

**RESEARCH ARTICLE**

**A Temporally Relaxed Theory Models for Non-Equilibrium Solute Transport in Layer Media**

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**ABSTRACT**

This study uses a mathematical model based on the temporally relaxed theory of Fick's law to describe the one-dimensional (1D) non-Fickian transport of solutes in a layered heterogeneous porous medium. The methodology introduces two relaxation times to accurately consider solute particle collisions and attachment, resulting in the development of new advection-dispersion equations (ADEs) for each layer. In this scenario, it is assumed that each layer of the porous medium is initially contaminated by a background source. Additionally, we are taking into account a time-dependent input source located at the origin of the domain. The semi-analytical solution of the proposed model is obtained using Laplace Transform Techniques and a numerical inversion of the transformation. All graphic plots are obtained using MATLAB software. The results show that the temporally relaxed theory can reproduce the solutes transport behaviour described by the existing two-stage models, 1D equilibrium models in homogeneous and layered media. Additionally, relaxation times significantly affect the spatial distribution of solute concentration in layered media and the remediation time. This innovative approach provides a deeper insight into solute transport in layered media and its impact on groundwater contamination. It can serve as a preliminary tool for future researchers studying decaying solute migration such as radionuclides in groundwater and their impact on water quality.

**Keywords:** Advection; Dispersion; Times laggings; Sorption; Two-stages models.

**1. INTRODUCTION**

The increasing human activities have led to a significant rise in pollution levels, which is a major concern for environmental researchers. When pollutant concentrations are significantly elevated, this poses a potential risk to ecological receptors. This situation leads to widespread pollution of the atmosphere, soil, and notably, water bodies. Water pollution in urban areas is particularly troubling, as water is the ultimate recipient of various forms of pollution (Kengni et al., 2012). Groundwater contamination renders it unsuitable for human use and presents significant challenges in terms of cleaning, requiring substantial time and resources. Understanding the hydrological processes that govern the transport of pollutants in groundwater is essential for developing effective strategies for remediation and management of contaminated sites, and for mitigating the impacts of pollution on aquatic ecosystems. This involves the development of new mathematical models that can facilitate the study of pollutant behaviour in groundwater.

The Advection-Dispersion Equation (ADE) is often used to describe the transport of solutes in groundwater. Sorption processes can be approximated by a linear relationship, allowing for a single equation to describe the transport (Thorne 2014). Various studies have examined the transport of pollutants in homogeneous porous media using different techniques (Van Genuchten 1981). Sim and Chrysikopoulos (1996) studied the impact of time-dependent distribution coefficients on virus transport with pseudo-first-order inactivation. Smith (2000) examined solute transport in a deformable medium with sorption processes. Van Genuchten et al. (2013) introduced ADEs for solute transport in surface waters. Sudheendra et al. (2014) used solutions for solute transport analysis in soil columns. Niranjan et al. (2015) studied pollutant transport in unsaturated porous media. Raij & Sudheendra (2018) presented a solution for sorbing solute transport in porous formations. Moranda et al. (2018) proposed an analytical solution for contaminant transport in soils. Considering heterogeneity in the ADE is essential for analysing pollutant transport in real-world environments, but also their impact on the water cycle.

Media can exhibit heterogeneous behaviour due to variations in properties with position or the presence of different geological formations, leading to layered media. There is extensive research on the 1D Fickian transport of pollutants in a medium with space-dependent coefficients (Freeze and Cherry 1979; Dagan 1984; Chrysikopoulos et al. 1990; Liu et al. 2000; Ghosh and Sharma 2006; Guerrero and Skaggs 2010; Sing and Das 2015; Bharati et al. 2017, 2018 and 2019; Chaudhary et al. 2020; Sobhi Gollo et al. 2022). Tjock-Mbaga et al. (2022) studied the impact of pollution sources localized at the boundaries of a domain on pollutant dispersion in heterogeneous groundwater reservoirs. Paul et al. (2024) developed a model for solute migration under spatially dependent sorption in heterogeneous groundwater reservoirs. These models explored the influence of the degree of heterogeneity on contaminants dispersion in groundwater.

