Experiments and models for contaminant transport in unsaturated and saturated porous media – A review

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ABSTRACT

Soil column experiments in both saturated and unsaturated conditions are widely used for practical and theoretical research in a variety of domains, including the assessment of transport models, the fate and transport of pesticides, explosives, microorganisms, heavy metals, and non-aqueous phase liquids. And the application of models associated with experiments has grown in popularity, owing mostly to their predictive capacity. This paper discusses the complex interactions between saturated/unsaturated porous media and the mechanisms of contaminant migration in column experiments, with an emphasis on the relevant environmental factors affecting the migration of various types of contaminants in column experiments and an analytical summary of the mechanisms affecting contaminant migration factors. The modeling of contaminant transport in unsaturated and saturated groundwater zones is integrated and presented, and research on the coupling of related models with other modeling algorithms is presented. The assessment of regional-scale pollutant transport models is integrated with other assessment models and algorithms to arrive at the appropriate groundwater management options.

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Contents

1. Introduction

Soil and groundwater environments are important connotations of the lithosphere and hydrosphere. The spatial and temporal distribution characteristics and changes of their physical, chemical, biological and environmental parameters can change, which have important theoretical and practical values for understanding and studying the macro-micro processes in the subsurface environment as well as the environmental quality on which human beings depend (Williams, 2020; Bell et al., 2000; Yu et al., 2022). Pollutant migration behavior and patterns in the groundwater environment vary with the geographical and temporal distribution features of environmental factors, and there is significant heterogeneity in groundwater flow and pollutant migration patterns in each location (Dobrovol'skii, 2006). Therefore, the application of experimental and mathematical modeling research methodologies to examine the flow and pollutant transport characteristics of unsaturated and saturated groundwater zones plays an essential role in human protection and usage of groundwater environments. Fig. 1 presents the history of the development of the column

experiment and the development and application of the model.

There are numerous sources of groundwater contamination, including both anthropogenic or human-created substances dissolved or mixed in supplementary aquifers, such as nitrate pollution from surface sewage (waste) water discharges and agricultural pollution and landfill leakage, and natural contaminants, such as naturally occurring excess iron, manganese, and arsenic, radioactive contaminants in bedrock, and saltwater intrusion from coastal areas. To study the migration mechanisms of groundwater contaminants, contaminant migration in column experiments can be divided into different types based on its characteristics: multicomponent multiphase flow issues and dissolved contaminant migration in groundwater. Transport of dissolved pollutants has been extensively studied, while contaminants in multicomponent multiphase flows are more challenging to manage. For instance, heavy non-aqueous phase liquids (DNAPL) in multi-phase flows are denser than water and can sink rapidly into the ground, making DNAPL spills more challenging to manage than oil spills, and it is difficult to remediate groundwater by pumping and injecting
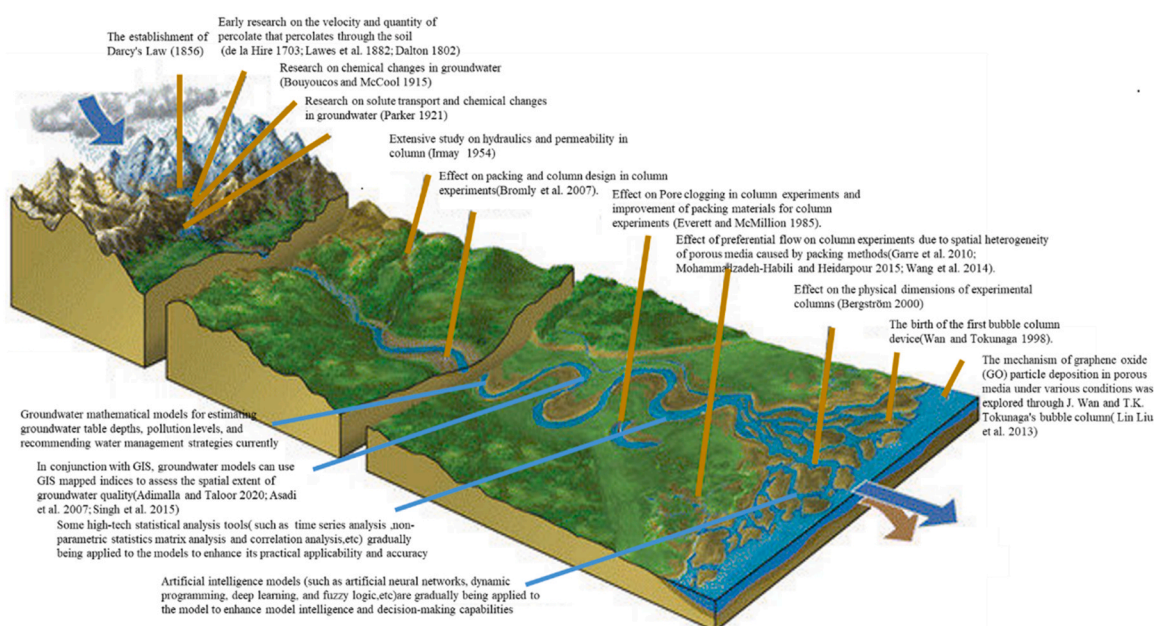

Fig. 1 – A chart of the history of the development of the column experiment and the development and application of the model.

water as opposed to dissolved contaminants. Therefore, the mechanisms of contaminant transport in multi-component multiphase flows are essential for remediation of groundwater. The study of multi-phase flow and multi-component contamination transport focuses on how to create contaminant mass transfer connections during the transfer of pollutants between phases and which mathematical models can effectively represent mass transfer patterns between phases. The use of soil column experiments allows for the downscaled study of pollutant transport and the demonstration of contaminant movement at the interface between two phases.

Soil column experiments have been used for more than three centuries in the study of hydrogeological properties (Liu et al., 2022). Soil columns and instrumentations have been applied in recent years to test transport models and monitor the movement patterns of contaminants in soils (Bachhuber et al., 1982; Langner et al., 1998; Liu et al., 2018; Martinez et al. 2013; Mukhlisin et al., 2021; Tao et al. 2021; Zhang et al., 2013). Soil columns are typically constructed with discrete soil blocks wrapped in a rigid impermeable material, which are controlled or measured for infiltration parameters and associated effluent data measurements by discrete soil blocks located outdoors or in the laboratory. Following Darcy's (1856) pioneering work on groundwater seepage (Darcy, 1856), groundwater-related studies were gradually developed. Earlier research concentrated on the rate and amount of percolation through the soil (de la Hire, 1703; Lawes et al. 1882; Dalton, 1802). Solute transport and chemical changes in pore water were studied at the beginning of the 20th century (Bouyoucos and McCool, 1915; Parker, 1921). Additionally, extensive study has been conducted on hydraulics and permeability in column studies (Gao et al., 2021; Santos et al., 2012). Numerous studies in the domains of hydrogeology, agriculture, and soil science have been published that heavily rely on results from soil column investigations(Yu et al., 2021). Despite this, there has never been an attempt to define or compile best practices for soil column building.

