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Enhancing hydrological analysis by incorporating environmental and artificial tracers of an altered vadose zone: A systematic review

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ABSTRACT

This review investigates the integration of environmental and artificial tracers for evaluating water flow within modified vadose zone environments and assesses how heterogeneous structures and preferential flow influence transport mechanisms, residence times, and flow pathways. Utilising both single and multiple tracers the precision of flux estimations between the vadose zone and water table can be enhanced. Altered vadose zones substantially influence tracer storage and release based on shifting moisture levels, highlighting the hydrological importance of these altered zones. The review underscores the importance of high-frequency measurements for diverse hydrological systems and understanding contaminant transport processes, with vadose zone thickness influencing residence times and hydrological behaviour and enhancing groundwater protection. Insights into the study of karst aquifers using fluorescent dyes and natural tracers shed light on rapid flow dynamics, and how to improve modelling techniques to capture these complexities. This further highlights the need to address safety and regulatory considerations related to tracer use, particularly toxicity and ecotoxicity effects, which are critical when borehole water is utilised for domestic purposes. In this regard, the development of a standardised regulatory framework in South Africa, given the absence of specific tracer test guidelines, drawing from international examples should be established. Numerical models for vadose zone flow and contaminant transport tackle challenges like non-equilibrium processes, complex geometries, and heterogeneity. Methods like Picard and Newton iterations can therefore enhance model accuracy, vital for sustainable water resource management and understanding modified vadose zone processes.

1. Introduction

Groundwater constitutes 96% of the Earth's liquid (unfrozen) freshwater and is vital in sustaining the baseflow in rivers, lakes, wetlands, and ecological systems (Poeter et al., 2020). On a global scale, nearly 2 billion people rely on groundwater from various aquifer systems as their main source of freshwater (Velis et al., 2017). Currently, groundwater is estimated to provide 40% of the world's water needs for agriculture, 36% of its domestic water needs, and 27% of its industrial water needs (Taylor et al., 2013). This makes it a strategic resource, especially from the perspective of mitigating the effects of changing climatic patterns in many areas globally, where surface water and precipitation are limited and highly variable. Changes in rainfall patterns and evapotranspiration create challenges for surface water to meet the demands for clean water. During times of drought, groundwater acts as a buffer against a lack of rainfall and water scarcity (Green et al., 2011; Kaveh et al., 2017; Cobbing, 2020).

The vadose zone is that key area that connects the land surface to the underlying aquifers, representing a critical zone that controls its hydraulic response to rainfall and the extent to which pollutants are delayed or attenuated before reaching the water table. Consequently, the heterogeneity of the vadose zone plays a very important role in the transfer of water and pollutants because of the presence of temporary storage zones and preferential flows. A better knowledge of the physical processes in the vadose zone allows an improved assessment of the natural recharge of an aquifer and of its vulnerability to surface-applied pollution.

However, when it comes to establishing an early warning system for groundwater contamination, the vadose zone, positioned above the water table, has often been overlooked as a crucial monitoring area (Dahan, 2020). Notably, it's worth mentioning that between the 1980's and around 2010, Germany conducted numerous relevant studies in this

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field. These studies, primarily conducted in German, may not have received the international attention they deserved during that time. Ultimately, the quality of water that traverses this critical zone has a direct influence on the groundwater system. Improvements in characterising flow and transport in the vadose zone have been attributed to the development of the vadose-zone monitoring system (VMS) for continuous real-time tracking of water quality and hydraulic parameters (Dahan et al., 2003, 2014; Ghashghaie et al., 2022).

Work done by Dahan et al. (2014) in Israel showed that nitrate concentrations leaching from organic greenhouses (>100 mg/L) were observed in the deeper parts of the vadose zone, where it is out of reach for plant uptake, and poses a direct threat to groundwater quality. The leachability of nitrate occurring below the root zone was shown to be independent of the general agrotechnical regime of organic versus conventional agriculture, but rather as a result of the method of fertiliser application (i.e., solid fertiliser vs. fertigation). This was further demonstrated by Turkeltaub et al. (2016) when they implemented a vadose-zone monitoring system to track the water percolation and nitrate migration from the surface of the land through the vadose zone to the water table at 18.5 m depth. The data showed that it took approximately 5.9 years for the nitrate to migrate from the land surface to the water table. Therefore, it is evident that monitoring the vadose zone is critical in preventing groundwater contamination, especially where this water is used for drinking purposes.

As indicated above, this area of the subsurface has not been given much attention as compared to groundwater monitoring, when it comes to the vadose zone serving as either a buffer or a source of contaminants for the underlying aquifer. Hydrogeologists usually monitor the quality of aquifer systems by collecting water quality data from springs and boreholes. However, by the time contamination is observed in boreholes and springs it might already be too late as it takes a considerable amount of time for pollutants to spread in the aquifer with the next step generally being remediation. Groundwater contamination can be prevented if efficient real-time in situ monitoring of the vadose zone is implemented. Enhancing this approach involves integrating sensor networks, geophysical methods, satellite imaging, and community-based initiatives.

Depending on the climatic conditions, matrix flow in the vadose zone can range in the order of magnitudes within a year (Gurdak et al., 2007; Bruneau et al., 2022; Ostad-Ali-Askari, 2022). In humid areas it is normally directed vertically downwards, and in arid climates like South Africa (average annual precipitation of 464 mm) it is also vertically upwards if the water table is not too far below the land surface (Seiler and Schneider, 2001; Zhu et al., 2011; van Tol, 2020; Nimmo, 2021). In addition to matrix flow, other events occur during infiltration; these include bypass or preferential flow, which interacts with the matrix by ion-exchange processes, retardation processes producing perched groundwater or interflow. Conceptual models that simulate seepage conditions typically assume that fluxes are homogeneous within small compartments and vertical; these boundary conditions are not easy to control using statistical estimation of matric suction and volumetric water content values and therefore remain theoretical (Mali and Urbanc, 2009). One way to reduce this measurement uncertainty is to apply tracer methods (environmental and artificial tracers) to support and improve the estimation of subsurface hydraulic properties (Meyer et al., 2013; Lauber and Goldscheider, 2014).

The application of tracer methods can yield satisfactory results for the hydraulic characteristics of the vadose zone when used in conjunction with detailed conceptual models and numerical methods of a particular area. Tracer studies can be used for depicting groundwater flow paths, mean residence times and mixing processes among different end-members, identifying connectivity between surface water and groundwater, estimating recharge from infiltration and percolation following a rainfall event, and quantifying pre-infiltrative evaporative processes.

The altered vadose zone, as described in this review paper, refers to the region of the Earth's subsurface that has been modified by human activities. Examples of such modifications include excavation, adding or removal of overburden, and exposure of underlying layers, which disrupts the natural soil profile and affects physical and chemical properties. These alterations can occur in various settings, such as changing the surface nature through ploughing, quarries, construction sites, mines, roads, and landfill sites. Changes in the vadose zone affect hydrological processes, influencing moisture content, organic matter, nutrient availability, and properties like permeability, porosity, and hydraulic conductivity. Consequently, nearby surface water bodies and groundwater systems can be affected. Understanding and managing these anthropogenically altered vadose zones is crucial for minimising environmental effects and preserving water resources.