Pollutant transport in layered media has garnered limited attention and remains an area of ongoing research. Layered porous media are often found in natural and engineered settings, like stratified soils and landfill liners (Liu et al. 1998). In this context, the transport coefficients exhibit piecewise constancy. Al-Niami and Rushton (1979) used the Laplace technique to derive solutions for solute transport in finite layered media. Similarly, Leij et al. (1991) applied the Laplace transform to derive an analytical solution for the 1D ADE in a semi-infinite two-layer medium. Subsequently, Liu et al. (1998) used the Generalized Integral Transform Technique (GITT) to solve a 1D multilayer conservative solute transport problem in finite media with arbitrary time-varying inlet concentration. Guerrero et al. (2013) utilized the GITT to find an analytical solution for the ADE of a decaying solute transport with a constant inlet boundary. Carr (2020) suggested reutilizing the Laplace transform and introducing unknown functions at each interface to simplify solving multilayer problems. Carr (2021) used the same method to solve multispecies transport problems in layered media. Tjock-Mbaga et al. (2023) extended the work of Carr (2020) to transport problems in groundwater reservoirs with spatiotemporal variable coefficients and two input sources. They show that the multilayer analysis can accurately reproduce solute transport with position- and time-dependent coefficients.

Classical ADEs are derived from Fick's law, which establishes a constant relationship between concentration gradient and mass flux. Complex physical and chemical processes in a medium often involve mass continuity equations (Carr, 2020, 2021). While conventional ADEs based on Fick's law are commonly used, they may not fully account for observed concentration increases due to non-Fickian behaviors, or anomalous transport. This phenomenon would be influenced by the heterogeneity of the porous medium (Benson et al. 2013; Kelly and Meerschaert, 2017). There are very few studies in the literature on the non-Fickian transport of pollutants in layered media. Filistovič et al. (2015) introduced a semi-analytical solution for modeling contaminant transport in lake water and 1D sediment solute transport. This solution includes non-equilibrium processes for a more accurate depiction of the dynamics involved. This problem involves several parameters. Lin et al. (2023) introduced the "temporally relaxed theory" on solute transport, a two-phase lagging model based on Fick's theory. They used this concept to develop a new ADE and a new model for non-Fickian transport of a contaminant in porous media.

This research aims to extend the work of Lin et al. (2023) regarding temporally relaxed theory to the study of the non-Fickian transport behavior of solutes transport in layered porous media. This will be applied to the analysis the interaction between times lagging, solute concentration distribution, and some hydrological processes in groundwater. The approach incorporates relaxation times into the ADE describing contaminant transportation within each layer. This will lead to the development of new ADEs and a new model for non-Fickian transport in layered media. The research will consider an arbitrary number of layers and a general Robin-type input condition with an arbitrary time distribution. To address the issues caused by the inclusion of time lags, the relaxation times are assumed to be significantly smaller than the overall time scale under study. The first-order approximation of the Taylor series expansion is employed to capture the major time lag effect on the concentration response. The resulting system of equations will be solved semi-analytically using the Laplace transform technique. The study will examine how relaxation times affect contaminant distribution in each layer, the rehabilitation of contaminated environments, and their impact on specific hydrological processes.

**2. MATERIALS AND METHODS**

**2.1** **Problem formulation**

This study focuses on solute transport in a layered porous medium, incorporating processes like advection, dispersion, sorption, decay reactions, and production. Understanding and quantifying these processes is essential for managing and mitigating environmental pollution and ensuring groundwater safety. Let  be the number of layers and assume the medium is layered as follows (Fig. 1). The governing ADE of contaminant transport in layer can be expressed in general form as:

 (1) For each layer ,  is the retardation factor,  is the aqueous solute concentration at the position and at a time ,  is the dispersion coefficient,  is the pore water velocity, and  is the first order decay rate.  represents a zero-order production.

The advective-dispersive terms in right-hand side of Eq. (1) may be expressed in terms of the mass flux in the layer as follows:

 (2)

Eq. (2) suggests a constant relationship between mass flux and concentration gradient in a layer, implying that mass particles could theoretically move at infinite speed. However, this assumption inadequately represents certain groundwater interactions. In practice, the relationship between concentration gradient and mass flux may change over time due to inertial forces and particle collisions. To address this issue, a proposal has been made to modify Eq. (2) for Fick's law, considering the mass flux and concentration gradient occurring at different times:

 (3)

 and  are flux lagging and storage lagging parameters in each layer, respectively.