The design of soil column experiments has received relatively little attention, even though packing and column design can have a significant effect on the solute transport behavior of column experiments (Bromly et al., 2007). The purpose of packing is to produce homogenous soil columns with a capacity close to that observed naturally, while reducing the formation of stratified layers or preferential flow routes. Solute transport tends to establish preferential flow routes due to the spatial heterogeneity of porous media, which might produce bias in experimental results (Garre et al., 2010; Mohammadzadeh-Habili and Heidarpour, 2015; Wang et al., 2014). Since the physical dimensions of experimental columns have not been standardized, their widespread application research has resulted in a wide range of column sizes. the short columns enable rapid tests with several replicates, while longer columns require more time for equilibration before the beginning of the experiment, resulting in longer reaction times and more complicated setups. The shorter experimental columns are barely 1.5 cm in length, while the larger ones exceed 15 m[23,24]. To avoid scaling effects and sidewall flow, it is critical to select an acceptable aspect ratio. A thorough examination of column experimental designs indicated that diameter to length ratio of 1:4 effectively avoids scaling effects. This ratio, however, is rarely mentioned in the published literature (Bergström 2000). To research and

comprehend the consequences of soil column heterogeneity and scale effects, Huang et al. defined and analyzed solute transport processes in saturated and extremely diverse soil columns by comparing five distinct models, (CDE, MIM, CLT, FADE, CTRW). Sharma et al. explains the scale effect by employing constant dispersion, linear and asymptotic distance-dependent dispersion functions and by considering varied mass transfer coefficients as a function of pore velocity and distance traveled to column experiments for heterogeneity [24]. Using the Laplace transform technique and the power series method, a semi-analytical solution to the governing equations with asymptotically distance-dependent dispersivity was found [26]. For research pertaining to priority pathways and soil column formation stratified, Sudicky et al. investigated the solute transport process for non-reactive as well as reactive solutes in layered porous media and found that the solute breakthrough curves were formally consistent, although there was variability in the time of appearance and peak concentration[27,28]. Sharma et al. constructed a physical model to represent a layered porous medium, introducing equilibrium adsorption and first-order degradation constants to investigate the reactive transport processes used to pass through the layered porous medium [29]. Brusseau created the MPNE model to accurately characterize the transport of non-equilibrium, adsorption-restrained solutes through multilayer porous media at a given velocity[30]. And Zhang et al. offered a semi-analytic solution of a two-dimensional (2-D) solute transport model taking lateral dispersion and linear reactions into account for the preferential flow problem appearing in layered heterogeneous media, this study provides a fully analytical solution [31,32]. Pore clogging is a significant issue when using rigid porous sample materials, and Everett and McMillion (1985) advocate sandwiching the rigid porous material between the experimental soil and a silica flour pack to prevent colloids in the soil from reaching and blocking the rigid porous surface (Everett and McMillion, 1985).

If the numerical simulation of solute transport in soil columns is to be successful, the boundaries and initial conditions must be well defined. The beginning settings are intended to replicate the predominant environmental variables, but actual geographic conditions are considerably changeable. Soil column experiments to explore solute transport processes under laboratory settings can typically be simplified by solute transport in a homogenous single environment in a two-dimensional rectangular patch of media, when coupled with ADE equation solving and Type I boundary conditions. In practice, however, environmental changes in salt water intrusion processes, which are frequently accompanied by factors such as heterogeneous heavy flow with variable density or medium transport with variable porosity, are controlled using mathematical models with density matrices or porosity matrices in order to overcome environmental change properties [29,30]. The majority of cases cannot be explored just through experiments, and it is critical to employ mathematical models in these instances (Barovic and Boochs, 1981).

Mathematical models for groundwater pollution investigations have grown in prominence in recent decades due to their predictive power (Dhingra and Shah, 2021). Groundwater mathematical models can currently estimate groundwater table depths, pollution levels, and recommended water management strategies (Xie et al., 2011; Tilahun and Merkel, 2010; Chowdary et al., 2005; Shrestha

and Ladah, 2002). With the ongoing evolution of modeling tools, the models in widespread usage today are essentially mathematical models based on mass, momentum, and energy conservation, solving partial differential equations under specified boundary or initial conditions. These models can be straightforward one-dimensional solutions or extremely intricate three-dimensional structures. Numerous numerical models have already been created to simulate pollutant migration in aquifers. With further technological developments in related domains, researchers have increasingly applied advanced geospatial, statistical, mathematical modeling, and artificial intelligence tools to properly characterize groundwater quality in the region. With the growing usage of Geographic Information Systems (GIS), A recent study by Machiwal et al. (2018) reviewed all of the methods currently in use to assess the quality of groundwater. As GIS technology has become more widely adopted, it has become possible to use indices mapped with GIS to evaluate the spatial extent and variation of groundwater quality (Adimalla and Taloor, 2020; Asadi et al. 2007). Some common statistical analysis tools, such as time series analysis and non-parametric statistics, principal component analysis, cluster analysis, regression analysis, matrix analysis, and correlation analysis, are gradually applied to mathematical models (Sidauruk et al., 1998; Moncaster et al., 2000; Lee et al. 2003; García-Díaz 2011; Nanni et al., 2008; Bordbar et al., 2019). Meanwhile, advanced artificial intelligence models, such as artificial neural networks, dynamic programming, deep learning, and fuzzy logic, have been applied to groundwater contaminant transport prediction and management strategies (Bagheri et al., 2017; Pal and Chakrabarty, 2020; Dhar and Datta, 2007; Elzain et al., 2021).

Contaminants formed by excessive use of fertilizers in agriculture and effluent discharge in industry progressively infiltrate the unsaturated and saturated zones of groundwater, which in turn causes groundwater pollution. Contaminants enter into different groundwater environments with a variety of pollutant migration (Weber Jr et al., 1991). Thus, the patterns that contaminate migration in groundwater are a topic worthy of in-depth study. This paper summarizes the mechanism of contaminant transport in groundwater systems from both experimental and modeling perspectives, and presents the progress of experimental studies on contaminant transport in saturated and unsaturated groundwater regions, respectively.

Additionally, mathematical models of groundwater pollutant movement in saturated/unsaturated environments are studied and summarized.

2. Types of contaminant migration

The movement of pollutants in soil porous media in aquifers is depicted in Fig. 2, which typically passes through the soil root zone beneath the surface, the percolation filter zone, the tension-saturation zone, and the saturated aquifer. So contaminant migration in column experiments can be divided into different types based on its characteristics (Mackay et al., 1985): (1) multicomponent multiphase flow issues (LNAPLs and DNAPLs migration problems), which primarily replicate the migration of immiscible fluids in multiphase media systems; (2) dissolved contaminant migration in groundwater. For multicomponent multiphase flow issues, colloidal particles in the subsurface environment are regarded as potential pollutant carriers that might dramatically amplify the migration of contaminants. Colloidal contaminants are frequently found in surface and groundwater sources, typically with particle sizes of less than $1\,\mu m$, and these contaminants remain in suspension. Colloidal contaminants are composed of a variety of organic or inorganic components as monomeric compounds, or may be a composite compound of multiple compounds. Colloids pose an alarming threat to the subsurface environment due to the adsorption of numerous heavy metals, radionuclides, and pesticides on their surface. Colloidal transport in porous media and the interaction between dissolved pollutants and mobile colloids have become major areas of study in recent years. For dissolved contaminant migration in groundwater, dissolved pollutants are carried through convection, dispersion, and the reactive reactions that occur during transport. To investigate the convective dispersion properties of pollutants, tracer and column studies are often employed. Current research on the transport of dissolved pollutants in groundwater is relatively exhaustive and sufficient.

2.1. Migration of colloidal contaminants

Colloids may interact with contaminants to breach the surface soil and vadose zone and reach the aquifer as shown in Fig. 3, posing a threat to groundwater safety. Colloids in porous
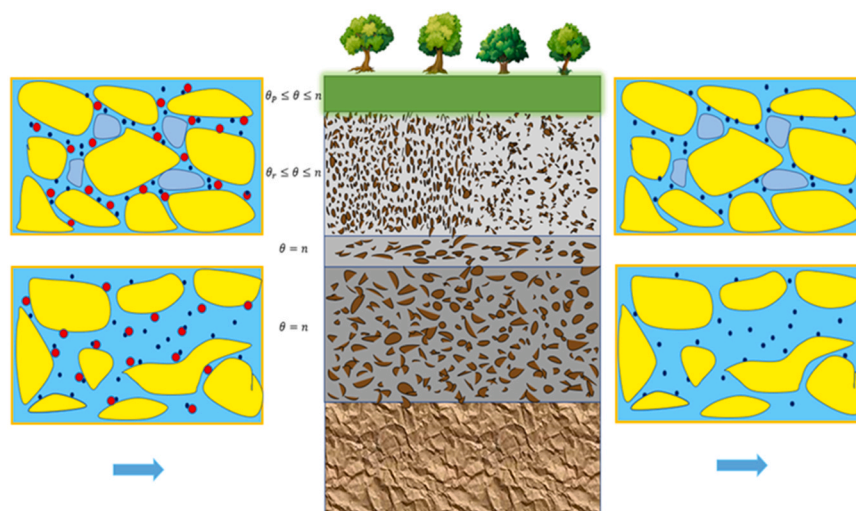