This review consequently seeks to provide an overview for the selection and utilisation of tracers within the vadose zone, while addressing regulatory considerations. The analysis encompasses both environmental and artificial tracers, highlighting commonly used ones and their typical applications. With a focus on elucidating flow and transport dynamics within the altered vadose zone, the review also addresses the critical choice between single and multi-tracer approaches, taking into consideration the vadose zone's thickness and its influence on mean residence times. Furthermore, when considering the complexities surrounding flow and contaminant transport modelling within the vadose zone, it is crucial to highlight the significance of experimental investigations as an essential component of these modelling efforts.

1.1. *Article search strategy and screening phase*

Literature review searches were carried out on 1 September 2023 using Science Direct, Scopus, Google Scholar, Semantic Scholar, and Web of Science search engines. Multiple keywords were used as a basis to identify relevant research articles with Boolean combinations ("AND", "OR", "WITH", "SAME") to further constrain the search results. In addition, eligibility criteria (inclusion/exclusion) were applied at various stages of the literature screening phase. The preliminary search returned 2070 articles, and after careful review, duplicate articles (n = 240) and those that did not have any relevance to the research questions (n = 489) were eliminated using the Endnote Reference Manager software online. Further analysis based on titles and abstracts (n = 1341) resulted in the removal of 1037 articles as they centred predominantly around groundwater-surface water interaction and groundwater recharge estimations using various tracer techniques.

Finally, after reviewing the full text of the remaining literature (n = 304) the selection was reduced to a total number of 98 published items in this review paper. Fig. 1 illustrates the screening process flow chart.

Among the 98 peer reviewed publications listed in this review, the

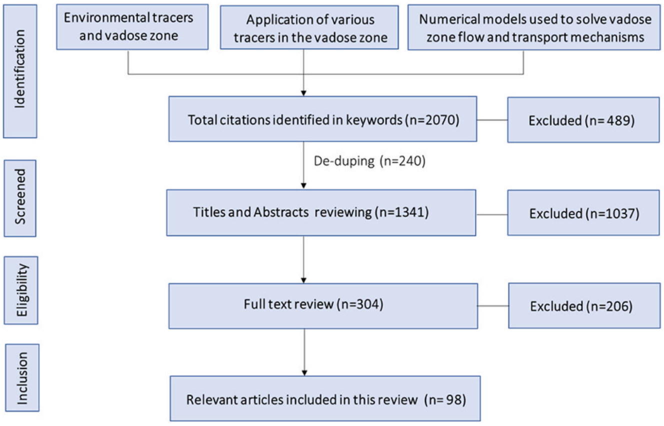

Fig. 1. Flow chart illustrating the literature search methodology.

United States of America and Germany accounted for the highest number of vadose zone environmental and artificial tracer studies conducted internationally. South Africa, along with eight other countries, had a total of two studies each within the search enquiry and Tunisia was the only other African country listed (Fig. 2).

In addition to analysing the number of publications from different countries, it was important to consider the geographic distribution of the conducted studies. The locations of the studies have been extracted and are presented on a global map, which provides insights into the spatial patterns of research efforts in the vadose zone environmental and artificial tracer studies (Fig. 3). The map shows clusters of darker purple shading, indicating regions with a higher number of conducted studies, reflecting substantial research activity and knowledge accumulation. Conversely, areas with light purple shading represent research gaps, emphasising the need for further investigations and a more comprehensive representation of global research efforts. It's important to note that processes often exhibit similarities regardless of geographical location.

Although this study draws conclusions based on a comprehensive search of publications in the Science Citation Index (SCI), it is important to acknowledge the potential bias inherent in this approach. The reliance on SCI publications may inadvertently overlook research from countries where financial constraints and limited motivation to publish in international journals exists. Consequently, the findings should be interpreted with caution, as they may not fully reflect the global research landscape. Future studies should strive to incorporate a broader range of sources to ensure a more inclusive representation of research efforts worldwide.

2. Use of tracers in vadose zone hydrology

Generally, contaminants that are released at the surface can migrate through the vadose zone and pollute the underlying aquifer (Zhuang et al., 2021). In terms of the risks associated with contaminating an aquifer system, it is vital to gain an understanding of the fate and transport of contaminants in the vadose zone. Although advection and dispersion are considered the main transport mechanisms, further evidence suggests that solute diffusion in the vadose zone is a key parameter that affects solute residence times in both the liquid and gas phase.

While the flow mechanisms in unsaturated unconsolidated material have been studied in considerable detail (Freeze and Cherry, 1979; Nimmo, 2005; Bear et al., 2012), the practical implications of this research for monitoring groundwater contamination within the vadose zone have often been neglected. Despite the advancement in understanding contaminant dispersion in relation to soil water content (Bear et al., 2012), the vadose zone has not received sufficient attention as a crucial monitoring area above the water table. As mentioned, the principal fate and main transport mechanisms of concern in the subsurface include advection, molecular diffusion, mechanical dispersion, hydrodynamic dispersion, sorption, and decay. In terms of solute migration, the solute can only be transported by one or a combination of the above-mentioned transport processes if it is dissolved in water. Colloid transport is also a significant factor to consider, involving the movement of suspended particles through the subsurface and can act as carriers for adsorbed pollutants and influence the overall fate and mobility of contaminants.

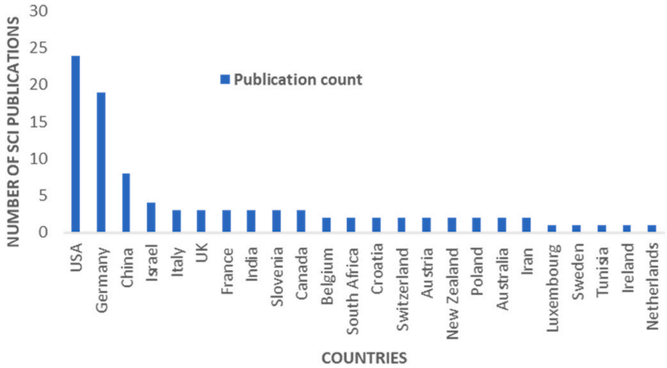

Fig. 2. The total number of environmental and artificial tracer studies published in each of the countries identified within this review paper.

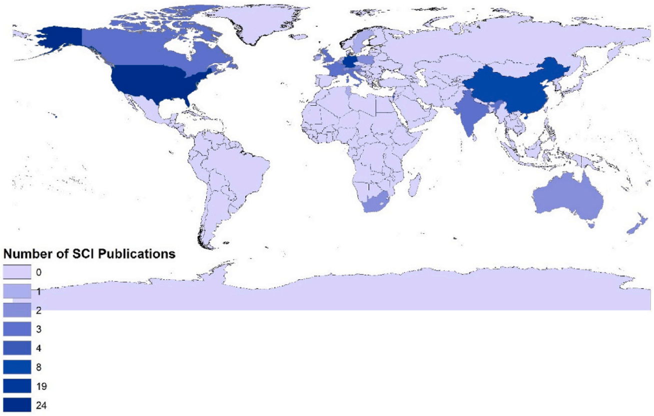

Fig. 3. Geographic distribution of environmental and artificial tracer studies in the vadose zone worldwide.