The flux lagging parameters represent the relaxation times of a system due to various factors.  and reflect respectively the inertial effects of mass particle collisions and structural interactions like sorption and secondary pore water interactions in a layer . These parameters can vary between layers due to their dependence on the properties of the medium. The comparison between the values of  and provides information about the process that precedes the other one, as consequently indicates the causal factor of concentration gradient. When , the mass flux and concentration gradient occur simultaneously, then Eq. (3) can be reduced to its simpler form given by Eq. (2). The analysis of these two parameters enhances our understanding of the complex physical and chemical interactions within porous media, enabling researchers to gain insights into dynamic processes and their effects on solute transport. Relaxation times are inversely proportional to the transfer rate coefficients of Rate Limited Sorption (RLS) and Mobile-Immobile Models (MIM), adjusted by different constants (Lin et al., 2023). Conventional two-stage models (RLS and MIM) involve numerous parameters for each layer, complicating manipulation (Filistovič et al., 2015). In contrast, the temporally relaxed theory approach simplifies this by removing the need to understand matrix blocks or the sorption properties and interactions of each layer.

Assuming that  and  are quite small compared to the overall time 𝑡, applying the Taylor series expansion to Eq. (3), and taking its first-order approximation (Tzou, 1995) leads to:

 (4)

Substituting Eq. (4) into Eq. (1), the temporally relaxed ADE in layer  is then obtained as:

(5)

In Eq. (5), the reactive terms in the modified ADE of layer j has been multiplied by the first-order approximation of the concentration gradient . This aims to maintain consistency with the classic ADE in terms of the relationship between the reactive terms and the concentration gradient.

The medium is assumed to contain constant background contamination in each layer before introducing pollutant sources. The initial condition can be expressed as:

 (6)

A robin boundary condition is considered at the inlet of the porous medium (). It is also assumed that no mass crosses the other end of the domain. It is expressed by a flux-type condition at the other end. Thus, boundary conditions are written in general form as follows:

 (7)

 (8)

In Eq. (7), represents the Kronecker delta function. For , Eq. (7) represents an input condition of increasing nature, while for , it reduces to an input condition of uniform nature.  is an arbitrary time function specifying the rate of contaminant entering in the first layer.

The contaminant concentrations in layers () and () are related by assuming the continuity of concentration and dispersive flux at the interfaces between adjacent layers (). The perfect contact at layer interfaces is assumed in this study so, the continuity of concentration and dispersive flux are written as (Leij et al. 1991; Liu et al. 1998; Pérez Guerrero et al. 2013):

 (9)

 (10)

**2.2** **Semi-analytical solution**

The system of eqs. (5)–(10) addresses a non-traditional contaminant transport problem in layered media, featuring time lags that render conventional methods unsuitable. Instead, we apply the Laplace transformation technique and the generalized semi-analytical method proposed by (2020) to solve these equations. This versatile approach adapts to various transport problems in layered media, regardless of boundary conditions. Following this approach as detailed in Appendix A, the Laplace domain expression for the pollutant concentration in the layer  is defined as:

 (11)

 (12)

 (13)

where the functions  , and  () are defined in Table 1.

The unknown interface functions  () are determined by imposing the continuity of concentration in the Laplace domain () in each interface layer (Carr, 2020, 2021):

 (14)

A substitution of Eqs. (11)–(13) into the system of Eqs. (14), yield to the following resulting linear system:  (15)

where is a column matrix with elements, elements of tridiagonal matrix () and -length vector  () (), are given by:





















The solution of solute concentration for () in the time domain can be obtained using the numerical inversion schemes of . The numerical inversion of the Laplace domain solution is performed using the CMS-S method (Horváth et al., 2023). The CME-S method is renowned for its exceptional numerical stability, as it effectively circumvents issues of overshooting and undershooting, and yields precise results with increasing order.

**3. RESULTS**

This section verifies the semi-analytical model through comparisons with existing models and numerical solutions. It also discusses the effects of time lagging on solute distribution and groundwater remediation.