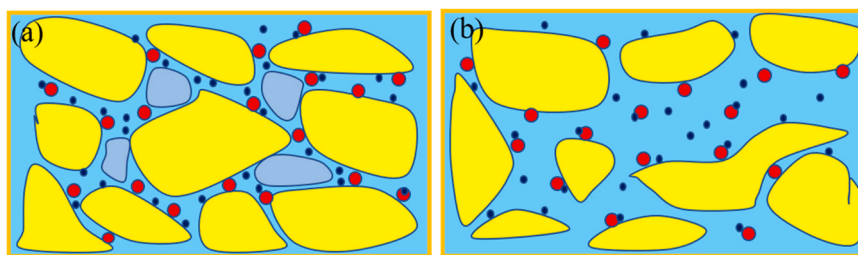**Fig. 2 – A conceptual model of groundwater contaminant transport.**

Fig. 3 – Contaminant transport in unsaturated (a) and saturated (b) colloidal porous media in groundwater.

media move quicker than solutes under the impact of physical, chemical, and their combined effects (Šimunek et al., 2006). The primary physical parameters consist of the size of the pores, the size and form of the colloidal particles, and the hydraulic circumstances (such as flow rate, water saturation, etc.). The chemical variables include pH, ionic strength, and redox potential, among others. Moreover, the release and deposition and filtration of colloids on solid-phase media, the plugging of colloids in porous media and the retention effects at the solid-liquid interface and the gas-liquid interface all have an important influence on the migration of colloids, which is further complicated by the presence of the gas phase in the vadose zone (Gao et al., 2006). Advection-dispersion, aggregation-dispersion, attachment-detachment, filtering, blockage, straining, and preferential flow are the primary mechanisms that govern colloidal movement.

2.1.1. Co-migration of colloidal contaminants in saturated porous media

In saturated porous media, changes in environmental conditions are an important factor in the migration of colloids in Table 1. In acidic environments, soil colloids migrate easily and Enhanced pH increased the retardation factors and K_F values of Cd^{2+} in column studies with and without colloids (Chotpantarat and Kiatvarangkul, 2018). Dissolved organic matter (DOM) is usually capable of influencing the surface chemistry of colloids, promoting their flocculation or dissolution. Wang et al., (2015) discovered that modifying the surface of illite with humic acid improved illite's spatial repulsion and encouraged colloidal migration. The ionic strength of the colloid can change the thickness of the double electric layer on its surface, which in turn affects the colloid's migrating behavior in groundwater (Samari-Kermani et al., 2021). In situations with high ionic strength, the repulsion between colloids and saturated porous media is weak, and

colloids bound to porous media are difficult to separate from the surface, inhibiting colloid migration as well. Simultaneously, changes in hydraulic conditions affect the migration of contaminants carried by colloids. The percolation rate of the fluid influences the migration of colloidal contaminants by affecting the sieving effect of colloidal particles in porous media (Göppert and Goldscheider, 2008).

2.1.2. Co-migration of colloidal contaminants in unsaturated porous media

Typical unsaturated porous media in the vadose zone are usually multi-phase complex systems in Fig. 4a. The alternating wet and dry environmental characteristics result in alternating shear, ionic strength, pH, and water content in the vadose zone. The migration of colloids is further complicated by the presence of the gas phase in the vadose zone (McCarthy and McKay, 2004).

Ionic strength and sand size have an important influence on the fate and transport of colloids in unsaturated porous media (Mitropoulou et al., 2013). Mitropoulou et al. (2013) found that Smaller and more cautiously sized colloids were much easier to migrate than the larger colloids. The increase in ionic strength makes it more difficult for colloidal contaminants to migrate. Colloidal pollutants migrate more complex when the sand size and ionic strength are taken into account. Breakthrough points on the breakthrough curve occur more quickly in moderately sized sand columns with smaller saturation and higher void velocities. Simultaneously, the intensity of contamination adsorption at the gas-liquid interface is greater than at the solid-liquid interface, indicating the gas-liquid interface's potential to significantly restrict the transit of colloidal contaminants (Syngouna and Chrysikopoulos, 2011; Fountouli and Chrysikopoulos, 2020). Qin et al. (2020) reported that silica hampered viral movement in saturated sand columns but

| Table 1 – The effect of changing environmental conditions on the transport of colloidal contaminants in saturated porous media.			
Environmental parameters	Major FEATURES	Mechanisms	References
pH	increasing the pH increased the retardation factors and KF values	pH variations can affect colloidal release and deposition in the subsurface environment	Chotpantarat and Kiatvarangkul (2018)
DOM	modify the surface of illite with humic acid to improve illite's spatial repulsion and encouraged colloidal migration	Influence the surface chemistry of colloids and promote their flocculation or dissolution.	Wang et al. (2015)
Ionic strength	In situations with high ionic strength, the repulsion between colloids and saturated porous media is weak and inhibit colloid migration	change the thickness of the double electric layer on its surface	Samari-Kermani et al. (2021)
Hydraulic conditions	colloids and solutes travel at similar velocities in low flow; colloids and solutes travel at similar velocities in high flow.	affecte the sieving effect of colloidal particles in porous media	Göppert and Goldscheider (2008)
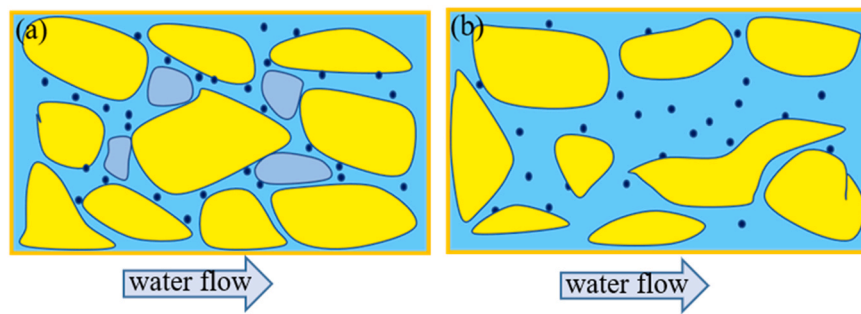
Fig. 4 – Contaminant migration in unsaturated (a) and saturated (b) porous media.

promoted virus transmission in unsaturated sand columns in his investigation of the role of inorganic colloids in the transport of bio-colloids across porous media (Qin et al., 2020). Silica occupies Adsorption sites at the air-water interface (AWI) during the early stages of injection in unsaturated column tests, inhibiting virus retention via electrostatic repulsion with charged particles, hence promoting virus movement. Bio-colloids, in comparison to silica model colloids, act as a barrier to contaminant migration. Preferential flow phenomena are more prominent in groundwater environments, which is critical for colloidal pollutant transmission (Kjaergaard et al., 2004). Hoogland et al. (2017) determined the velocity distribution and its effect on colloidal transport by employing the soil foam drainage equation (SFDE) as a substitute framework for modeling unsaturated flow in laminar porous media (Hoogland et al., 2017).

As mentioned above, environmental parameters in the Table 2 such as ionic strength, sand size, colloid size, pH, saturation, and preferred flow all have a major effect on colloidal contaminant transport in unsaturated porous media. Ionic strength can affect the transport of pollutants by varying the thickness of the colloidal surface double layer, whereas pH variations can affect colloidal release and deposition in the subsurface environment. Sand size has an indirect effect on changes in porosity, which in turn influences pollutant movement via the porous medium's filtering effect. When the saturation of groundwater changes, fluctuations at the gas-liquid interface can strip hydrophobic colloids (e.g. bacteria) deposited at the solid-liquid interface, causing them to migrate with the gas-liquid interface fluctuations, indicating a stronger affinity for colloids at the gas-liquid interface. Mineral colloids have an affinity for the gas-liquid interface that is determined by their structure, surface charge distribution, and is inversely proportional to their cation exchange capacity(CEC). Additionally, the filtering effect of the water film on colloids inhibits their migration. The spatial heterogeneity of porous media results in favorable hydraulic conditions in local areas, and preferential flow takes use of these favorable hydraulic conditions to impact colloidal pollutants' movement.

