \cdot n_i . \quad (\text{A.6})$$

The boundary condition on Γ_2 , (2.19), is modified as

$$\int_0^\infty t \left[D_{ij} \frac{\partial c}{\partial x_j} \right] \cdot n_i dt = \left[D_{ij} \frac{\partial}{\partial x_j} \left(\int_0^\infty c t dt \right) \right] \cdot n_i = \left[D_{ij} \frac{\partial E}{\partial x_j} \right] \cdot n_i . \quad (\text{A.7})$$

By modifying the ADE as shown in (A.1) - (A.7), the ADE, (2.16) to (2.19), becomes

$$-\theta M - \rho_b M_s = \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial E}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\theta v_i E) \quad (\text{A.8})$$

$$-\rho_b M_s = \rho_b \alpha_s (K_d E - E_s) \quad (\text{A.9})$$

$$\left[D_{ij} \frac{\partial E}{\partial x_j} - v E \right] \cdot n_i = 0 \text{ on } \Gamma_1 \quad (\text{A.10})$$

$$\left[D_{ij} \frac{\partial E}{\partial x_j} \right] \cdot n_i = 0 \text{ on } \Gamma_2 . \quad (\text{A.11})$$

We can obtain a relationship between M and M_s by defining M_s as $M_s = \lim_{t^* \rightarrow \infty} \int_0^{t^*} c_s dt$.

For a solute that exhibits linear kinetic sorption, $c_s \rightarrow K_d c$ as time approaches infinity. Thus, M_s becomes

$$M_s = K_d \lim_{t^* \rightarrow \infty} \int_0^{t^*} c dt = K_d M . \quad (\text{A.12})$$

We make this substitution in (A.8) to (A.11) and divide by M . Using the definitions $A = E/M$ in (2.15) and $A_s = E_s/M$, (A.8) to (A.11) become (2.20) to (2.23), respectively.

Appendix B

Solute age distribution for the entire domain

Figure B.1 to B.8 show solute age distributions at different locations downstream of the recharge boundary for different conditions: (1) tracer (Figure B.1 and B.2), (2) linear equilibrium sorption (Figure B.3 and B.4), (3) first-order decay (Figure B.5 and B.6), and (4) linear equilibrium sorption and first order decay (Figure B.7 and B.8). The CDFs are obtained from solving (2.31) at different positions. The PDFs are obtained from the CDFs using (2.33). Mean ages at different locations shown in Figure 2.5 are obtained from the following PDFs.

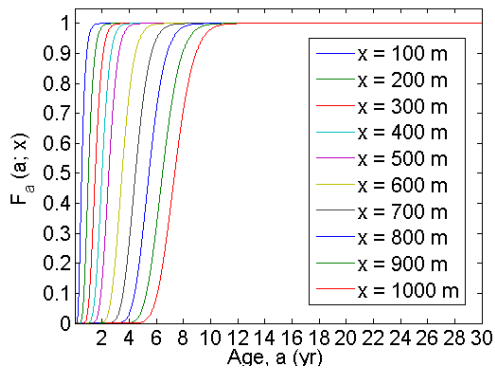


Figure B.1: CDFs of groundwater age at various downstream locations.

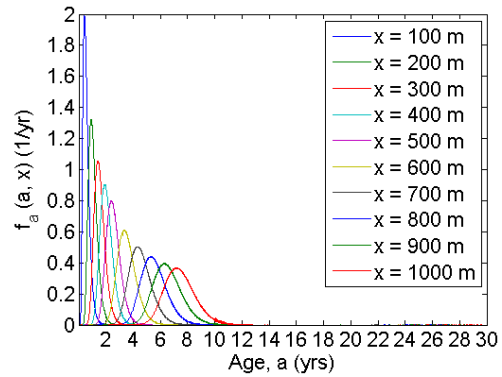


Figure B.2: PDFs of groundwater age at various downstream locations.