**3.1** **Verification of the developed solution**

In this subsection, we evaluate the capabilities of the temporally relaxed theory model to replicate solute concentration distributions obtained by various models based on linear equilibrium and NE concepts. We are using three analytical solutions from the literature to validate the model for both two-stage and linear equilibrium models. To perform this validation, we are simplifying the temporally relaxed theory model in layered media into the LE one layer, MIM one layer, and LE multilayer models by selecting specific values for various coefficients. The MATLAB code obtained from github.com/elliotcarr/Carr2020a has been employed, undergoing modifications to accommodate the temporally relaxed theory, the CMS-S method, as well as the inclusion of each relevant comparison case.

***3.1.1 Comparison with linear-equilibrium one-layer model***

Van Genuchten and Alves (1982) developed analytical solutions for solute transport in both finite and semi-infinite media using the linear equilibrium model. The temporal relaxed model is transformed into the linear equilibrium model by encompassing two layers with identical transport parameter values in each layer and considering in each of the layers. The supplementary parameters needed for this comparison are explicitly enumerated in the linear equilibrium column of Table 2. Figure 2 presents a comparison between the solute concentration derived from the temporally relaxed theory (shown as solid lines) and the LE model (indicated by markers) for a pulse injection originating from a source of uniform and increasing nature. The curves illustrate that under both input conditions, the concentration gradually decreases with position during the injection period until it reaches zero. Upon removal of the source, the concentration exhibits an increase with position up to a maximum value, after which it begins to decrease. The curves also show that the results obtained for both models are in good agreement, suggesting that the temporally relaxed theory can accurately replicate solute concentration patterns for the LE model.

***3.1.2 Comparison with linear-equilibrium multilayer model***

 Carr (2020) presented a semi-analytical solution for 1D solute transport in a porous medium with an arbitrary number of layers using the Laplace transform. The semi-analytical solution of the temporally relaxed model in layer media can be reduced to the linear equilibrium model in layer media by consideringin each of the layers as in the previous subsection. The input parameters are given by Guerrero et al. (2013) and are shown in Table 2. Figure 3 compares solute concentrations obtained using the temporally relaxed theory (solid lines) and linear equilibrium multilayer model (markers) for a pulse injection from a uniformly increasing source. Figs. 3(a) and 3(b) depict this comparison for a two-layer medium, while Figs. 3(c) and 3(d) depict this for a five-layer medium, both representing cases studied by Guerrero et al. (2013). Figure 3 depicts a noteworthy alignment between the temporal relaxed theory and linear equilibrium models for each of the cases examined. This finding implies that the temporal relaxed theory can replicate the solute transport behavior described by the LE transport model in layer media.

***3.1.3 Comparison with non-equilibrium mobile immobile model (MIM)***

Van Genuchten and Wlerenga (1976) developed an analytical solution to study chemical movement through porous materials, considering lateral or intra-aggregate diffusion. They described the liquid phase in the material as having mobile and immobile regions, assumed instantaneous sorption processes, a linear adsorption isotherm, and a Cauchy-type input boundary condition with a pulse-type source. For comparison, the model proposed in our study can be simplified as two layers with the same relaxation time values in each layer. The formulas proposed by Lin et al. (2023) to connect the parameters of the MIM model with those of the temporally relaxed theory (please see Table 1, page 4), are used to calculate the values of , and . We obtain the values , et ​. The ratio  is greater than 1, showing that the solute transport is dominated by , indicating resistance from structural interactions in the medium. The comparison is based on parameters outlined by Van Genuchten and Wlerenga (1976), as delineated in Table 2. In Figure 4, the breakthrough curves of contaminant concentration at various positions are depicted using the temporally relaxed theory (solid lines) and the MIM model (markers) for two values of the ratio. The curves show that the concentrations obtained by both initially increase rapidly at low times, then show a slight increase at intermediate times up to a certain value. After that, the concentrations decrease rapidly with time until they reach an asymptotic value that depends on the position. The contamination concentration trend is a reflection of the dynamic pulse form of the input source. The curves also demonstrate an excellent agreement between the concentrations obtained with the temporally relaxed theory and those of the MIM. This finding indicates that the temporally relaxed theory can replicate the solute transport behavior described by the MIM model, contingent on the appropriate specification of values for both and .