Environmental (or natural) tracers are chemical substances measured in groundwater that are either naturally present or produced because of man's activities, but not specifically released for tracing purposes; in contrast, artificial tracers are deliberately introduced into a system. In addition, tracers can be categorised in terms of being stable (e.g. ^{18}O, ^{2}H, salts, solid tracers and fluorescent dyes) or unstable (e.g. radioactive; subject to biodegradation; ^{14}C; rhodamine WT); whether they are of natural or anthropogenic origin; whether their delivery to the environment is natural, accidental, or deliberate (Ho et al., 2006).

Tracers are useful for characterising water flow in the vadose zone and to infer environmental processes. In terms of practicality of use, the main differences between environmental and artificial tracers are the spatiotemporal timescales about which they provide information; environmental tracers generally provide information on processes that have occurred over many years and over larger spatial scales, while artificial tracer studies have a shorter time frame (usually measured up to several years) over a relatively small area (Cook, 2015). A prerequisite for the application of tracers is that the spatial or temporal differentiation of tracer signatures should exceed the sampling and analytical precision. These differentiated tracer signatures can be inherent from the infiltrating water or acquired during passage of water through the vadose zone and rocks where the addition of dissolved substances takes place (Wachniew, 2015).

The ideal characteristics of tracers include being non-toxic and easily transportable, soluble, and clearly visible (in the case of dye tracers), possessing a stable spectrum, exhibiting high detection sensitivity, and being affordable and widely accessible. Moreover, tracers should not experience significant hindrance from the soil or aquifer matrix, ensuring their non-reactive (conservative) nature and facilitating easy measurement. (Flury and Wai, 2003; Geyh et al., 2008). An ideal tracer should display these characteristics; however, no single tracer may meet all these requirements (Singhal and Gupta, 2010). The subsurface displays substantial heterogeneity and anisotropy, creating an opportunity for the application of tracer techniques. Consequently, these techniques aid in effectively narrowing down the properties of the system under investigation. (Leibundgut et al., 2011). In this review, the focus is on tracers primarily used within the vadose zone, recognising their importance in improving understanding of vadose zone hydrology and contaminant transport dynamics.

3. Environmental and artificial tracers

There are two basic groups of tracers (Table 1).

1. Environmental tracers encompass naturally present dissolved constituents, isotopes, and physical properties as well as chemical components found in water. By examining their spatial and temporal variations, valuable insights can be gained regarding the movement and behaviour of water and solutes within the environment.
2. Artificial tracers, on the other hand, are deliberately introduced into the hydrological system in order to deduce information about environmental processes.

Environmental tracers serve as valuable indicators of long-term processes in hydrology, offering insights into events that have unfolded over extended periods. These tracers can originate from natural sources or be unintentionally released into the environment through human activities, eventually becoming persistent and useful hydrological markers. With their widespread distribution across Earth's surface, most environmental tracers have the capacity to provide valuable information on processes occurring on much larger spatial scales (Clark, & Fritz, 2013). They are widely employed to identify and analyse the sources of water or contaminants. Their primary role is twofold: first, to pinpoint unique signals linked to geological formations or aquifers, and to enhancing our understanding of vadose zone water dynamics, subsurface flow pathways, groundwater flow, and recharge processes.

One crucial application of environmental tracers involves estimating the age or average residence time of pore water and/or groundwater. Various types of environmental tracers have been utilised for this purpose, with naturally occurring stable and radioactive isotopes being the most commonly employed. These include isotopes of the water molecule (such as δ^{18}O and δ^{2}H) and tritium (δ^{3}H), a radioactive isotope of hydrogen that was released during atomic bomb tests in the 1960s (Clark, & Fritz, 2013). By determining the mean residence time of water, it becomes possible to deduce water velocities, aquifer recharge rates, and the vulnerability of water supplies to contamination. (Leibundgut et al., 2011).

Table 1
Relevant hydrological tracers (adapted from Leibundgut et al., 2011).

- **Environmental Tracers**
  - **Stable Isotopes**
    - Deuterium (^{2}H) [a]
    - Oxygen-18 (^{18}O) [a]
    - Carbon-13 (^{13}C)
    - Nitrogen-15 (^{15}N)
    - Sulphur-34 (^{34}S)
  - **Radioactive isotopes**
    - Tritium (^{3}H) (and helium-3 (^{3}He)
    - Carbon-14 (^{14}C)
    - Argon-39 (^{39}Ar)
    - Krypton-85 (^{85}Kr)
    - Radon-222 (^{222}Rn)
    - Radium-226 (^{226}Ra)
    - Silicon-32 (^{32}Si)
    - Chlorine-36 (^{36}Cl)
  - **Categories of Gases and Compounds**
    - Anthropogenic trace gases
    - Chlorofluorocarbons (CFCs)
    - Sulphur hexafluoride (SF_6)
    - Geochemical compounds
    - e.g., silicate, chloride, DOC
  - **Physicochemical parameters**
    - e.g., Electrical conductivity, temperature
- **Artificial Tracers**
  - **Solute tracers**
    - Fluorescent dyes
    - Naphthionate
    - Pyranine
    - Uranine
    - Eosin
    - Rhodamine WT
  - **Non-fluorescent dyes**
    - e.g., brilliant blue
  - **Salts**
    - Sodium/potassium chloride
    - Sodium/potassium bromide
    - Lithium chloride
    - Potassium iodide
    - Sodium borate (borax)
  - **Fluorobenzoic acid**
  - **Deuterated water (^{2}H)**
  - **Radionuclides**
    - e.g., Tritium (^{3}H) [b]
    - Chrome-51 (^{51}Cr)
    - Bromide-82 (^{82}Br)
    - Iodine-131 (^{131}I)
- **Activatable radionuclides**
  - Dissolved gas tracers
    - Helium
    - Neon
    - Stable isotopes of krypton
    - Sulphur hexafluoride (SF_6)
  - **Particulate tracers**
    - Lycopodium spores
    - Bacteria
    - Viruses
    - Phages
    - DNA
    - Synthetic microspheres
    - Phytoplankton

[a] Typical applications include origin and mixing of waters, residence time of water in the vadose zone and small catchments, estimation of recharge rates.

[b] Identification and dating of young groundwater, estimation of recharge rates.

In contrast, artificial tracers can be defined as substances which are added intentionally to either the hydrological or vadose zone systems in planned experiments for detection downstream (Wolkersdorfer and LeBlanc, 2012). In terms of characterising flow paths and estimating groundwater velocities, applied tracers using either single or multiple wells have been applied since the 19th century and have become a standardised hydrogeological characterisation tool (Käss, 1998; Divine and McDonnell, 2005).

In a sense, groundwater contamination typically originates at the surface and then enters the vadose zone, through the application of agricultural chemicals, or chemical organisms released from waste repositories (Arora et al., 2019). This can be from landfill leachate, mine waste discard dumps, leaking underground storage tanks, unlined pits, ponds, and lagoons, household septic systems, and surface hydrocarbon spills. These contaminants leach through the vadose zone and end up polluting the groundwater (Flury and Wai, 2003).