2.2. Migration of dissolved contaminants

2.2.1. Migration of contaminants in saturated porous media
Seepage is the driving force for contaminant migration in groundwater, and the Fig. 4b presents the process of contaminant migration is the result of a combination of molecular diffusion and convective dispersion in the pore medium (Shackelford, 1993). A stable external environment is more likely to develop in column experiments of contaminant migration in saturated porous media, so most early

Table 2 – The effect of changing environmental conditions on the transport of colloidal contaminants in unsaturated porous media.

Environmental parameters	Major FEATURES	Mechanisms	References
pH	pH can affect changes retardation factors and KF values	pH can change colloidal release and deposition in the subsurface environment	Chotpantarat and Kiatvarangkul (2018)
Sand Size	Smaller and more cautiously sized colloids were much easier to migrate than the larger colloids	Influence pollutant movement via the porous medium's filtering effect	Mitropoulou et al. 2013
Ionic Strength	The increase in ionic strength makes it more difficult for colloidal contaminants to migrate	Affect the transport of pollutants by varying the thickness of the colloidal surface double layer	(Mitropoulou et al. 2013)
Hydraulic Conditions		the velocity distribution can affect on colloidal transport	Hoogland et al. (2017) (Kjaergaard et al. 2004)
Saturation of Groundwater	a stronger affinity for colloids at the gas-liquid interface and inhibit transport behavior	Fluctuations at the gas-liquid interface can strip hydrophobic colloids (e.g. bacteria) deposited at the solid-liquid interface	Syngouna and Chrysikopoulos, 2011; Fountouli and Chrysikopoulos, 2020)
Bio-colloids	Silica occupies Adsorption sites at the air-water interface during the early stages of injection in unsaturated column tests, inhibiting virus retention via electrostatic repulsion with charged particles, hence promoting virus movement.	In comparison to silica model colloids, act as a barrier to contaminant migration	Qin et al. (2020)

column experiments began with column experiments in saturated media. Breakthrough curves (BTCs) are commonly used to describe the migration trends of contaminants in subsurface saturated aquifers. It should be noted that the fundamental challenges for analyzing and interpreting data from column experiments are the same for diverse organic compounds, namely interactions with surfaces and the ionic or neutral nature of the molecules. In column experiments, the breakthrough curves of organic solutes are frequently compared with the breakthrough curves of a conservative tracer to describe their transport behavior. To simulate the actual groundwater situation, Silliman and Simpson (1987) used tubular fine sand in a coarse sand medium and discovered that the trends in the penetration curves (BTCs) were significantly different for different porous media environments and that the dispersion coefficients increased with migration distance (Silliman and Simpson, 1987). Groundwater contaminant transport research is currently focusing on novel environmental contaminants of contemporary relevance, including environmental endocrine disruptors (EDCs), novel persistent organic pollutants (POPs), microplastics, and antibiotics. The majority of these new contaminants are non-aqueous phase liquids (NAPL), which are largely non-miscible with groundwater and predominantly non-soluble. Due to polarity, it is difficult for hydrophilic remediation reagents to dissolve into hydrophobic NAPL for reaction, and the solubility of NAPL is often poor, significantly restricting the effectiveness of reaction mass transfer, hence diminishing the efficacy of future groundwater remediation operations. Future studies must pay close attention to the transport characteristics of this novel groundwater pollutant. Lyu et al. (2019) studied the impacts of PFOA migration in saturated groundwater under various ionic strength, ion type, and pH conditions (Lyu et al., 2019). In saturated porous media, migration is influenced by ionic strength and ion type (valence), pH, flow rate, and surfactant. All of these factors affect the migration of pollutants in saturated porous media, either directly or indirectly.

2.2.2. *Migration of contaminants in unsaturated porous media*

In 1998, Wan and Tokunaga (1998) built the first bubble column apparatus to address future problems about the mechanism of colloid partitioning at the liquid-gas interface (Wan and Tokunaga, 1998). Additional column experiments were conducted to determine the migration of pollutants in unsaturated media. Lin Liu et al. (2013) based the study on Wan and Tokunaga (1998) bubble column to explore the deposition mechanism of graphene oxide (GO) particles in porous media with various combinations of moisture content and ionic strength, understanding that the recovery of GO in unsaturated sand columns is lower than in saturated columns under the same ionic strength conditions. Kamrani et al. (2018) evaluated the transport and retention of carbon dots (CD) in saturated and unsaturated porous media considering three different parameters: ionic strength, pH, and collector particle size (Kamrani et al. 2018). The mobility of CDs in saturated and unsaturated porous media increases with decreasing ionic strength, increasing pH, and increasing grain size of the collector. Perfluorooctanoic acid (PFOA) distribution in unsaturated sandy porous media also changes with ionic strength and cation type (Li et al. 2021), as well as a surface roughness (Lyu et al., 2020). Higher ionic strength or cationic valence considerably enhances PFOA adsorption at

the gas-water interface, resulting in a larger PFOA delay during transport across unsaturated porous media. The rougher surface texture and smaller particle size dramatically increase PFOA's delay in unsaturated conditions. The effect of HA content and ionic strength (IS) on the transport of Cu 2 + in unsaturated columns was investigated by synthesizing composites of Fe_3O_4 nanoparticles coated with HA (HA@NPs) (Lin et al., 2021). In the presence of HA@NPs, it was discovered that HA had a severe inhibitory effect on Cu 2 + mobility, whereas greater ionic strength boosted Cu 2 + mobility in unsaturated porous media. Frederic Leuther (2020) researched the transport and retention of silver sulfide nanoparticles in porous media at the air-water interface in the presence of flow velocity and natural organic matter, and found that the hindrance of particles depends mainly on the interfacial area between the solid and air-water phases, and that the decrease in particle penetration at reduced saturation depends on the increase in AWI and the decrease in flow velocity (Leuther et al., 2020). The influence of air pressure fluctuations on the non-equilibrium transport of volatile organic pollutants in the seepage zone was investigated using a non-equilibrium computational model (Qi et al., 2021). Solute dispersion is explicitly dependent on soil water saturation, and the resulting relationship is non-monotonic, particularly for coarser media. The relationship discovered between solute dispersion and water saturation may be beneficial for modeling pollutant transport in unsaturated zones at the field scale (Zhuang et al., 2021).

As mentioned above, it is clear in Table 3 that ionic strength and ion type (valence), pH, base-electric particle size, air-water interface area, flow rate, soil moisture saturation, sand grain coarseness, surfactants, and atmospheric pressure fluctuations all have a significant effect on the transport processes of contaminants in unsaturated porous media. Higher ionic strength promotes contaminant adsorption at the air-water interface by shielding organics from electrostatic repulsion and decreasing the thickness of the interfacial water layer. Ca^{2+} promotes more adsorption of pollutants at the air-water interface than Na^+ at the same ionic strength because Ca^{2+} induces a greater drop in the surface tension of the contaminated solution than Na^+. Additionally, pH and surfactants can affect a liquid's surface tension. In comparison, parameters such as the area of the air-water interface, the flow rate, and the water saturation of the soil all have an indirect effect on the rate of adsorption, which in turn prevents pollutants from migrating across unsaturated media.