**3.2 Effects of times laggings**

In this subsection, our focus lies on evaluating the influence exerted by the parameters andon the concentration distribution and the rehabilitation of the medium. Figures 5(a) and (b) depict the spatial distribution of the contaminant concentration at  and respectively, in a medium with two layers. The curves illustrate a uniform input distribution of increasing nature. The values of  and are assumed to be the same for each layer. The parameters used are identical to those depicted in Figures 3(a) and 3(b). It is shown that increasing the value of leads to an increase in concentration level in both layers. This is because the continuous injection of mass particles leads to an accelerated saturation of the soil pore at the origin. An increase in  precipitates the swift liberation of contaminant particles from the soil, consequently culminating in an increase of concentration at each of the positions. Conversely, increasing causes a decrease in concentration values in the first layer. This is because the consistent influence of inertial force on the continuously injected mass particles results in the particles being held near the inlet. The graphs also demonstrate that the concentration values are higher in Fig 5 (a) compared to those in Figure 5 (b) as increases, while the concentration values are lower in Fig 5 (a) compared to those of Fig 5 (b) as increases. This is because, as time progresses, the particles interact with the soil, leading to decreased concentration at all positions with the increase of . Conversely, an increase in  prompts the movement of all particles, including newly injected ones, toward the exit, resulting in increased concentrations over time. Ultimately, the results of relaxation times differ based on the type of interaction.

Figs 5(c) and (d) depict the spatial distribution of the pollutant concentration at  and respectively, in a medium with five layers. The curves illustrate a uniform input distribution of increasing nature. The parameters used are identical to those depicted in Figs 3(c) and (d). It reveals that increasing the value of leads to a decrease in concentration level at lower distances and an increase in concentration at greater distances for both times. It can be observed that at , the trend of concentration changes at the end of the first layer while for , this trend changes approximately in the middle of the third layer. Two main factors can explain the observations. First, near the entrance of the domain, collisions between particles push the particles forward, leading to a decrease in concentration at lower distances. This causes an accumulation of particles and increased concentration at long distances. Second, with the continuous injection of mass, the number of injected particles increases over time, resulting in more collisions. As a result, the distance over which collisions are important also increases over time. Conversely, an increase in results in the appearance of concentration peaks at short distances and a rapid decrease in concentration values at long distances. Furthermore, it can be observed that the concentration peaks obtained at t = 10 days are more pronounced and occur at greater distances compared to those at . Additionally, the concentration level increases and decreases rapidly at  in comparison to . These observations arise from the fact that an increase in leads to a swift release of particles injected at the inlet of the domain due to continuous mass injection, thus causing a buildup of particles near the entrance. Subsequently, there is a considerable absorption of pollutants by the solid particles in the medium as they travel, resulting in a decline in concentration with distance. Moreover, an increase of injected pollutants over time results in a progressive rise in concentration and a shift of concentration peaks to the right. It is clear that the effects of time laggings show the same results for different observation times but the concentration level depends on the observation time.

In summary, relaxation times significantly affect contaminant distribution in a layered medium, making it essential to include these variables in the solute transport equation when analyzing environmental dynamics.

Figs. 6 illustrates the concentration pattern in absence of source () at different times, for different combination of (,) in a medium with five layers. The time of elimination of the source of pollution is considered as . It reveals for each combination of (,) and at each time, that concentration values increase with positions until a maximum value depending on time and the values of and, then the concentration starts to rehabilitate toward harmless level. The increase and the decrease rates are higher for larger values of and lower for higher values of . Few times after the source’s removal (), the peaks of concentration are obtained near the inlet boundary. As times increases, the peak of concentration moves forward, the maximum concentration values for fixed value of increase for first periods and then decrease while for fixed value of  the maximum concentration values then decrease with time. On the other hand, increasing the value of  leads to a higher maximum concentration and a shift of the peak to the left while, increasing causes a decrease in the concentration peak and shifts the peak to the right. It can be also observed, that a greater  leads to lower concentration values at lower positions and higher concentration values at greater positions. However, as time increases, the concentration values at lower positions decrease and slightly increase for higher positions. Those observations can be attributed to the fact that, just after the source removal, the number of collisions of mass particles is greater near the inlet, resulting in some particles being pushed forward. As time increases, the pushed particles collide with those encountered along the way. On the other hand, that a greater  leads to higher concentration values at lower position and lower concentration values at greater positions. However, as time increases, the concentrations values at lower positions decreases while, the concentration values increase at intermediary positions and slightly increase at higher positions. a large value of indicates a stronger interaction between the mass particles and the soil resistance due to structural interaction. This is because, just after the source removal, we assist in a stronger release of particles from the soil near the inlet, resulting in higher concentration values. Later, the particles attached to the soil start to release along the medium, leading to a large amount of mass being released into the flow path. This results in a higher peak in the intermediate position. Rehabilitation rate is faster for higher values of  and slowly for higher values of . Overall, these findings demonstrate the importance of considering the time lag effects when studying the rehabilitation of a contaminated medium such as groundwater.