Following the invention of sodium fluorescein in the 19th century, artificial tracer experiments have become more widespread and have been continuously used in karst systems (Käss, 1998). In general, artificial tracers are used in systems which have a residence time of less than one year (Poulain et al., 2015).

A tracer test employing uranine (500 g), with a minimal water flush of less than 500 L, was conducted in the Han-sur-Lesse Cave, Belgium, to investigate the long-term behaviour of the unsaturated zone karst (Poulain et al., 2015). The test revealed flow rates of 6.5 m/h over a distance of 90 m, highlighting the transmissivity of the limestone massif and the existence of preferential flow pathways. Remarkably, maximum concentrations of the tracer (72.2 μg/L) were observed after only 80 h, indicating a minimum modal velocity of 0.88 m/h (for a distance of 90 m).

Artificial tracer studies, due to their short time frame, prove most useful in shedding light on rapidly occurring processes. They can aid in identifying flow pathways in fractured rocks, understanding transport mechanisms, determining residence times, flow velocities, and aquifer parameters by analysing tracer breakthrough curves (BTCs) and tracking the movement of water in the vadose zone. (Cook, 2015; Benischke, 2021). A sound knowledge of the characteristics of the tracer substances and the respective measurement techniques is required to perform experiments successfully, both in the laboratory and at field scale.

4. Multiple vs single tracer use in the vadose zone

The understanding of vadose zone flow pathways within the vadose zone plays a pivotal role in effective water resource management and the analysis of pollutant transfer to underlying aquifers (Nimmo, 2005; Ma et al., 2017). To assess groundwater recharge, stable isotopes of oxygen (δ^{18}O) and hydrogen (δ^{2}H), along with the radioactive isotope of hydrogen (δ^{3}H), are widely employed, leveraging seasonal variations in the isotopic compositions of precipitation (Barbecot et al., 2018; Li et al., 2019). In the field of artificial tracers, fluorescent dyes have emerged as a key group, with xanthene dyes such as uranine, eosin, rhodamine WT, and erythrosine being at the forefront. These dyes offer several advantages, including high detection sensitivity, minimal or negligible background presence in the natural environment, ease of detection, reliable quantifiability, and robust environmental resilience. Their sorptive behaviour varies across the spectrum, ranging from low for uranine to moderate for eosin and stronger for sulforhodamines and rhodamine WT. This variability is influenced by both the characteristics of the sorbing material, and the pH of the water being traced. Additionally, the advent of field fluorimetry enables the acquisition of in-situ time series data for fluorescent tracer concentrations with exceptional temporal precision. It is important to note that a wide array of dyes is available for hydrological tracing, each selected with a specific purpose in mind (Käss, 1998).

Ma et al. (2017) conducted a study in the Northern China Plains, investigating subsurface water flow patterns in three distinct land-use areas: non-irrigated grassland, poplar forest, and irrigated arable land. They collected samples from precipitation, groundwater, and soils, focusing on stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) as tracers. Notably, the $\delta^{18}O$ and $\delta^{2}H$ values in the upper 10 cm of soil water at all three sites were substantially influenced by evaporation and infiltration processes. These values were enriched ($\delta^{18}O = -4.2‰$ to $-7.0‰$) compared to precipitation ($\delta^{18}O = -10.1‰$), reflecting the effect of low soil water content. This enrichment, despite occurring at depths greater than 10 cm, is attributed to the infiltration of surface runoff during storm events, where water from precipitation penetrates the soil and mixes with antecedent soil water. The presence of short residence times at shallow depths (10–40 cm) reflects the rapid mixing of these waters during such events. Additionally, the study identified the coexistence of both diffuse and preferential flow within the active plant root zone, with local-scale heterogeneities influencing subsurface flow paths. These heterogeneities, including variations in soil properties and the presence of root channels, contribute to the observed complexities in subsurface water movement.

Factors such as antecedent moisture content, vegetation type, precipitation intensity, and soil texture played crucial roles in shaping preferential flow paths in the vadose zone, corroborating findings from earlier work by Stumpp and Maloszewski (2010). Where they deployed lysimeters with undisturbed soil, demonstrating seasonal variations in preferential flow driven by vegetation cover and highlighted that preferential flow can occur even when the soil is not near saturation, particularly during high-intensity rainfall. To delve further into the intricacies of flow and transport at much smaller scale, Scaini et al. (2019) used laboratory tracer experiments with NaCl and a multiple interacting pathways (MIPs) model. This model incorporated transition probability matrices (TPMs) to account for exchanges between flow pathways of varying velocities, simulating effects such as capillarity, connectivity, and preferential flow. Laboratory column experiments with NaCl revealed modifications in the soil's internal pore structure. The MIPs model was applied to test hypotheses related to velocity distribution shape, TPM influence, immobile storage zones, and time variability. The best model performance was achieved when TPMs and local immobile storage zones were included, underscoring the influence of macropore structures on soil water infiltration.

In a study by Filipović et al. (2020), the evaluation of soil pore systems and preferential flow in vineyard soil was carried out using a combination of laboratory and numerical methods, dye staining, and X-ray imaging. While single-porosity models adequately simulated leaching, the extensive macropore network revealed by dye staining and X-ray imaging led to the adoption of dual-permeability modelling, which provided a more accurate representation of preferential flow ($R^2 = 0.987$). Approximately 23% of the vertical column sections exhibited dye patterns, indicating the presence of macropore flow primarily driven by biopores, such as earthworm burrows and old root channels. Dual-region transport modelling was essential for capturing non-equilibrium flow patterns in complex pore systems. This comprehensive approach enabled a thorough assessment of vineyard soil structure and the extent of preferential water flow.

Building on the insights gained above, Koeniger et al. (2010) conducted experiments to assess water movement in both saturated and unsaturated conditions, offering valuable data on tracer behaviour in various settings. In their column experiments, stable isotopes of deuterium ($\delta^{2}H$, D) and oxygen 18 ($\delta^{18}O$) exhibited faster breakthrough (at 3.5 mL/min; t_t: 507.1 min; P_D: 0.023) and smaller dispersion coefficients compared to uranine dye (at 3.5 mL/min; t_t: 510.6 min; P_D: 0.028). This indicated the isotopes had a more conservative behaviour through the column setup. Expanding to field-scale investigations, they simulated a rain event of 26 mm over 20 min, by releasing a tracer solution of 6.25 L containing 1.6 g/L uranine (10 g) and a δD of +272‰ (0.4 mL of a 99.8% D_2O solution). The resulting data revealed unsaturated flow rates of 0.03–0.04 m/d for a floodplain site and 0.002–0.004 m/d for a snowmelt study site over a six-month period. Interestingly, the vadose zone flow velocities observed in this field-scale study were roughly an order of magnitude lower than those reported in the Rhine River floodplain study. This variation can be attributed to factors such as lower infiltration capacities in the loess soils and higher simulated rainfall intensity during the irrigation experiment. Importantly, this study reaffirmed the utility of stable isotopes of water as tracers in understanding vadose zone dynamics.