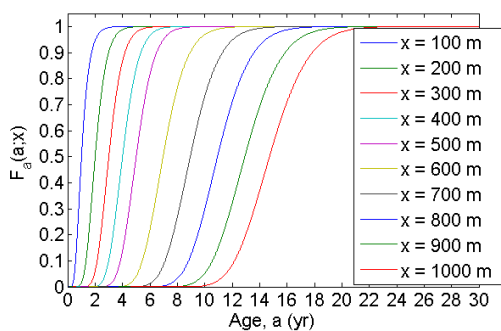


Figure B.3: CDFs of solute age for a sorbing solute at various downstream locations.

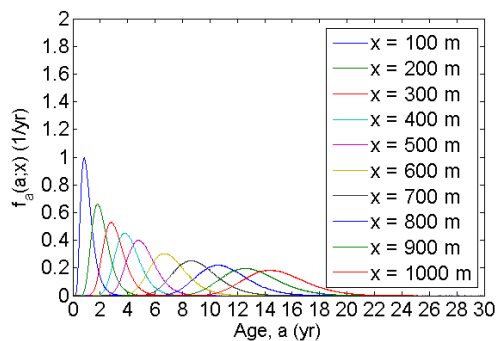


Figure B.4: PDFs of solute age for a sorbing solute at various downstream locations.

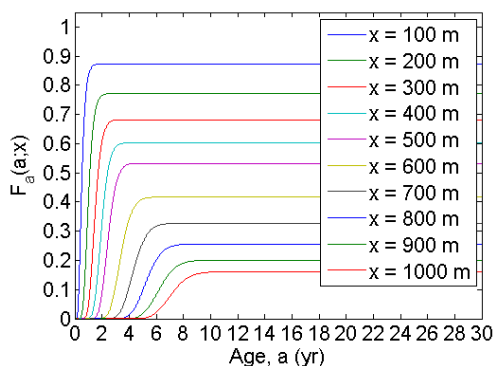


Figure B.5: CDFs of solute age for a decaying solute at various downstream locations.

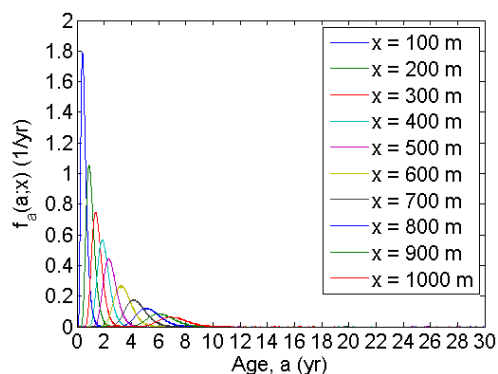


Figure B.6: PDFs of solute age for a decaying solute at various downstream locations.

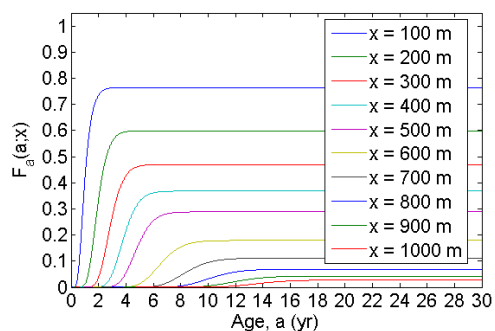


Figure B.7: CDFs of solute age for a sorbing and decaying solute at various downstream locations.

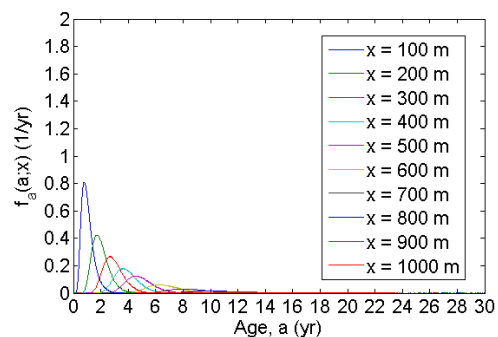


Figure B.8: PDFs of solute age for a sorbing and decaying solute at various downstream locations.