**4. DISCUSSION**

The results presented above are based on the temporally relaxed theory of contaminant transport in layer media. This theory is a two-stage model of non-fickian transport that includes two relaxations times and in each of the layer. The two times laggings arise from different structural interactions, influencing hydrological processes, solute distribution in groundwater, and its quality in different ways. Moreover, hydrological processes and environmental factors also affect relaxation times. Factors such as solute concentration, porosity of the porous media, flow rate, temperature, pressure, water density, and viscosity can cause particle collisions (McDowell-Boyer et al., 1986; Elimelech and O’Melia, 1990; Panfilov et al., 2008). Factors such as the surface charge of the solute particles, grain shape parameters, pore connectivity, surface area of the porous matrix, interfacial tension, chemical composition of both the solute and the matrix, and fluid properties such as friction forces may play a role for particles retention (Bradford et al., 2002; Yang et al., 2022; Ogolo and Onyekonwu, 2022).

The temporal relaxation theory effectively replicates concentration profiles from Fickian models in both homogeneous and layered media, as demonstrated in Figures 2 and 3. Notably, when the same parameter values are applied across all layers, and the same values of and , are considered, the resulting concentration profiles align with those predicted by Van Genuchten and Alves (1982) for uniform and increasing nature of input distributions. These findings align with Lin et al. (2023), who suggested that simultaneous mass flux and concentration gradient simplify the model to a linear isothermal equilibrium transport model. When relaxation times are non-zero, the inertial forces on particles are balanced by retention and release processes. As a result, relaxation times have minimal influence on pollutant dispersion, adsorption, retention, and flow velocity, leading to a limited impact on water quality and pollutant distribution as well as the water cycle. This observation is further substantiated by the results presented in Figure 3, which pertains to layered media. By considering the same values of and in each layer, the temporally theory enables the obtaining of concentration distributions predicted by the Fickian models of Pérez Guerrero et al. (2013) and Carr (2020). Non-Fickian transport can be regarded as a limiting case of the temporally relaxed theory when it is assumed that the two aforementioned phenomena occur simultaneously.

The temporally relaxed theory accurately reproduces the concentration profiles from the MIM, as shown in comparison with Van Genuchten and Wierenga (1976) in Figure 4. The MIM, the RLS model, and the temporally relaxed theory are three transport models based on distinct concepts, yet sharing the same two-stage process. The MIM is based on mass transfer between primary and secondary pores, whereas the RLS model is based on mass exchange between liquid and solid phases. The mass exchange between mobile and immobile phases (MIM) and the sorption kinetics (RLS) can influence contaminant migration, and contaminant retention, and consequently impact water quality and human and environmental health (Bear, 1972; Van Genuchten, 1980; Weber and DiGiano, 1996). Both models involve several parameters, including matrix blocks and sorption properties, that must be well understood. Adjusting these, especially in a layered medium, is complex. The temporally relaxed theory addresses this issue by characterizing the two-stage transport process using two empirically determined relaxation times and. Therefore, the temporally relaxed theory resolves the problem associated with the use of numerous parameters related to the MIM and RLS models.