3. Contaminant migration experiments in porous media

3.1. *Contaminant migration experiments in saturated porous media*

Based on the Darcy experiment, the pollutant transport experiment was gradually built up. Darcy(1856) used macroscopic instead of microscopic averaging to deduce the fundamental rules of percolation in porous media (Darcy, 1856). Slichter's (1905) research confirmed that not all solutes transport at the same pace in soil (Slichter, 1905). The hydrodynamic dispersion theory was defined as a theory of soluble fluid dispersion and summarized the methods used to investigate the dispersion mechanism and identify the required parameters (Bear and Braester, 1972). The study of organic contaminant migration in subsurface inhomogeneous porous media began with

Table 3 – The effect of multiple environmental factors on the migration of contaminants in porous media.

Multiple Environmental Factors	Major FEATURES	Mechanisms	*References*
Moisture Content and Ionic strength	(1)the recovery of GO in unsaturated sand columns is lower than in saturated columns under the same ionic strength conditions (2) Increased ionic strength resulted in an increase in GO retention.	Additional retention mechanisms (GO did not attach to the air–water interface), such as film straining,	Lin Liu et al. (2013)
pH, and Collector Particle Size	Mobility of CDs in both saturated and unsaturated porous media increases with the decrease in ionic strength, increase in pH, and increase in collector grain size.	CD surface functional groups, surface charge and aggregation	Kamrani et al. (2018)
ionic strength and cation type	Increased ionic strength or cationic valence significantly improves PFOA adsorption at the gas-water interface, resulting in a longer PFOA transport delay through unsaturated porous media.	the air-water interfacial (AWI) adsorption coefficients calculated from surface tension isotherms also increased with increasing ionic strength or in the presence of Ca^{2+} in comparison to $Na+$.	Li et al. (2021)
surface roughness and moisture content	Larger surface roughness leads to greater retardation of PFOA in unsaturated media. Lower moisture content result in higher air-water interfacial adsorption of PFOA	Rougher surface cause larger air-water interfacial areas and more PFOA adsorption.	Lyu et al. (2020)
HA content and ionic strength (IS)	HA had a severe inhibitory effect on Cu 2 + mobility, whereas greater ionic strength boosted Cu 2 + mobility in unsaturated porous media.	HA embedded in the sand matrix could bind $Cu2+$ by forming stable chelate, while the IS-dependent $Cu2+$ transport could be attributed to the competitive adsorption between $Na+$ and $Cu2+$.	Lin et al. (2021)
Air-Water Interfaces, Flow Velocity, and Natural Organic Matter	(1) The addition of NOM to S-Ag-NP dispersion significantly increased NP mobility; (2) the difference between saturated and unsaturated transport increased with decreasing flux and, consequently, water content; (3) both solid-water and air-water interfaces were involved in the retention of NOM-aged S-Ag-NPs.	(1)A strong link between transport behavior of NPs and the structure of the phase distribution including the different interfaces (2) The retardation of particles was mainly dependent on the interfacial areas between the solid-water and air-water phase. The decreasing amount of particle breakthrough at reduced saturation was dependent on both, the increasing AWI and the decreasing flow velocity field-scale models	Leuther et al. (2020)
Saturation and Particle size	Between the dispersivity and soil water saturation, a definite non-monotonic relationship was discovered.		Zhuang et al. (2021)
solute size, pore water velocity, and intraparticle porosity	dispersivity is essentially independent of solute size; the importance of axial diffusion decreases as pore water velocity increases	Hydrodynamic dispersion is the predominant source of dispersion	Brusseau (1993)

mechanistic studies, which included the use of sand column tracer experiments and laboratory-based contaminant leaching migration simulation experiments. These studies revealed the presence state, migration mode, hysteresis effect, wettability, and infiltration pattern of organic contaminants in porous media. Based on a review of the literature, it is feasible to examine tracer migration in non-homogeneous porous media. The breakthrough curves are increasingly being used to explain the migration tendencies of pollutants in groundwater during contaminant migration tests in the saturated porous medium. By examining the results of multiphase flow in non-homogeneous porous media, a physical model was created to examine the migration mechanism of multiphase fluids in non-homogeneous porous media (Kueper and Frind, 1991). Swami et al. created a physical model to represent a layered porous medium, and an implicit finite difference numerical technique was used to solve the advective dispersion transfer equation for reactive transfer through the layered porous medium, including equilibrium adsorption and first order degradation constants[80]. A two-dimensional sandbox experiment was conducted in porous media to evaluate the distribution of non-dissolved fluids and thus to investigate the effect of oil permeability surfaces, water capillarity, and hysteresis on oil

recovery. Brusseau et al. discovered that regional differences in intrinsic permeability were the primary cause of flow diversion and dilution, and that changes in the aqueous phase's relative permeability in NAPL-contaminated areas also resulted in flow diversion and decreased effluent concentrations (Brusseau et al., 2002). A sequential successive linear estimation technique (SSLE) was developed and utilized to calculate parameters such as permeability coefficients and DNAPL sorption distributions by integrating hydraulic tests with zonal tracer tomography (Illman et al., 2008). Further investigation of the geographical and spatiotemporal scale impacts of pollutant transport experiments is conducted to capture the scale dependency of coupled response transport processes (Majdalani et al., 2018; Steefel et al., 2005). The experimental study of contaminant transport in saturated porous media is developing.

3.2. Contaminant migration experiments in unsaturated porous media

In order to answer future questions about the mechanism governing the partitioning of colloids at the liquid-air interface, devices for studying the transport of unsaturated

porous media and photographic measurements of bubble diameters for each solution (suspension) type were developed as a result of the bubble method's success[28]. Tian et al.(2011) investigated the transport mechanisms of single-walled nanotubes (SWNT) in saturated and unsaturated sand columns based on the bubble column to explore ultrasonically shortened sodium dodecylbenzene sulfonate (SDBS) dispersion (Tian et al., 2011). As research related to unsaturated column contaminant transport experiments has increased, more and more studies have been developed on the effects of environmentally relevant factors (e.g. ionic strength and type, water content, pH, surfactants, hydraulic conditions, soil organic matter, etc.) on transport in unsaturated column experiments. In recent years, it has been proved experimentally that the use of bubble column devices to explore contaminant transport in unsaturated porous surfaces is of practical interest.

The retardation factor R is a critical parameter in unsaturated column experiments on contaminant transport because it influences the transportation, transformation, and fate of organic matter in groundwater. When adsorption has linear or non-linear features, the relevant R equations are available and have been effectively employed to describe solute transport. The measured delay factors are therefore determined for each mixed-phase displacement experiment by the standard method of calculating the area above the breakthrough curve. Their uncertainties are very small and are related to the uncertainties in concentration and flow rate. These retardation factors account for the effects of all retention processes that affect transport. The retardation factor for aqueous-phase transport of a solute subjected to solid-phase adsorption and air-water interfacial adsorption is determined as

$$R = 1 + K_d \rho_b / \theta_w + K_{ai} A_{ai} / \theta_w \tag{1}$$

Where K_d is the solid-phase adsorption coefficient (cm^3/g), K_{ai} is the air-water interface adsorption coefficient (cm^3/cm^2), A_{ai} is the specific air-water interface area (cm^2/cm^3), ρ_b is the bulk density of the porous medium (g/cm^3), θ_w is the volumetric water content. By phase balance, $\theta_w + \theta_a = n$, where θ_a is the volumetric air content and n is the porosity. Water saturation is defined as $S_w = \theta_w/n$. The fraction of the overall retention rate evaluated at the air-water interface attributed to adsorption is determined as

$$F_{AWIA} = [(R - 1) - (K_d/\rho_b)]/[R - 1] \tag{2}$$

Where K_{ai} is determined by rearranging Eq. 1 based on the miscible-displacement experiments. R was calculated using the breakthrough curve analysis and all other variables were determined independently.