Appendix C

The derivation of adjoint equation for solute age

In this appendix, we show the details for obtaining (3.24) to (3.30) from the ADE, (3.13) to (3.19). Following the approach of Sykes et al. [55], a performance measure, P , that quantifies some state of the system, is defined as

$$P = \iint_{\Omega, t} h(c, c_s, c_N) d\Omega dt \quad (\text{C.1})$$

where h is a functional of the state of the system, and Ω is the spatial domain.

We define P as flux concentration, c^f , at the observation point, $P = c^f(\mathbf{x} = \mathbf{x}_w, t = t_w)$, \mathbf{x}_w is the observation location and t_w is the observation time. We assume that the well can be approximated as a point in space. Also, since our observation point is a pumping well we assume $c = c^f$; therefore, $P = c(\mathbf{x} = \mathbf{x}_w, t = t_w)$ [37]. To use (C.1) to obtain this defined P , the appropriate performance functional is defined as $h = c(\mathbf{x}, t)\delta(\mathbf{x} - \mathbf{x}_w)\delta(t - t_w)$ [41], and (C.1) becomes

$$P = \iint_{\Omega, t} c(\mathbf{x}, t)\delta(\mathbf{x} - \mathbf{x}_w)\delta(t - t_w) d\Omega dt. \quad (\text{C.2})$$

We define the marginal sensitivity of P by differentiating P in (C.2) with respect to the source concentration, c_N , as given by

$$\frac{dP}{dc_N} = \iint_{\Omega, t} \psi\delta(\mathbf{x} - \mathbf{x}_w)\delta(t - t_w) d\Omega dt \quad (\text{C.3})$$

where $\psi = \partial c / \partial c_N$ is the marginal sensitivity of c . To eliminate the state sensitivity, ψ , from (C.3), firstly, we obtain a governing equation for ψ by differentiating each term in (3.13) to (3.19) with respect to c_N to obtain

$$0 = -\theta \frac{\partial \psi}{\partial t} - \rho_b \frac{\partial \psi_s}{\partial t} + \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial \psi}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\theta v_i \psi) \quad (\text{C.4})$$

$$-\lambda_a \theta \psi - \lambda_s \rho_b \psi_s + q_I - q_O \psi$$

$$0 = -\rho_b \frac{\partial \psi_s}{\partial t} + \rho_b \alpha_s (K_d \psi - \psi_s) - \lambda_s \rho_b \psi_s \quad (\text{C.5})$$

$$\psi(\mathbf{x}, 0) = 0 \quad (\text{C.6})$$

$$\psi_s(\mathbf{x}, 0) = 0 \quad (\text{C.7})$$

$$\psi(\mathbf{x}, t) = 0 \text{ on } \Gamma_1 \quad (\text{C.8})$$

$$\left[D_{ij} \frac{\partial \psi}{\partial x_j} \right] \cdot \mathbf{n}_i = 0 \text{ on } \Gamma_2 \quad (\text{C.9})$$

$$\left[D_{ij} \frac{\partial \psi}{\partial x_j} - v_i \psi \right] \cdot \mathbf{n}_i = 0 \text{ on } \Gamma_3 \quad (\text{C.10})$$

where $\psi_s = \partial c_s / \partial c_N$ is the state sensitivity of c_s . The next step is to take the inner product of each term in (C.4) and (C.5) with arbitrary functions, ψ^* and ψ_s^* , respectively, and add the result to (C.3). Let the inner product of two real functions, φ^* and ξ be $\int_t \int_\Omega \varphi^* \xi \, d\Omega dt$. Since the right hand sides of (C.4) and (C.5) equal zero, their inner products can be added to the right hand side of (C.3) without changing the equality, resulting in

