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Residence time distributions for hydrologic systems: Mechanistic foundations and steady-state analytical solutions

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SUMMARY

This review presents the physical mechanisms generating residence time distributions (RTDs) in hydrologic systems with a focus on steady-state analytical solutions. Steady-state approximations of the RTD in hydrologic systems have seen widespread use over the last half-century because they provide a convenient, simplified modeling framework for a wide range of problems. The concept of an RTD is useful anytime that characterization of the timescales of flow and transport in hydrologic systems is important, which includes topics like water quality, water resource management, contaminant transport, and ecosystem preservation. Analytical solutions are often adopted as a model of the RTD and a broad spectrum of models from many disciplines has been applied. Although these solutions are typically reduced in dimensionality and limited in complexity, their ease of use makes them preferred tools, specifically for the interpretation of tracer data. Our review begins with the mechanistic basis for the governing equations, highlighting the physics for generating a RTD, and a catalog of analytical solutions follows. This catalog explains the geometry, boundary conditions and physical aspects of the hydrologic systems, as well as the sampling conditions, that altogether give rise to specific RTDs. The similarities between models are noted, as are the appropriate conditions for their applicability. The presentation of simple solutions is followed by a presentation of more complicated analytical models for RTDs, including serial and parallel combinations, lagged systems, and non-Fickian models. The conditions for the appropriate use of analytical solutions are discussed, and we close with some thoughts on potential applications, alternative approaches, and future directions for modeling hydrologic residence time.

1. Introduction

Residence time is one of the most general, widespread concepts in all of hydrology. This generality stems from the fact that, regardless of any specific system being considered (watershed, lake, ocean, etc...), water is moving and cycling into and out of neighboring systems, and the amount of time spent in any section of the connected network is an important consideration for many problems. Residence time has application to water quality, risk assessment, contaminant remediation, characterization, habitat restoration, toxicity, reaction rates, age dating, turnover times in lakes, and ocean circulation, amongst others (Cirpka and Kitanidis, 2001; Delhez et al., 1999; Maxwell et al., 2003; Neumann et al., 2008; Seeboonruang and Ginn, 2006; Solomon et al., 2010). Despite this wide range of applications, the principles of residence time are fundamentally the same in that they are all concerned with the amount of time water, or some element transported by it, has spent in the system.

The common mechanistic framework that unifies residence time theory in hydrology is often masked by the terminology and assumptions adopted for a particular study or application. This raises confusion since two studies on residence time may be referring to something altogether different. The definition adopted here will be general, but robust: the residence time is defined as the amount of time a moving element has spent in a hydrologic system, which is typically the water mass but could be solutes. Alternative names for residence time include transit time, travel time, age, and exposure time (Ali et al., 2014; Beven, 2010; Campana, 1987; Ginn, 1999; Gomez and Wilson, 2013; McDonnell et al., 2010; Schwientek et al., 2009). The latter is strictly the most general, but we will consider all of these as equivalent, at least mechanistically, for our discussion of residence time. For any finite

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volume of water (e.g. a water sample), a single residence time cannot be defined since the sample is composed of a mixture of water and this introduces the concept of a residence time distribution (RTD) (Bethke and Johnson, 2008), which will be the focus of this article.

The geometry, boundary conditions, and physical aspects of hydrologic systems cause RTDs to take on unique shapes that reflect the processes occurring within that system. A variety of solutions to the governing equations have been developed over the years for a range of systems including batch reactors, oceanic systems, aquifers, etc. To name but one, the most popular example is probably the so-called "exponential" model (Benettin et al., 2013; Danckwerts, 1953; Delhez et al., 1999; Luo and Cirpka, 2008). The simplest, and most common, of these solutions arise from the assumption of a steady-state system with respect to time. Many of these solutions are further simplified in dimensionality, which could mean assuming a 1-D model for a 3-D system and disregarding system's heterogeneity. All of these assumptions and simplifications can be constraining to such an extent that these analytical solutions might seem inapplicable or unsuitable. Still, they constitute a physical framework to understand what and how generic features, such as geometry or boundary conditions, generate the RTD. They provide a link between observations and system's characteristics that can help in testing quickly different conceptual representations and help in understanding why real hydrologic systems deviate from reference simple ones (Eberts et al., 2012; Leray et al., 2012). Another advantage of simple analytical models is that they are often formulated with a few parameters only. This allows for a straightforward characterization of the system with a small amount of data, hence offering an appealing approach to get a first approximation of hydrological processes even in data poor areas. In contrast, distributed models are more complicated to develop and require much more data to be fully characterized but offer a much greater flexibility for representing heterogeneity and unsteady conditions of a field situation. Both approaches (analytical and distributed models) are in fact complimentary.