In a related context, Cremer and Neuweiler (2019) investigated the influence of dynamic boundary conditions on solute transport within heterogeneous media under unsaturated conditions. They employed eosin Y and brilliant blue FCF as tracers in laboratory and numerical simulations. Their findings revealed that when high infiltration rates approached the hydraulic conductivity of the materials, downward flow and transport differed extensively from upward transport. This observation reveals a departure from traditional interpretations of breakthrough curve tailing (BTC tailing) commonly associated with structural heterogeneities, particularly dual-domain heterogeneities. Instead of being exclusively attributed to inherent structural variations, the pronounced BTC tailing during infiltration emerges from an intricate interplay shaped by the dynamic evolution of boundary conditions and the actively fluctuating hydraulic properties within the vadose zone. This interplay involves factors such as the rapid changes in moisture content, variations in soil matric potential, and shifts in soil hydraulic conductivity. This nuanced understanding highlights the need to delve beyond static structural factors and delve into the specifics of dynamic boundary conditions and actively changing hydraulic properties for a more comprehensive understanding of flow and solute transport dynamics in such intricate environments.

Continuing from the previous studies, Mali et al. (2007) conducted a comprehensive tracer experiment in a highly permeable coarse gravel vadose zone within the Selniska Dobrava aquifer of Slovenia. They employed both deuterated water and uranine to assess the transport processes, where the water table typically lies at depths ranging from 25 to 37 m. Their tracer test results revealed that deuterated water proved to be a more suitable tracer compared to uranine for studying vadose zone water flow. Deuterium exhibited more conservative behaviour, with mean flow velocities based on $\delta^{2}H$ concentrations ranging from 0.014 to 0.017 m/d, whereas uranine exhibited slower movement at 0.008 m/d. Dispersion increased with depth, highlighting the complexity of flow in this setting. Additionally, the retardation factor of uranine compared to deuterium fell within the range of 1.13–1.75, consistent with previously published findings. Moreover, the study illustrated that preferential flow paths, particularly on the north side of the lysimeter, exerted a substantial influence on vadose zone water flow properties, leading to variations in the arrival times of tracers at different depths. In a different setting, Fank (2001) conducted a tracer experiment in the vadose zone of a quaternary gravel fill in Austria. This experiment involved injecting 6 kg of sodium bromide (NaBr) through sprinkler irrigation (approximately 30–40 mm) over a 6-h period. Small, monolithic field lysimeters were installed at various depths (40 cm, 70 cm, 110 cm, 150 cm, and 300 cm) to sample solute movement. Results from this study indicated a mean residence time in the vadose zone of more than 3 years under the hydro-meteorological conditions at the test site. This resulted in a mean flow velocity of approximately 1.4 m/year, with a maximal flow velocity of 1.6 m/year, corresponding to a residence time of over 2.5 years. The study also revealed a longitudinal dispersivity in the soil ranging from 0.4 to 0.8 cm, demonstrating the influence of varying depths on solute movement.

Expanding the scope to contaminant transport in the vadose zone, (Viccione et al., 2020) utilised numerical modelling to assess the fate and transport of contaminants, specifically benzene and tetrachloroethylene, under different infiltration scenarios. Their study highlighted the critical role of sorption (Kd) phenomena in shaping the fate of contaminants. Using HYDRUS 2D/3D numerical modelling, they demonstrated that water flow through the vadose zone occurred primarily via preferential flow paths, bypassing considerable portions of the soil matrix. This phenomenon not only reduced the availability of water and nutrients to plants but also led to the leaching of chemicals, including pesticides, from the vadose zone to the water table.

Nützmann et al. (2001), further assessed a 2-m-thick layer of fine sands with a bulk density of 1.73 g/cm^3 in the vadose zone. Employing a dual tracer test, they introduced 60 g of sodium bromide (NaBr) and 0.5 L of deuterium (δ^2H) dissolved in 200 L of water onto a 10 m^2 surface area at a rate of 20 mm/h. This setup resulted in an initial concentration (C_0) of 300 mg/L for bromide and $C_0 = 2.6$ mg/L for deuterium. Their analysis of normalised breakthrough curves revealed interesting findings. The longitudinal dispersivity α_L, ranging from 2.75 to 7.5 cm, exhibited an increase with depth (30–120 cm). Mean lateral and vertical flow velocities were quantified at 0.31 cm/d and 3.8 cm/d, respectively. Shifting to a different geological setting, Veselič et al. (2001), embarked on a comprehensive exploration of flow and solute transport in fractured and karstified rocks at the Sinji Vrh experimental site in Slovenia. Their experimental setup comprised a 340-m-long artificial research tunnel positioned 5–25 m below the surface. Seeping water from this tunnel was meticulously collected in 1.5 m long sheet segments, each covering a 2.2 m^2 surface area. To investigate the intricate vadose zone processes, two distinct tracer tests were executed using a suite of six tracers, including NaCl, uranine, KCl, $MnCl_2$, $CuSO_4.5H_2O$, and $NiSO_4.6H_2O$, spanning both dry and wet seasons. Notably, NaCl exhibited rapid movement through the vadose zone, with its maximum concentration appearing just 2 h after injection, highlighting the presence of rapid conduit flow. Uranine, injected at a depth of 0.65 m below the surface, displayed unique transport behaviour. It peaked 8 days post-injection with a velocity of 1.2 m/d, and when rain arrived, its velocity further increased to 9.5 m/d, demonstrating minimal retardation at the soil-rock interface. Vincenzi et al. (2009) extended their focus to explore the effects of a 15 km long railway tunnel on groundwater and surface water in the Northern Apennines in Italy. Through two multi-tracer tests employing uranine and sulforhodamine G, they uncovered profound alterations in the regional flow system. The consequences included the drying up of springs and elevated drawdown, with total baseflow losses reaching 245 L/s (40–80%). Breakthrough curve analysis, leveraging the conventional one-dimensional advection-dispersion model (ADM), provide crucial insights.

In the northern region, flow velocities of 135.4 m/d were observed over a 135 m distance. In the southern part, linear flow paths exceeded 1 km in length, with maximum flow velocities ranging from 18.8 to 63.3 m/d. This interesting variability was attributed to the divergent tectonic domains characterised by distinct compressive and extensional stress fields, thereby establishing a critical connection between the streams and the tunnel. This emphasised the essential role of multiple factors encompassing soil saturation rates, geological structures, and precipitation events in enabling piston-like flow and efficient tracer movement through the modified vadose zone system, profoundly influenced by anthropogenic interventions.

In Southern Germany, Seiler and Schneider (2001) conducted a series of deuterium tracer experiments in Quaternary and Neogene sediments within an agricultural area. They employed multiple suction lysimeters at various depths, observing deuterium breakthrough at 10, 20, 50, 90, 130, and 180 cm below the surface. These experiments, conducted at eight different sites, showed the highly heterogeneous nature of vadose zone flow, characterised by distinct forms of slow matrix flow and rapid bypass flow. In loess and tertiary sands/gravels, matrix flow rates ranged from 0.7 to 1.2 m/a, while bypass flow rates spanned from 0.7 m/d to 2 m/d across all sediment types. Bypass flow velocities even approached those of overland flow, with observations at a depth of 1 m for loess, down to 1.5 m for Neogene sands, and exceeding 3 m in quaternary gravels, highlighting the complexity and variability of subsurface flow dynamics.