$$\begin{aligned} \frac{dP}{dc_N} = & \iint_{\Omega, t} \left\{ -\psi^* \theta \frac{\partial \psi}{\partial t} - \psi^* \rho_b \frac{\partial \psi_s}{\partial t} + \psi^* \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial \psi}{\partial x_j} \right) - \psi^* \frac{\partial}{\partial x_i} (\theta v_i \psi) \right. \\ & - \psi^* \lambda_a \theta \psi - \psi^* \lambda_s \rho_b \psi_s + \psi^* q_I - \psi^* q_O \psi \\ & - \psi_s^* \rho_b \frac{\partial \psi_s}{\partial t} + \psi_s^* \rho_b \alpha_s K_d \psi - \psi_s^* \rho_b \alpha_s \psi_s - \psi_s^* \lambda_s \rho_b \psi_s \\ & \left. + \psi \delta(\mathbf{x} - \mathbf{x}_w) \delta(t - t_w) \right\} d\Omega dt. \end{aligned} \quad (\text{C.11})$$

Then, we use the product rule on each derivative term in (C.11) to obtain derivatives of ψ^*

and ψ_s^* and divergence terms. The time derivative term in aqueous phase of (C.11) becomes

$$\iint_{\Omega,t} -\psi^* \theta \frac{\partial \psi}{\partial t} d\Omega dt = \iint_{\Omega,t} \left[-\theta \frac{\partial(\psi \psi^*)}{\partial t} + \theta \psi \frac{\partial \psi^*}{\partial t} \right] d\Omega dt. \quad (\text{C.12})$$

The time derivative term in sorbed phase (with function ψ^*) becomes

$$\iint_{\Omega,t} -\psi^* \rho_b \frac{\partial \psi_s}{\partial t} d\Omega dt = \iint_{\Omega,t} \left[-\rho_b \frac{\partial(\psi_s \psi^*)}{\partial t} + \rho_b \psi_s \frac{\partial \psi^*}{\partial t} \right] d\Omega dt. \quad (\text{C.13})$$

The time derivative term in sorbed phase (with function ψ_s^*) becomes

$$\iint_{\Omega,t} -\psi_s^* \rho_b \frac{\partial \psi_s}{\partial t} d\Omega dt = \iint_{\Omega,t} \left[-\rho_b \frac{\partial(\psi_s \psi_s^*)}{\partial t} + \rho_b \psi_s \frac{\partial \psi_s^*}{\partial t} \right] d\Omega dt. \quad (\text{C.14})$$

The dispersion term becomes

$$\begin{aligned} \iint_{\Omega,t} \psi^* \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial \psi}{\partial x_j} \right) d\Omega dt &= \iint_{\Omega,t} \left[\frac{\partial}{\partial x_i} \left(\theta D_{ij} \psi^* \frac{\partial \psi}{\partial x_j} \right) - \frac{\partial}{\partial x_i} \left(\theta D_{ij} \psi \frac{\partial \psi^*}{\partial x_j} \right) \right. \\ &\quad \left. + \psi \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial \psi}{\partial x_j} \right) \right] d\Omega dt \end{aligned} \quad (\text{C.15})$$

where we used the fact that the dispersion tensor is symmetric. The advection term becomes

$$\iint_{\Omega,t} -\psi^* \frac{\partial}{\partial x_i} (\theta v_i \psi) d\Omega dt = \iint_{\Omega,t} \left[-\frac{\partial}{\partial x_i} (\theta v_i \psi^* \psi) + \theta v_i \frac{\partial \psi^*}{\partial x_i} \right] d\Omega dt. \quad (\text{C.16})$$

No manipulation is done to the remaining terms in (C.11). We substitute (C.12) to (C.16) into (C.11), and rearrange the terms to isolate ψ^* and ψ_s^* as given by