The absorption coefficient at the air-water interface, K_{ai}, can also be determined through using surface-tension function. In the Gibbs equation, the surface excess Γ (mol/cm^2) is related to aqueous-phase concentration (C)

$$\Gamma = \frac{-1}{RT} \frac{\partial \gamma}{\partial InC} = K_i C \tag{3}$$

$$K_i = \frac{\Gamma}{C} = \frac{-1}{RTC} \frac{\partial \gamma}{\partial InC} \tag{4}$$

Where K_i is the interfacial adsorption coefficient, γ is the interfacial tension, C is the concentration of the aqueous phase (mol/cm^3), and R is the gas constant (erg/mol K). This is accomplished by determining the local slope of the $\partial \gamma / \partial In\,C$ function at the appropriate solute concentration and then

applying Eq. 4. Determination of K_{ai} is difficult at substantially lower doses due to the surface-tension function's insensitivity at those concentrations. K_{ai} can be determined these by determining the relevant parameters in transport experiments and then inferring the relevant parameters and comparing them to the measured values to analyze structural impacts.

4. Mathematical modeling of groundwater contaminant transport

The transport of contaminants in groundwater porous media is based on a percolation model, therefore to understand the transport of contaminants in groundwater porous media it is necessary to first construct a groundwater flow model of the study area. It is critical to adopt a suitable mathematical model for the geographic attributes of the various porous media (saturated and unsaturated groundwater) and the fluid's physical state (heterogeneous flow or saltwater intrusion) in the groundwater region. The main framework of mathematical models has now been developed to describe groundwater contaminant transport processes. Even though numerous biochemical processes are involved in contaminant transport, only a few have been simulated. These are described below.

4.1. Advection

Convection is often a relative movement that occurs when a fluid flows to transport itself and the pollutants it contains to a certain spatial position. When the fluid flow rate is increased in porous media systems, the flow velocity increases, enhancing convection and dilution of pollutants. The convective flux J_v is usually used to describe the convective transport of pollutants

$$J_v = nuC \tag{5}$$

Where n is the porosity of the porous medium, u is the average flow rate of the fluid through the porous medium void and C is the average concentration of the contaminant.

4.2. Dispersion

The diffusion of pollutants in an environmental medium follows Fick's law. When a pollutant's diffusion in an environmental medium is steady-state, it obeys Fick's first law; otherwise, it obeys Fick's second law. The intensity of diffusion is frequently expressed in terms of the ratio of the diffusion flux to the concentration gradient.

$$J_f = -D \frac{dC}{dx} \tag{6}$$

Where J_f is the diffusion flux kg/(m^2s) , D is the diffusion coefficient (m^2/s), C is the volume concentration of the diffusing substance; $\frac{dC}{dx}$ is the concentration gradient of the substance.

4.3. Sorption

Absorption is the process by which ions and molecules in solution are absorbed onto the surface of porous media particles and removed from the solution; desorption is the inverse process. The essence of adsorption and desorption is the mutual exchange of the solid and liquid

phases. The adsorption process is divided into equilibrium isothermal adsorption and non-equilibrium isothermal adsorption.

In equilibrium isothermal adsorption, the components of the solid surface are in continuous equilibrium with the liquid's component mass changes. The amount of adsorption in a porous medium is proportional to the concentration of the contaminant dissolved in the solution under isothermal linear adsorption conditions.

$$F = K_d C \tag{7}$$

Where F is the isothermal linear sorption concentration; K_d is the partition coefficient; C is the concentration of contaminant dissolved in the solution.

In non-equilibrium isothermal adsorption processes, the mass change of the solid surface component and the liquid composition cannot approach transitory equilibrium, but can progressively reach a given adsorption rate. In many cases, the adsorption is not transient. The simplest empirical equation for adsorption (Langmuir, 1967) can be described.

$$\frac{\partial F}{\partial C} = K_3 C \tag{8}$$

Where K_3 is constant.

4.4. Pollutant decay and transformation

Contaminants enter the groundwater system and undergo a variety of component changes as a result of a variety of environmental conditions (e.g. temperature, microbial and other factors). As a result, the source sink will undergo its processes throughout the migration of contaminants, such as radioactive decay, multi-component chemical reactions, redox reactions, and microbial degradation.

When radioactive or other chemicals capable of attenuating radiation are present in groundwater fluids, The source sink term for pollutant transport can be described as

$$\left(\frac{d(nC)}{dt}\right)_r = -n k_f C \tag{9}$$

Where k_f is the decay rate constant for the number of decaying nuclei in the fluid, C is the concentration of the solution; n is the porosity.

When a chemical reaction occurs in component A of the groundwater fluid medium, an increase in pollutants occurs.

$$\left(\frac{dC}{dt}\right)_r = \sum_{j=1}^{m} R_{aj} \tag{10}$$

Where R_{aj} is the rate of production of the mass of the jth reaction a-component per unit volume of porous medium and R_{aj} is a function of the concentration of the a-component.

When a redox reaction occurs in a component of the groundwater fluid medium

$$\left(\frac{dC}{dt}\right)_{red} = -k_{red}[N^+][R] \tag{11}$$

Where k_{red} is the oxidation/reduction rate coefficient per unit volume.

When a biochemical reaction occurs in component B of the groundwater fluid medium, a change in pollutants occurs.

For the Monod biochemical model

$$\left(\frac{dC}{dt} = \right)_{bio} = -\frac{k_{max} X_a S_f}{k_s + S_f} \tag{12}$$

Where $(\frac{dC}{dt} =)_{bio}$ is the rate of metabolic utilization per unit volume of cells, k_{max} is the maximum rate of metabolic utilization, X_a is the concentration of living cells, S_f is the concentration of the metabolic limiting rate in cell contact, and k_s is half of the maximum probable rate of metabolic utilization.

4.5. Advective-dispersive-reactive transport equation

Without taking into account the mass change of the solid phase inside the porous media of the groundwater system, the process described above enables the construction of the basic differential equation for contaminant transport in porous media.

$$\frac{\partial(nC)}{\partial t} + \frac{\partial}{\partial t}[(1-n)\rho_s F] = \nabla \cdot (n\mathbf{D} \cdot \nabla C - n\mathbf{u}C) + \left(\frac{d(1-n)C}{dt}\right)_s + RC_R - PC + \left(\frac{d(nC)}{dt}\right)_r \tag{13}$$

Where n is the porosity of the porous medium, R, P in the source sink term represents the rate at which pollutants are injected into and removed from solution per unit time per unit volume of porous media, respectively. C_R is Concentration of injected pollutants, $(\frac{d(nC)}{dt})_r$ is the rate of biological or chemical reaction in the liquid phase.

5. Model of contaminant transport in groundwater

In a real groundwater system, the irregular shape of the study area and the complexity of the mathematical model make it difficult to have an analytical solution to the convective transport response equation, and the numerical solution is usually obtained by discretizing the groundwater area and the mathematical model separately. Numerous models have been constructed to simulate contaminate transport in groundwater, utilizing a variety of discrete approaches to mathematical modeling and the inherent flexibility of control equations for a variety of external contexts. There are primarily saturated and unsaturated groundwater zones in each stratigraphic setting, and the separate model presentations for the unsaturated and saturated zones are described below (seen in Table 4).

5.1. Models of pollutant migration in saturated groundwater

There are numerous software programs available for studying the migration of saturated groundwater contaminants. Some of the more commonly used saturated groundwater migration software programs include GMS, GroundWater Vistas, Tough2, Visual MODFLOW, and others. The majority of these aboveground water modeling software is built on modules such as MODFLOW, MT3DMS, and RT3D to simulate and analyze groundwater and pollutant migration patterns.

Groundwater Modeling System (GMS) is a powerful and widely used software for groundwater simulation, which was first developed by the United States Army Corps of Engineers

Table 4 – The effect of multiple environmental factors on the migration of contaminants in porous media.