The risk is high with analytical RTDs to take them as black box models of which parameters can be easily calibrated while the formal conditions and assumptions required to use them are overlooked, or are not clearly stated, causing confusion about the choice of a particular RTD model and about the consequences of this choice. In order to help in avoiding this, the intent of this paper is to expose clearly the physics behind the various models that are available for modeling steady-state RTDs analytically. To achieve this, this paper reviews and classifies available analytical solutions according to physical processes. This strategy is distinct from previous reviews on this topic (Małoszewski and Zuber, 1982; McGuire and McDonnell, 2006; Raats, 1974; Turner and Barnes, 1998), which presented *mathematical* models of RTDs (e.g. the exponential model or the linear model) and subsequent discussion of possible physical interpretations. In no way should these past reviews be viewed as incorrect but their presentation seems backwards to us for two reasons. First, it creates confusion regarding the use of mathematical models that can have different physical interpretations. For example, the exponential model is often associated with "perfect mixing" but exponential behavior can also emerge from other mechanisms such as the sampling of different flow paths. Second, it can be unclear whether a mathematical model selected for an RTD has any physical basis or whether it is selected simply because it provides a reasonably good fit; our aim is to assist readers in avoiding the latter whenever possible. The focal point of the paper is not the RTDs in themselves whose expressions are mostly well-known but the physical and operational (sampling) conditions, and their interplay for generating a RTD. The aim is to give clues for better understanding and modeling of the RTDs of real hydrologic systems. The introduction of additional little known solutions helps in that approach.

This paper focuses on steady-state solutions of RTD. While some of the limitations related to the steady-state assumption are discussed in Section 5, a companion paper fully addresses the topic of transient RTDs (Engdahl et al., 2016) which have received more attention in the recent years (Duffy, 2010; McDonnell and Beven, 2014; Rinaldo et al., 2015). The article is organized into three main sections, each of which is designed to be useful on its own. Section 2 is a detailed overview of the mechanistic basis for the governing equations and their theoretical development. The different derivation techniques are described as well as the basic solution techniques of the differential equations. Section 3 describes the origins of the commonly applied analytical solutions. The assumptions and conditions for these solutions are detailed with a focus on their applications to real-world scenarios. Both similarities and differences in concept between different analytical RTDs are highlighted. Emphasis is also placed on the kind of physical systems where these solutions are reasonable approximations. Section 4 discusses some of the more complicated analytical models for residence time including serial and parallel mixing models, lagged systems, and non-Fickian models. This section revises some of the earlier central assumptions (Section 2) and explains why more complicated models may be required. Lastly, a broad discussion of potential applications is provided (Section 5). Alternatives to physically-based RTDs are also presented there: they are based on more abstract concepts and introduced as complementary approaches. All of these sections are intended to be somewhat independent of each other. For instance, those readers that are only interested in applying a specific model for residence time may wish to skip Section 2 since sufficient detail about each model and its intended use are given in Section 3, and so forth. References to specific applications of each kind of model are included but we do not discuss any of the applied studies in detail. Instead, we focus on explaining the mechanistic origin and utility of the different models and leave it to the reader to critique the validity of individual studies.

2. Governing equations and generic properties of RTDs

The question of residence time in hydrologic systems always reduces to a mass balance. The difference between what follows and classical approaches for groundwater is that the mass will be formally distributed over an additional dimension of the problem space, creating the RTD. Eulerian and Lagrangian methods can be used to construct the appropriate mass balance statements but there are a few preliminary remarks that should be mentioned first.

The most precise accounting of mass possible is at the molecular level, where each water molecule has a Dirac delta distribution of mass and residence time. Obviously this is not a practical approach for hydrologic problems, but it is a useful conceptual starting point. The residence time is defined as the time since that molecule entered the hydrologic system up to the observation time. Physical processes may move the molecule but its mass is constant and its residence time is always Dirac delta distributed, linearly increasing over time. Addition of a second molecule to a sample creates the possibility for a non-uniform RTD so any sample of water is distributed over residence time whether it is a single molecule or all the water on the planet. Any difference in the residence time of the molecules creates a distribution that is no longer a Dirac delta and the more water molecules are sampled, the broader and more complex the RTD is expected to be (Fig. 1). The goal of this section is to present the governing equations for the aqueous phase mass balance, distributed over residence time,

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