$$\begin{aligned} \frac{dP}{dc_N} &= \iint_{\Omega,t} \left\{ \psi \left[\theta \frac{\partial \psi^*}{\partial t} + \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial \psi}{\partial x_j} \right) + \theta v_i \frac{\partial \psi^*}{\partial x_i} - q_O \psi^* + \psi_s^* \alpha_s \rho_b K_d - \psi^* \lambda_a \theta \right. \right. \\ &\quad \left. \left. + \delta(\mathbf{x} - \mathbf{x}_w) \delta(t - t_w) \right] + \psi_s \left[\rho_b \frac{\partial \psi^*}{\partial t} + \rho_b \frac{\partial \psi_s^*}{\partial t} - \alpha_s \rho_b \psi_s^* - \lambda_s \rho_b \psi^* - \lambda_s \rho_b \psi_s^* \right] \right. \\ &\quad \left. - \frac{\partial}{\partial t} \left[\theta \psi^* \psi + \rho_b \psi_s \psi^* + \rho_b \psi_s^* \psi_s \right] \right. \\ &\quad \left. + \frac{\partial}{\partial x_i} \left[\theta D_{ij} \psi^* \frac{\partial \psi}{\partial x_j} - \theta D_{ij} \psi \frac{\partial \psi^*}{\partial x_j} - \theta v_i \psi^* \psi \right] + \psi^* q_I \right\} d\Omega dt. \end{aligned} \quad (\text{C.17})$$

The goal of this process was to eliminate the unknown ψ and ψ_s from (C.17) by appropriately defining ψ^* and ψ_s^* . The first term in the double integral in (C.17) can be eliminated if we define

$$\begin{aligned} \theta \frac{\partial \psi^*}{\partial \tau} &= \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial \psi^*}{\partial x_j} \right) + \theta v_i \frac{\partial \psi^*}{\partial x_i} - q_O \psi^* + \psi_s^* \alpha_s \rho_b K_d - \psi^* \lambda_a \theta \\ &+ \delta(\mathbf{x} - \mathbf{x}_w) \delta(\tau - \tau_w) \end{aligned} \quad (\text{C.18})$$

where $\tau = t_f - t$ is backward time, t_f is the upper limit of the forward time domain, and τ_w is the observation time in backward time. The second term in the double integral in (C.17) can be eliminated if we define

$$\rho_b \frac{\partial \psi^*}{\partial \tau} + \rho_b \frac{\partial \psi_s^*}{\partial \tau} = -\alpha_s \rho_b \psi_s^* - \lambda_s \rho_b \psi^* - \lambda_s \rho_b \psi_s^*. \quad (\text{C.19})$$

The third and fourth terms in the double integral in (C.17) are temporal and spatial divergence terms. These terms are eliminated by defining the final and boundary conditions, respectively, on the adjoint states, ψ^* and ψ_s^* , such that these terms containing unknown values of ψ and ψ_s^* vanish. The first term of the temporal divergence term in (C.17) can be simplified as

$$\iint_{\Omega, t} -\frac{\partial(\theta \psi \psi^*)}{\partial t} d\Omega dt = -\int_{\Omega} \theta \psi \psi^* \Big|_{t=0}^{t=t_f} d\Omega. \quad (\text{C.20})$$

If we substitute (C.6) in (C.20), ψ is eliminated if we define

$$\psi^*(\mathbf{x}, t = t_f) = \psi^*(\mathbf{x}, \tau = 0) = 0. \quad (\text{C.21})$$

Equation (C.21) represents the initial condition on ψ^* in backward time. The second term of the temporal divergence term in (C.17) can be simplified as

$$\iint_{\Omega, t} \rho_b \psi_s \psi^* d\Omega dt = -\rho_b \int_{\Omega} \psi_s \psi^* \Big|_{t=0}^{t=t_f} d\Omega = 0 \quad (\text{C.22})$$

where we used (C.7) and (C.21). The third term of the temporal divergence term in (C.17) can be simplified as

$$\iint_{\Omega, t} -\frac{\partial(\rho_b \psi_s \psi_s^*)}{\partial t} d\Omega dt = -\int_{\Omega} \rho_b \psi_s \psi_s^* \Big|_{t=0}^{t=t_f} d\Omega. \quad (\text{C.23})$$

If we substitute (C.7) in (C.23), ψ_s is eliminated if we define

$$\psi_s^*(\mathbf{x}, t = t_f) = \psi_s^*(\mathbf{x}, \tau = 0) = 0. \quad (\text{C.24})$$

Equation (C.24) represents the initial condition on ψ_s^* in backward time.