MODEL	Module Components	Application	References
Saturated zone			
GMS	MODFLOW, FEMWATER, MT3DMS, RT3D, etc.	In conjunction with GIS for soil and water evaluation Combine with SWAT model to simulate and reconcile groundwater systems Coupled with model SWAT, ModFLOW and model RT3D to analyze the fate and transport of nitrate in the watershed system Couple the (SWAT), (MODFLOW), and (MT3DMS) models to predict changes in flow and salt concentration in groundwater systems	(Lu et al. 2020) Shrestha et al. (2020) Wei et al. (2019) Ehtiat et al. (2018)
Visual MODFLOW	MODFLOW-2000, MODPATH, MT3DMS, and RT3D model	Couple with An artificial neural network (ANN) model to investigate the process of predicting groundwater pH	Mol et al. (2020)
FEFLOW	Intuitive GIS data interface, optimized dissecting mesh procedures, tools for graphical display and analysis of data outputs	To establish fluoride index,simulate and assess the impact of the new fluoride index Simulation of the effect of subsurface barriers on saltwater intrusion using the FeFlow model based on sandbox tests a one-way sequential coupling of the unsaturated water transport model SIMWASER/STOTRASIM with FEFLOW to analyse the distribution of nitrogen flow	Kalpana et al. (2019) Li et al. (2018) Klammler et al. (2013)
Stanmod	CFITM, CFITIM, CXTFIT, CHAIN, SCREEN, 3DADE and N3DADE,etc.	To investigat the effect of pH and starting concentration on the Cr(VI) sorption process To explore the effect of initial concentration and input flux on the migration of Zn contaminants in soil columns; initial concentration	Zhang et al. (2018) Shahmohammadi-Kalalagh and Taran (2019)
UnSaturated zone			
UnSaT Suite (UNSAT/UNSAT2 model)	SESOIL, VSADT, VLEACH, PESTAN, and HELP module,etc	To simulate unsaturated flow field motion To simulate unsaturated soil water and heat flow conditions	Fayer and Jones (1990); Fayer et al. (1986)
SWMS-2D/3D		To simulate water and solute movement in variably saturated media	Simunek et al. (1992)
CHAIN-2D		To Simulate the movement of water, heat and multiple solutes in two-dimensional variably-saturated porous media	Simunek and Van Genuchten (1994)
UNSATCHEM-2D		To simulates water, heat, carbon dioxide and solute movement in one-dimensional variably saturated media	Šimůnek and Suarez, (1993)
HYDRUS	UNSATCHem, Wetlands, DualPerm、C-Ride and HP2 Additionally, Type-analytic functions such as van-Genuchten model, Brooks-Corey model, Kosugi's lognormal pore-size distribution model, Durner's bimodal pore-size distribution model	To simulates water, heat and solute movement variably-saturated porous medium	Simunek et al. (1998) (Tafteh and Sepaskhah (2012); Varvaris et al. (2021); Mallants et al. (2017); Kodešová et al. (2005)
PetraSim (TOUGH2)	TOUGH2, TOUGH2-MP, EWASG, T2VOC, TMVOC, and TOUGHREAT. TOUGH2 module,etc.	Apply in multi-phase flow migration movements of air, water, and miscible gels and can also be used for the evaluation of pollutant migration sorption	Pearson et al. (2012); Finsterle et al. (1994)
GMS	/	to simulate coupled three-dimensional finite element models of water flow and solute transport in unsaturated water flow scenarios, as well as challenges involving water flow and transport with varying densities.	
FeFLOW	/	To simulate unsaturated zones using a range of parametric models	

Hydraulics Laboratory in partnership with Brigham Young University. This is mainly due to his collection of a large number of early saturated groundwater contaminants transport mathematical models, such as MODFLOW, FEMWATER, MT3DMS, RT3D, and other modules. The MODFlOW module is based on a three-dimensional finite-difference approach to groundwater flow and solute transport, while FEMWATER can be used to simulate flow and

solute transport in both saturated and unsaturated flow environments, as well as flow and transport with varying densities such as saltwater intrusion. The MT3DMS module is used to simulate convection, dispersion, and chemical reactions in groundwater systems. For simulation calculations, MT3DMS is frequently used in conjunction with MODFLOW. RT3D is a three-dimensional transport model dealing with multi-component reactions and is suitable for simulating natural attenuation and biological recovery.

In practice, GMS can also be used in conjunction with remote sensing, geographic information systems (GIS), and instruments for soil and water evaluation. A combined SWAT/ GMS model was used to simulate and reconcile groundwater systems on the North China Plain to capture extreme hydrologic events in the Fuhe River Basin of the Poyang Lake (Lu et al., 2020). GMS-MODFLOW was used in cooperation with the SWAT model to assess groundwater resilience in the Kathmandu Valley under various climate change scenarios and to assess the impact of climate change on groundwater resources (Shrestha et al. 2020). The semi-distributed watershed model SWAT was coupled with the groundwater flow model MODFLOW and the groundwater solute response transport model RT3D to analyze the fate and transport of nitrate in the watershed system (Wei et al., 2019). Ehtiat et al. (2018) proposed an integrated modeling strategy for groundwater systems by coupling the (SWAT), (MODFLOW), and (MT3DMS) models in terms of flow and salt concentration, resulting in a joint model capable of predicting changes in flow and salt concentration in groundwater systems (Ehtiat et al., 2018).

The USGS created Visual MODFLOW as a visual version of MODFLOW. It is the most comprehensive and user-friendly simulation platform for practical applications of 3D groundwater flow and pollutant transport simulation. It is primarily based on the GWF and GWT models, but also includes the MODFLOW-2000, MODPATH, MT3DMS, and RT3D model simulation modules for simulating groundwater flow and pollutant transport models. An artificial neural network (ANN) model was coupled with Visual MODFLOW to investigate the process of predicting groundwater pH during the migration of contaminants with groundwater, using pH as the target value (Mol et al., 2020).

FEFLOW (Finite Element subsurface FLOW system) is a finite element approach for modeling groundwater flow and pollutant transport that features an intuitive GIS data interface, optimized dissecting mesh procedures, and a plethora of useful tools for graphical display and analysis of data outputs. Listed below are a few successful examples. The new fluoride index was simulated by Fellow software for the Panbal river basin in southern India and confirmed the positive impact of the established fluoride index (Kalpana et al., 2019). Simulation of the effect of subsurface barriers on saltwater intrusion using the FeFlow model based on sandbox tests (Li et al., 2018). The results of a simulation of the influence of subsurface barriers on saltwater intrusion, conducted using FeFlow software and based on sandbox tests, indicate that low permeability is successful at avoiding saltwater intrusion. Simulating multiple scenarios assuming high surface nitrogen inputs using a one-way sequential coupling of the unsaturated water transport model SIMWASER/STOTRASIM with FEFLOW in the Westliches Leibnitzer Field aquifer in Austria, it was discovered that nitrogen inputs to groundwater are dominated by contributions from agricultural land (Klammler et al., 2013).

Along with the GMS, Visual MODFLOW, and FeFLOW software modeling tools, there are also more practical models available, such as Stanmod, a Windows-based computer package for analyzing solute transport in soil and groundwater using an analytical solution of the convection-diffusion equation. It includes one-dimensional transport models such as CFITM, CFITIM, CXTFIT, CHAIN, and SCREEN, as well as multidimensional transport models such as 3DADE and N3DADE. One of the most common models used is the CXTFIT model. Zhang et al. (2018) investigated the effect of pH and starting concentration on the Cr(VI) sorption process and demonstrated that the parameters computed using CXTFIT can be used to explain Cr(VI) migration and transformation behavior in soil columns (Zhang et al., 2018). Shahmohammadi-Kalalagh and Taran (2019) used CXTFIT to investigate the effect of initial concentration and input flux on the migration of Zn contaminants in soil columns; initial concentration was found to be negatively and linearly correlated with sorption (delay factor), whereas input flux was found to be positively correlated with sorption (Shahmohammadi-Kalalagh and Taran, 2019).