Figures 5 and 6 illustrate that relaxation times significantly affect pollutant concentration distribution in layered media. In the two-layer medium, no concentration peaks are observed, and an increase in raises overall concentration, while an increase in results in a decrease in concentration throughout the domain. In contrast, the five-layer medium shows opposite effects at short distances but similar effects at larger distances. This suggests that relaxation times impact concentration distribution based on transport parameters, including water flow velocity, dispersion coefficient, and sorption phenomena. Indeed, in highly dispersive media with high flow velocities and negligible sorption (such as the two-layer medium here), variations in time lags do not affect pollutant distribution in groundwater. However, they influence contamination levels and migration rates: an increase in raises pollutant migration velocity, while an increase in  lowers it. On the other hand, for a less dispersive medium, with low flow velocity and moderate sorption (such as the five-layer medium), variations in or affect the nature of pollutant distribution, the level of contamination, and the migration velocity of pollutants in the medium in groundwater. The behaviors observed align with the findings of Lin et al. (2023) regarding continuous mass injection into a single-layer medium with negligible sorption and low flow velocity. Relaxation times are connected to the mass transfer rate between solid and liquid phases, as well as the sorption process, which affects pollutant migration velocity (Bear, 1972). Thus, relaxation times influence certain hydrological processes in a porous medium during continuous mass injection, depending on dispersion, water flow velocity, and sorption effects.

The rehabilitation of a contaminated medium which determines the rate at which pollutants are eliminated or degraded in the medium is influenced by the relaxation times and as shown in Figure 6. The higher the collisions between particles (higher values of ), the longer it takes for the medium to be rehabilitated, because, after the removal of the source of contamination, the particles collide near the inlet boundary of the medium, causing some to move forward, which increases the concentration. On the other hand, the higher the sorption phenomena (higher values of ), the faster the medium is rehabilitated due to the attachment of particles to the solid particles of the soil. The relaxation times can influence the remediation of a medium in such a way that they can help evaluate the duration required to remediate a contaminated medium. This can enable the determination of the remediation duration necessary to achieve water or soil quality objectives (Bear, 1972). They can also influence the design of remediation strategies. For example, if relaxation times are short, it may be possible to use more aggressive remediation methods, such as pumping and treating water, to quickly eliminate pollutants. In contrast, if relaxation times are long, it may be necessary to use slower and more sustainable remediation methods, such as phytoremediation or bioremediation (Weber et al., 1991). Another manner which relaxation can influence the remediation process are the optimization of the remediation and long-term management. Indeed, relaxation times can indicate the areas of the medium where pollutants are most concentrated and where remediation efforts should be focused. This can enable the reduction of costs and remediation times by targeting the most critical areas (Fried, 1975). Relaxation times can indicate whether pollutants are likely to persist in the medium for an extended period. This can enable the determination of whether long-term management measures are necessary to prevent re-contamination of the medium (Freeze et al., 1979).

In summary, the structural interactions within the environments affected by pollutants influence the relaxation times, which in turn affect the distribution and concentration levels of these pollutants. This impact is observed during both the injection of the contamination source and its subsequent removal (affecting rehabilitation). The extent of this impact depends on the types of structural interactions involved. Certain irregularities observed in the water cycle, caused by the presence of pollutants in groundwater, can be effectively explained by temporally relaxed theory. These irregularities are primarily related to the increasing concentration of pollutants in the environment. The presence of contaminants in groundwater can diminish evapotranspiration (Freeze and Cherry, 1979), influence precipitation formation (Dagan, 1984), and reduce infiltration while increasing runoff (Sim and Chrysikopoulos, 1996). These phenomena can therefore considerably impact the water cycle. Furthermore, contaminants in groundwater can reduce groundwater recharge, which can have an impact on water availability (Todd, 1980). They can also influence recharge mechanisms, such as infiltration and percolation (Fetter, 2001) and recharge areas, which can have an impact on water distribution (Ridder, 1994). Finally, contamination of groundwater can reduce its velocity, flow paths, and dispersion and diffusion, all of which impact groundwater movement (Scheidegger, 1961; Perkins and Johnson, 1963; Bear, 1972It is essential to understand the actual level of groundwater contamination and its impact on water quality. The relaxed time theory allows for a more accurate estimation of pollutant concentration levels in groundwater within complex environments, where transport is described by two-stage processes. The results obtained ultimately show that for a layered media, the theory of relaxed times makes it possible to better locate the layer that needs treatment to be rehabilitated. The two major limitations of our work are that the relaxation times were approached in the macroscopic aspect and also the effects on hydrological processes were taken globally.