We use the divergence theorem, $\int_{\Omega} \nabla \cdot G d\Omega = \int_{\Gamma} G \cdot \mathbf{n} d\Gamma$, on the spatial divergence term in (C.17) to obtain the boundary conditions on ψ^* and ψ_s^* [38]. If we substitute (C.8), the spatial derivative term on Γ_1 can be eliminated if we define

$$\psi^*(\mathbf{x}, t) = 0 \text{ on } \Gamma_1. \quad (\text{C.25})$$

Similarly, if we substitute (C.9), the divergence term on Γ_2 can be eliminated if we define

$$\left[\theta D_{ij} \frac{\partial \psi^*}{\partial x_j} + \theta v_i \psi^* \right] \cdot n_i = 0 \text{ on } \Gamma_2. \quad (\text{C.26})$$

If we substitute (C.10), the divergence term on Γ_3 can be eliminated if we define

$$\left[\theta D_{ij} \frac{\partial \psi^*}{\partial x_j} \right] \cdot n_i = 0 \text{ on } \Gamma_3. \quad (\text{C.27})$$

Then, we need to arrange the terms in adjoint equation so that it has the same form as forward equation. We firstly multiply each term in (C.19) with K_d , rearrange terms to solve for $\psi_s^* \alpha_s \rho_b K_d$, and replace the fourth term in right hand side of (C.18) with this expression. In addition, we define $\phi = \psi^*$ and $\phi_s = K_d [\psi_s^* + \psi^*]$, and substitute them into (C.18) and (C.19) and rearrange

the terms. As a result, (C.18) becomes

$$\begin{aligned} \theta \frac{\partial \phi}{\partial \tau} + \rho_b \frac{\partial \phi_s}{\partial \tau} &= \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial \phi}{\partial x_j} \right) + \frac{\partial(\theta v_i \phi)}{\partial x_i} - \phi \frac{\partial(\theta v_i)}{\partial x_i} - \lambda_a \theta \phi - \lambda_s \rho_b \phi_s \\ &\quad - q_O \phi + \delta(\mathbf{x} - \mathbf{x}_w) \delta(\tau - \tau_w) \end{aligned} \quad (\text{C.28})$$

and (C.19) becomes (3.25). Making these substitutions in (C.21), (C.24), (C.25) to (C.27), we obtain the initial and boundary conditions shown in (3.26) to (3.30). The advection term in (C.28) is different than the advection term in the ADE, so we use the groundwater flow equations to modify this term. The groundwater flow equation under transient flow conditions is given by

$$S_s \frac{\partial h}{\partial t} = \frac{\partial}{\partial x_i} \left(K_{ij} \frac{\partial h}{\partial x_j} \right) + q_I - q_O = -\frac{\partial(\theta v_i)}{\partial x_i} + q_I - q_O \quad (\text{C.29})$$

where K_{ij} is the hydraulic conductivity tensor, S_s is specific storage, and h is hydraulic head. The spatial derivative term on the last equation of (C.29) is derived from Darcy's law $\theta v_i = -K_{ij}(\partial h / \partial x_j)$.

Using $\tau = t_f - t$, and rearranging (C.29) to solve for $-\partial(\theta v_i) / \partial x_i$, and substituting this into (C.28) leads to

$$\begin{aligned} \theta \frac{\partial \phi}{\partial \tau} + \rho_b \frac{\partial \phi_s}{\partial \tau} &= \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial \phi}{\partial x_j} \right) + \frac{\partial(\theta v_i \phi)}{\partial x_i} - \lambda_a \theta \phi - \lambda_s \rho_b \phi_s - q_I \phi \\ &\quad + \delta(x_1 - x_{1_w}) \delta(x_2 - x_{2_w}) \delta(x_3 - x_{3_w}) \delta(\tau - \tau_w) - \phi S_s \frac{\partial h}{\partial \tau}. \end{aligned} \quad (\text{C.30})$$

The term containing $S_s(\partial h / \partial t)$ can be treated as a first-order decay term. In this work, we assume negligible storage, so (C.30) becomes (3.24).