This was further illustrated by Rank et al. (2001) in sandy soils of the Great Hungarian Plain and the role of adhesive water in the water transport at a lysimeter station in Hungary. In total, eight tracer experiments were performed using δ^3H, δ^{18}O, NaCl and NO_3. For every experiment, 100 L of tracers were applied to four lysimeters at varying depths (60 cm, 110 cm, 160 cm, and 260 cm). The hydraulic conductivities at the lysimeter sites of about 2.10^{-4} to 1.10^{-5} m/s were estimated from grain size distributions. The results of the δ^3H tracer study showed that the discharge at lysimeter A (60 cm) consisted mainly of former adhesive water, while the main quantity of irrigated water appeared only with a considerable delay in discharge (i.e., approximately 13% of applied water appeared in the discharge at lysimeter A). Irrigation water with high δ^{18}O ($\delta^{18}O = -8.34‰$) applied in experiment 4 caused a temporary increase in the δ^{18}O values in all lysimeters with the NaCl and nitrate tracers not producing satisfactory results.

In a karstified limestone aquifer with a sandy loam overburden, Richards Coxon and Ryan (2005) assessed vadose zone travel times to groundwater using a bromide (Br^-) tracer. The experiment involved distributing 208 g of KBr dissolved in 2 L of deionized water evenly over 4 m^2 blocks. The application rate for Br and hydraulic loading rate (HLR) were 349.5 kg Br/ha and 0.5 mm/d, respectively. Suction lysimeters were placed at depths of 0.5, 1.0, and 1.5 m bgl. Within eight days after tracer application, the soil solution Br^- concentration increased from 0.02 to 0.22 mg/L, indicating a flow velocity of 6.3 × 10-2 m/d, with peak concentrations reached at a depth of 0.5 m after 34–65 days. This provided evidence of preferential flow through the vadose zone, with the tracer reaching 0.5 m depth within 8 days at both sites and 1.5 m depth within 27 days. Rainfall during the experiments played a crucial role in driving Br^- delivery through the vadose zone to the water table.

In a series of laboratory experiments conducted by Wang. et al. (2019), batch adsorption and column experiments were conducted on silty loam and silty clay soils to investigate the transport mechanisms of chloride and ammonia nitrogen. Three models, including the equilibrium advection-dispersion equation (ADE), mobile-immobile model (MIM), and continuous time random walk-truncated power law (CTRW-TPL), were employed. The results indicated that the CTRW-TPL model provided the best fit for the measured breakthrough curves (BTCs) of ammonia nitrogen in both soil types. Ammonia nitrogen adsorptive mass reached 90–100% of the maximum capacity within 5 min, displaying distinct non-Fickian features with earlier breakthrough and late tailing compared to chloride BTCs. The experimental adsorption data also revealed that the pseudo-second-order kinetic model and the Freundlich isotherm model best described the adsorption kinetics and equilibrium isotherms for both silty loam and silty clay soils. The maximum adsorption capacities were 811.49 μg/g for silty loam and 1399.45 μg/g for silty clay.

Perkins et al. (2011) investigated transport mechanisms within the vadose zone of the non-irrigated Bogue Phalia Basin in North-Western Mississippi, USA. They employed constant-head ponded infiltration tests, by inserting a 2-m diameter metal ring about 5 cm into the soil and sealed around the edges with bentonite to prevent leakage. Tracer-laden water, comprising a total volume of 3.45 m^3, was introduced to the ring infiltrometer. The tracers used were rhodamine WT at a nominal concentration of 2.68 kg/m^3 and calcium bromide at 2.37 kg/m^3. Rhodamine WT served solely as a visual marker for sample collection guidance. The bromide mass within the upper 1 m was 2.2 kg, with 2.3 kg below 1 m (total added amount: 8 kg). Consequently, the calculated preferential flow-transported tracer accounted for 43% of total flow, while the remainder was retained within the vadose zone. Additionally, the average field-saturated hydraulic conductivity (*Kfs*) values were measured at $4.7.10^{-4}$ cm/s and for the irrigated site and $1.9.10^{-2}$ cm/s for the non-irrigated site. This disparity indicated that in the absence of irrigation to maintain soil moisture, macropores, primarily composed of shrinkage cracks, developed, and facilitated preferential tracer transport to the water table. This significance of preferential flow was further shown by the observation that bromide reached a depth of 5 m before being detected at the 2-m level.

In a separate study, (Kaveh et al., 2017) explored the influence of soil moisture management techniques on soil properties and the output parameters of the SIRMOD model. The implementation of regular irrigation and increased soil organic matter influenced soil properties, preventing the formation of soil surface strength. Fluctuations between wet and dry periods had varying effects on soil characteristics. Modifications in infiltration coefficients systematically affected most output parameters, excluding the Time Watering Ratio (TWR). Elevated infiltration coefficients improved irrigation efficiency while decreasing TWR. The extension of irrigation borders enhanced irrigation efficiency, albeit at the cost of extended advance times and increased deep percolation. The quality of irrigation water introduced an element of sensitivity, particularly with parameters like the Deep Percolation Ratio (DPR) and Application Efficiency (Ea). Notably, the coefficient alpha exerted considerable influence over infiltration dynamics.

In a parallel investigation by Zaidman et al. (1999), the complexities of solute transport within the vadose zone of the chalk in East Yorkshire, UK were explored. They conducted two tracer infiltration experiments employing an electrically conductive tracer (NaCl) with a concentration of 60 g/L (105.8 g), applied at a rate of 49 mm/d over two days on an 18 m^2 plot. The evolution of these experiments was closely monitored using cross-borehole electrical resistivity imaging (ERI). The outcomes revealed interesting insights that are relevant to the earlier studies. Notably, they observed a rapid increase in heterogeneous conductivity at greater depths in both soil profiles, and this transformation occurred within just two days of tracer infiltration. This phenomenon was primarily attributed to the occurrence of bypass flow along steeply inclined joints, a behaviour that was particularly prominent during periods of high-intensity rainfall in autumn and winter following the tracer application, but notably absent during the summer months. The hydraulic implications of these findings suggest a strong correlation between fracture flow activation and high hydraulic loading rates. Furthermore, they highlighted that joint saturation manifested locally, advancing upward from horizons characterised by thin marl layers. These findings resonate with the observations of later studies by Isch et al. (2019) and Benettin et al. (2019), highlighting the importance of preferential pathways in solute transport, particularly in scenarios where hydraulic conditions and geological features lead to the activation of rapid bypass flow mechanisms, which can substantially influence the transport of solutes through the soil profile.

As shown above, the choice between using single or multiple tracers in vadose zone studies is influenced by several key considerations, including research objectives, site-specific characteristics, and the complexity of flow and transport processes. Single tracers are often employed when the research objectives are relatively straightforward and when a simplified representation of vadose zone processes is sufficient. As noted, 1-dimensional numerical models are commonly used in these cases because they provide a straightforward way to conceptualise vertical flow and transport. These models are practical when vertical flow and transport are the dominant mechanisms of interest, that focuses largely on understanding how substances move vertically through the vadose zone, neglecting lateral variations. Additionally, in situations where data availability, computational resources, or research budgets are limited, single tracers and simplified models offer a practical and cost-effective approach to gaining insights into vadose zone behaviour.