**5 CONCLUSIONS**

In this study, the temporally relaxed theory is introduced into an ADE to describe the non-Fickian behavior of solute transport in 1D layer media. The concentration-response is governed by an ADE that includes two relaxation times, and, which allows for differences in the timing of mass flux and concentration gradient in each layer. The solution of the problem is obtained semi-analytically with the help of the Laplace transform technique before being numerically inverted in the time domain. The results obtained show that the temporally relaxed theory model for layer media can replicate solute concentration behavior based on LE and NE concepts. The relaxation times, andsignificantly affect the spatial distribution of contaminants in a layered medium due to the presence of interactions between particles and particles and soil. The manifestation and magnitude of these effects are contingent upon the specific nature of the interactions under consideration, the observation time, and the precise composition and structural properties of the porous medium in question. Indeed, a medium with two and five layers has different concentration responses with the variation of and. The derived solutions extend recent work on temporally relaxed theory on solute transport in layer porous media. The present study seems to be a simple yet innovative and effective tool for analyzing contaminant transport in a layered medium exhibiting a two-stage model. This study may be helpful for ecologists or geologists to determine the harmless concentration level in a porous medium and can serve as an opening tool for contaminant migration for future researchers. It is particularly recommended for the study of transportation of radionuclides in deep geological repository systems. This present work can also be used by hydrologists to get an idea of ​​the effect of contaminants on the global water cycle. In future studies, we plan to conduct a numerical modeling analysis at the pore scale to explore the relationship between pore-fluid interactions and relaxation times. Additionally, we will need experimental data to examine the actual impact of relaxation times on various hydrological processes.

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**DATA AVAILABILITY**

Data will be made available from the authors on reasonable request.

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**Figures captions**

**Figure 1:** Schematic diagram of the one-dimensional solute transport in a layer medium affected by the temporally relaxed effects due to inertial force and sorption.

**Figure 2**: Spatial distribution of concentration predicted by the present study and van Genuchten and Alves (1982) for a pulse like input source: (a) input source of increasing nature, (b) uniform input source.

**Figure 3:** Spatial concentration distribution in different layer media predicted by the present study and Carr (2020) for a pulse like input source: (a) and (c) input source of increasing nature, (b) and (d) uniform input source.

**Figure 4:** Breakthrough curves predicted by the present study and MIM model (van Genuchten and Wlerenga, 1976) for a pulse like input source of increasing nature: (a) , (b) .

**Figure 5:** Spatial concentration distributions predicted by the temporally relaxed theory at different times for various combinations of (,) values, (a) and (b) case of two layers; (c) and (d) case of five layers.

**Figure 6:** Spatial concentration distributions predicted by the temporally relaxed theory at different times for various combinations of (,) values in a medium of five layers after the source removal.

**APPENDIX A: ANALYTICAL SOLUTION OF THE MULTILAYER TRANSPORT PROBLEM IN THE LAPLACE DOMAIN**

The transport problem in Eqs. (5)-(8) is rewritten into  separated single-layer problems (Carr 2020; 2021). After, unknown functions of time,  are inserted, to designate the scalar multiple of the (negative) dispersive flux at the layer interfaces (Carr and Turner 2016; Carr 2020; 2021):

 (A1)

yields Eqs. (5)-(8) to be written in the following equivalent model in each layer:

* First layer ()

 (A2a)

 (A2b)

 (A2c)

 (A2d)

* Intermediary layer ()

 (A3a)

 (A3b)

 (A3c)

 (A3d)

* Last layer ()

 (A4a)

 (A4b)

 (A4c)

 (A4d)

each problem is coupled together by imposing continuity of concentration at the interfaces between adjacent layers Eq. (9) (Carr and Turner 2016; Rodrigo and Worthy 2016; Carr and March 2018, Carr 2020; 2021).

Taking the Laplace transform of transport problem in Eqs. (A2a)-(A2d), (A3a)-(A3d), (A4a)-(A4d) yield:

* First layer ()

 (A5a)

 (A5b)

 (A5c)

* Intermediary layer ()

 (A6a)

 (A6b)

 (A6c)

* Last layer ()

 (A7a)

 (A7b)

 (A7c)

where, , denotes the Laplace transform of with Laplace parameter and for .

The boundary value problems (A5a)–(A5c), (A6a)–(A6c) and (A7a)–(A7c) all involve second-order constant coefficient differential equations and can be solved using standard mathematical techniques.