5.2. Models of pollutant migration in unsaturated groundwater

The earliest models for simulating the transport of unsaturated groundwater contaminants date back to the work of Israeli and Dutch researchers who developed the UNSAT and UNSAT2 models (Fayer and Jones, 1990; Fayer et al., 1986). These models have been refined into today's new software, UnSat Suite, for simulating vertical groundwater seepage and vertical transport mechanisms of dissolved contaminants, and have included various models such as SESOIL, VSADT, VLEACH, PESTAN, and HELP models. SWMS-2D (1992) by Simunek et al. (1992) improved the SWMII model and converted it to a solute model by a modification of the convective diffusion model, simulating water and solute mobility in a two-dimensional variable saturated medium. It was then expanded to three dimensions in 1995. Simunek and Van Genuchten (1994) simultaneously introduced modules for first-order solute decay chain, heat transfer, and volatile pollutant transfer to the SWMS-2D model, resulting in the new model CHAIN-2D. The SWMS-2D model was subsequently enhanced by adding ionic equilibrium and kinetic nonequilibrium chemical models via a finite element code, resulting in the development of the UNSATCHEM-2D model (Fig. 5).

HYDRUS was originally developed by Šimůnek et al. as a finite element computational model for the two- and three-dimensional motion of water, heat, and polysolutes in variable saturated porous media. It summarizes the type-analytic functions such as van-Genuchten model, Brooks-Corey model, Kosugi's lognormal pore-size distribution model, Durner's bimodal pore-size distribution model. These modifications expand on the description of the near-saturated state's hydrological features. Parkhurst and Appelo(1999) developed HP2-HYDRUS-PHREEQC-2D, a new integrated modeling tool that considers a range of mixed equilibrium/ dynamic biogeochemical reactions (Parkhurst and Appelo, 1999). As models have been developed and optimized, HYDRUS software has incorporated and enhanced previous models, and now includes a variety of modules (UNSATChem, Wetlands, DualPerm, C-Ride, and HP2) for simulating groundwater contaminant transport under a variety of
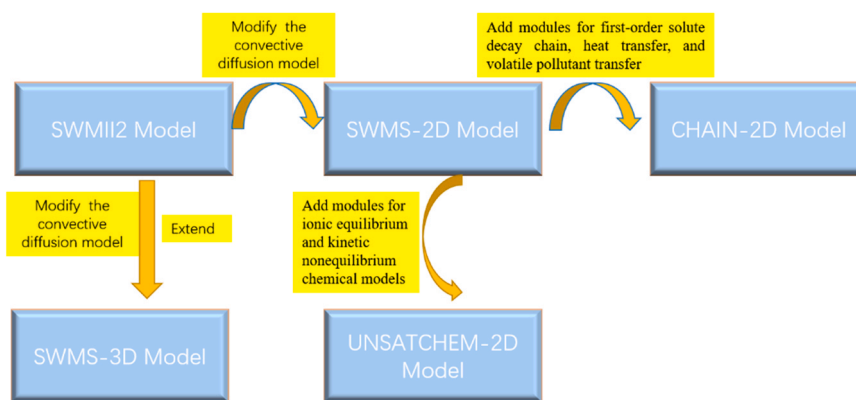
Fig. 5 – The development process of the early SWMII model.

conditions, as well as parallel computing tools and techniques that take advantage of multi-core and multi-processor computers to significantly accelerate time-consuming simulations (Tafteh and Sepaskhah, 2012; Varvaris et al., 2021; Mallants et al. 2017; Kodešová et al., 2005).

PetraSim software is used to create the graphical user interface for the TOUGH2 simulation program family. TOUGH2 and its derivatives were developed at the Lawrence Berkeley National Laboratory and are widely recognized for their ability to accurately simulate water flow and thermal transport in porous and fracture media. The PetraSim software now includes modules for TOUGH2, TOUGH2-MP, EWASG, T2VOC, TMVOC, and TOUGHREAT. TOUGH2 has been applied in multi-phase flow migration movements of air, water, and miscible gels and can also be used for the evaluation of pollutant migration sorption (Pearson et al., 2012).

In addition to UnSat Suite, HYDRUS software, and PetraSim software, the GMS and FEFLOW models used in saturated groundwater contaminant transport models can also be used in unsaturated groundwater contaminant transport models. Furthermore, the GMS FEMWATER Model module is used to simulate coupled 3D finite element models of water flow and solute transport in unsaturated water flow situations, as well as water flow and transport problems with variable densities, such as saltwater intrusion. FeFLOW software simulates unsaturated zones using a range of parametric models, including exponential, Van Genuchten, and several variants of Richard's equation. Although both are capable of simulating groundwater contaminant migration, each has limitations. The GMS-GIS module can only be used with steady-state data and FeFLOW is relatively difficult to reconcile, groundwater contaminant transport simulations for specific environments must be combined with actual engineering practice.

6.   Conclusion and outlooks

This paper summarizes the interaction between contaminant migration and the water environment in saturated/unsaturated porous media in column experiments, as well as the mechanisms of contaminant migration therein, with a particular emphasis on the relevant environmental factors affecting the migration of various types of contaminants in column experiments, as well as an analytical summary of the mechanisms affecting contaminant migration factors. Additionally, the mathematical modeling processes and

commonly used modeling software for pollutant transport in groundwater are discussed.

In recent years, we have seen the incorporation of contaminant transport models for the unsaturated and saturated zones of groundwater, as well as the coupling of relevant models with other modeling techniques. To make the best groundwater management decisions, the analysis of pollutant transport models at the regional level is coupled with other assessment models and artificial intelligence algorithms. However, certain issues warrant further investigation and attention during saturated/unsaturated porous media contaminant migration tests in column experiments. (1) Due to the short duration of column tests in the laboratory, whereas contaminants remain in porous media for years and years in the real world, this results in changes in the parameters associated with porous media. The porous medium, in particular, becomes clogged during the contaminant migration process, and the porous medium parameters induced by the variable void fraction in time (variable permeability coefficient) and the formation of randomised porosity in space have an effect on the contaminant migration process. (2) In the laboratory, column studies typically include the migration of a particular initial concentration of contaminant through a porous media. If contaminant migration occurs near the shore, the migration pattern of contaminants with varying densities in groundwater will be different than that observed in conventional column tests. (3) It is vital to be able to quantify the transport patterns of pollutants in column experimental contaminant transport investigations in terms of mathematical relationships rather than simply looking at environmental parameters. The mathematical equations will be used to improve existing models, laying the groundwork for developing pollution transport models.

As a result of the fact that the majority of comprehensive experiments are conducted under steady-state settings, there are still many unexplored areas for future research. Even though researchers have begun to investigate the mass transfer of contaminants in groundwater in unsaturated media in recent years, this is typically based on steady state unsaturated conditions, whereas in practice, preferential flow resulting from soil heterogeneity frequently results in changes to the steady state unsaturated condition after long experimental sessions. Current column experiments are typically conducted as pre-experiments to determine the length of time that the device is in a steady state prior to the actual experiment, so that future research can attempt to linearly vary the mass transfer process of contaminants in a

steady unsaturated state under dynamic equilibrium. In column experiments on the migration of colloidal contaminants in unsaturated media, we should be aware that the water content in the unsaturated region is typically variable, and changes in water content also cause adhesion of certain colloids and the release of contamination change process, so we need to pay close attention in advance to the investigation of regional infiltration water infiltration distribution, evapotranspiration and groundwater level fluctuations and other faunistic factors. For instance, when the external environment is at a constant temperature and pressure and the mass transfer process has reached dynamic equilibrium, the mass transfer process of low concentration volatile solute pollutants can attempt to apply Henry's law to describe the transport process of pollutants.

There are certain drawbacks to investigating the diffusion of contaminants from a modeling standpoint. (1) As demonstrated in the preceding examples, single model simulations are typically more accurate and reasonable; coupled models, on the other hand, are frequently used to decouple multiple environmental change processes occurring during contaminant transport, resulting in a coupled model that is less accurate, requires a large number of input parameters, and requires longer run times. To minimize mistakes induced by secondary components, it is recommended that the implementation of these coupled models requires an understanding of regional primary flow and solute transport. (2) With regards to the employment of models in forecasting studies, it is vital to analyze and comprehend the models' applicability and limitations for the study area, as well as to improve the models' accuracy by comparing the applicability of other models. On the other hand, suitable generalisations about the actual model for the actual study area are required through the addition of conditional assumptions about secondary elements, which not only enhances the model's accuracy but also decreases computational work.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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