On the other hand, the use of multiple tracers becomes essential when vadose zone systems are complex and heterogeneous. The reviewed studies demonstrated that vadose zone flow pathways can be highly variable, influenced by factors like soil texture, vegetation, and geological structures. In such cases, a single tracer may not capture the full range of processes at play. Multi-tracer experiments provide a more comprehensive understanding of vadose zone dynamics, that allows for the conservative and non-conservative behaviour, as well as the influence of sorption, adsorption, and retention mechanisms on tracer movement. The choice of tracers therefore depends on the specific goals of the study. For example, stable isotopes may be selected to investigate water sources and residence times, while fluorescent dyes offer advantages in terms of constraining the hydraulic flow regime and establishing connectivity between injection and monitoring points of interest.

When vadose zone systems require more detailed and accurate representations, complex numerical models such as 2-dimensional or 3-dimensional models may be employed alongside multiple tracers. These models account for lateral heterogeneity and can capture flow patterns that 1-dimensional models may overlook. In essence, the selection of single or multiple tracers and the associated modelling approaches are guided by the complexity of the vadose zone system and the research objectives. Careful consideration of the trade-offs between simplification for practicality and the necessity for a more comprehensive understanding of subsurface processes is therefore essential.

4.1. *Thickness of the vadose zone and residence times*

As previously discussed, it is well-established that the vadose zone exerts a substantial influence on the hydrological dynamics of aquifers, affecting both contamination processes and the patterns and timing of recharge events (Liu et al., 2021). Extensive research has been devoted to understanding how the thickness of the vadose zone effects residence times in diverse aquifer systems. While numerous studies have explored various aquifer types, there has been comparatively less emphasis on investigating the individual layers within the vadose zone, despite the use of a diverse array of tracers to investigate flow behaviours.

In a study conducted by Gal et al. (2009), the focus was on assessing the migration of perchlorate from a 25-year-old ammonium-perchlorate manufacturing plant, characterised by four unlined ponds, into the deep vadose zone extending to 40 m beneath the Israeli coastal aquifer. To achieve this, they employed mass balance calculations and stable isotopes, specifically $\delta^{18}O$ and $\delta^{2}H$. Their findings revealed that isotopically depleted samples, with values of −4.68‰ for $\delta^{18}O$ and −20.73‰ for $\delta^{2}H$, were observed at shallow depths ranging from 2 to 8 m. In contrast, deeper samples, situated between 20 and 40 m, displayed an average of +0.62‰ for $\delta^{18}O$ and −14.75‰ for $\delta^{2}H$. These isotopic compositions in the shallow vadose zone samples suggested a source of slightly evaporated rainwater, while the more positive samples at greater depths indicated water usage for perchlorate manufacturing approximately 14 years prior to drilling. Consequently, maximum infiltration rates of 1.4 m per year were estimated, with very limited flow rates observed in the deeper vadose zone layers. These findings strongly implied that perchlorate below the clay layers remained practically stagnant under the existing natural conditions.

In a related study by Schwientek et al. (2009), the team investigated the vertical distribution of mean transit times within an unconfined heterogeneous porous aquifer, featuring a vadose zone with varying thicknesses ranging from 4 to 60 m. To track the flow of water, they utilised tracers such as tritium ($\delta^{3}H$) and chlorofluorocarbons (CFC-11, CFC-12, CFC-113). Their data suggested that the transit time of water through the vadose zone could be calculated as the difference between mean transit times based on $\delta^{3}H$ and CFCs, augmented by the time lag attributed to CFC diffusion through the vadose zone. Notably, discrepancies between transit times based on $\delta^{3}H$ and CFC-12 data reached around 30 years (ranging from 100 to 69 years) at a depth of 13 m below the land surface, indicating an advective transit time of approximately 60 years through the vadose zone. Interestingly, the observed mean transit time data deviated substantially from the theoretically expected logarithmic increase with depth, implying that while local heterogeneities did influence the spatial structure of transit time profiles, the thickness of the vadose zone played a more dominant role.

In a complementary investigation by Kuntz Kuntz and Grathwohl (2009), the transport and fate of reactive compounds, specifically lindane and phenanthrene, within the vadose zone were assessed. Steady-state and transient numerical flow scenarios were employed to determine the accuracy of steady-state flow simulations in describing reactive contaminant transport under dynamic conditions in the field.

They found that for compounds degrading within a range of Damköhler numbers from 0.5 to 50, steady-state flow conditions resulted in longer residence times within the vadose zone, facilitating the degradation of a substantial portion of the contaminant mass. However, it was also observed that extreme infiltration events could lead to higher contaminant concentrations at the lower boundary in transient simulations due to the shorter residence time of seepage water in the vadose zone, consequently reducing biodegradation and sorption. Overall, the research highlighted the suitability of steady-state flow conditions for most field scenarios, though it underscored the need to consider extreme infiltration events in transient simulations due to their potential influence on contaminant behaviour.

Building on this knowledge, Gerber et al. (2018) employed nitrate time series data and gaseous tracers like ^{39}Ar, ^{3}He, and ^{4}He. They examined travel times in aquifers with varying vadose zone thicknesses, utilising an extended lumped parameter model (LPM). One key takeaway from their work was the importance of incorporating the vadose zone into the LPM. By doing so, they managed to separate travel times in both the saturated and vadose zones, reducing uncertainties in nitrate predictions at pumping wells and enhancing model accuracy. This highlighted the crucial role of the vadose zone in improving groundwater model predictions.

Furthermore, Petrič et al. (2018) conducted and compared two tracer tests in the mountainous karst aquifers of south-western Slovenia (Javorniki-Snežnik massif) to validate previous findings. The tests involved the use of different amounts of uranine (4 kg and 38 kg) flushed with varying volumes of water (11 m^3 and 8.5 m^3). The results further confirmed that the thickness of the vadose zone plays a crucial role in its protective functionality for the groundwater system. A thicker vadose zone, such as the 400 m deep one in this study, substantially enhanced the retention times of the tracer underground and facilitated dispersion. Conversely, in the 40 m thick vadose zone, the tracer reached the observed spring much earlier and exhibited a substantially higher recovery percentage (55% compared to just 8.4%). These findings provide further evidence that the greater the thickness of the vadose zone, the better it performs in protecting the groundwater system from contamination by dilution effects.

In a separate study conducted by Liu et al. (2021), the influence of a thick karst vadose zone on groundwater recharge in the Xianglushan karst system located in Xianglushan mountain, Lijiang, northwest Yunnan province, China was assessed. Various modelling codes, including two coupled saturated-unsaturated flow models (referred to as Model 1 and Model 2) and one saturated flow model (Model 3) were utilised, which did not consider vadose zone processes. Notably, Model 2 did not account for preferential infiltration. Comparing the root mean square error (RMSE) values for spring discharge and groundwater levels, both Model 1 and Model 2 exhibited lower errors than Model 3. Specifically, the RMSE values for Model 1 were more than 50% lower than those of Model 3, while for Model 2, the values were over 20% lower. The slight difference between Model 1 and Model 2 indicated that the exclusion of preferential infiltration in Model 2 had a limited effect on the overall performance. These results suggest that in karst areas with thick vadose zones, slow flow processes play a predominant role in controlling groundwater recharge. Furthermore, the study evaluated the influence of different parameters on recharge and found that the infiltration rate had the most relevant effect, followed by the specific yield, percentage of preferential infiltration, and the Brooks-Corey coefficient. Together, these findings reinforce the previous conclusions of Petrič et al. (2018) regarding the importance of the vadose zone's thickness in modelling groundwater dynamics and highlight the key parameters influencing recharge processes in karst regions.

The studies mentioned above have provided valuable insights into the relevance of the thickness of the vadose zone on the mean residence times of tracers. Investigating the distribution of studies across aquifer types and vadose zone layers, as well as the selection of which tracers to use, is still an area that requires more research. There does, however, appear to be a noticeable bias towards conducting studies in karst aquifers utilising fluorescent dyes and natural tracers. This preference can be attributed to several factors.

Firstly, karst aquifers possess geological characteristics that make them particularly interesting for studying vadose zone flow. These aquifers consist of soluble rock formations, such as limestone or dolomite, which exhibit complex fracture networks, conduits, and sinkholes. The presence of these distinct features creates rapid and preferential flow paths, resulting in highly dynamic and heterogeneous groundwater systems. This inherent complexity of karst aquifers offers valuable opportunities to investigate vadose zone flow characteristics, as they represent natural access points for studying the intricate interplay between surface water and groundwater. Secondly, fluorescent dyes and natural tracers are commonly employed in karst aquifers due to their suitability for capturing and tracing the rapid flow dynamics inherent in such systems. Fluorescent dyes, for instance, provide easily detectable markers that track the movement of water through the vadose zone and into the aquifer. Natural tracers, such as isotopes or naturally occurring chemicals, are advantageous as they mimic the behaviour of water molecules and can help discern flow pathways and rates in complex karst systems. These tracers allow us to gain valuable insights into the intricate hydrological processes occurring within karst aquifers. Artificial tracers should therefore always be measured with probes (online fluorimeters) or with fluorimeters in the lab.

Moreover, the challenges associated with modelling flow in karst aquifers contribute to the emphasis on studying these systems. Due to the rapid flow velocities, heterogeneity, and preferential pathways, accurately modelling karst hydrogeological systems is notoriously difficult (Goldscheider and Drew, 2014; Simaubi et al., 2023). Through conducting extensive research in karst aquifers and utilising a variety of tracers, it becomes possible to gather critical data and observations. These are essential for the refinement of existing models or the creation of novel ones. The insights gained from studying karst systems can then be extrapolated and applied to improve understanding and modelling techniques in other hydrogeological systems as well. In summary, the bias towards studying karst aquifers and employing fluorescent dyes and natural tracers is justified by the unique characteristics of karst systems, which offer unparalleled access to observing vadose zone flow dynamics. However, replicating such observations and data collection methods in geological settings characterised by hard fractured rock or different hydrogeological conditions can be exceptionally challenging due to the distinct and often limited accessibility of these systems.

4.2. Tracer safety and regulatory considerations

Fluorescent tracers have found extensive application in evaluating flow patterns, transport mechanisms, and mixing processes within subsurface environments, as demonstrated in studies by (Behrens et al., 2001; Cook, 2015; Skjolding et al., 2021). Despite their widespread use, a critical factor in selecting any tracer is its toxicity to humans and the environment. This becomes even more important where communities are solely reliant on borehole water for domestic and drinking purposes. However, data availability on many tracer classes are either incomplete and not readily comparable and therefore do not suffice for use-oriented toxicological assessment (Smart, 1982).

While this section focuses on the use and regulation of fluorescent tracers, it acknowledges that other environmental (Tritium, Iodine-131, and Bacteriophages) and artificial tracers (Potassium Bromide, Sodium Chloride and Sulphur Hexafluoride) also exist that should be considered in terms of safety and environmental influence. Behrens et al. (2001) showed that uranine, eosin yellow, amidorhodamine G, pyranine and tinopal CBS-X had no effect on either the genotoxicity or ecotoxicity tests. Rhodamine WT, B and 6G all have genotoxic and ecotoxic properties and should be used cautiously when conducting tracer tests. Bacteriophages on the other hand are commonly regarded as 'environmentally friendly' tracers. However, Florent et al. (2022) argue that introducing a substantial concentration of bacteriophages into the vadose zone may, in reality, constitute a form of pollution causing mutation and/or mortality of natural bacteria. This prompts concerns regarding the possible ecological ramifications of these exogenous agents on the natural environment. From an ecotoxicity standpoint, the release of bacteriophages has the potential to disrupt microbial communities and ecological processes within the vadose zone.

In a recent study comparing the ecotoxicity of two commonly used artificial tracers, rhodamine B and WT, Skjolding et al. (2021) examined their implications for assessing the environmental safety of chemicals. The ecotoxicity of rhodamine B and WT towards algae, daphnia and fish embryos were assessed. Under the present test conditions, it was observed that rhodamine B exhibited greater toxicity to *Raphidocelis subcapitata*, a freshwater green algae used as a test organism in ecotoxicology studies, compared to rhodamine WT. Specifically, the Effective Concentration 10 (EC10) values indicated that rhodamine B was 18 times more toxic to *Raphidocelis subcapitata* than rhodamine WT. Concentrations higher than 16 mg/L resulted in substantial mortality of daphnia exposed to rhodamine B, enabling the fitting of a concentration-response relationship to the dataset. For the controls used in the rhodamine WT experiment, 5% mortality was observed, and no control mortality was observed in the rhodamine B exposure. After 48 h exposure to rhodamine B, the estimated LC50 value was 25 mg/L with a 95% confidence interval from 15 to 32 mg/L. Toxicity of rhodamine B and WT towards fish embryos showed that after 96 h of exposure to 12.5 mg/L rhodamine B the mortality increased to 20%. At 25 mg/L the lethality increased to 85% and at concentrations above 25 mg/L 100% lethality was observed. In terms of the Annual Average Quality Standard (AA-QS), this can be taken to be equal to the Predicted No Effect Concentration (PNEC) values determined. For rhodamine B, the AA-QS is 14 μg/L and AA-QS for rhodamine WT it is $>$ 91 μg/L. When regulating the use of these tracers the PNEC values will be important from an environmental management standpoint. These studies emphasise the necessity of considering toxicity data and setting appropriate regulations to ensure the safe and environmentally friendly use of tracers in subsurface environments.

In South Africa, tracer tests are commonly employed to assess hydrogeological connectivity between surface water and groundwater. Despite their routine use, the country lacks specific guidelines and regulations governing tracer test implementation. This regulatory gap is particularly critical when considering the potential toxicity and ecotoxicity of tracers, which have substantial implications for safeguarding water resources, protecting the environment, and ensuring human health. Even within the framework of the South African National Water Act (Act 36 of 1998), acknowledged as progressive water legislation, explicit guidance on conducting tracer tests is absent. This regulatory void leads to a lack of clarity regarding reporting requirements, often resulting in investigators overlooking the necessity of notifying regulatory authorities before conducting tests.

Existing South African water laws, notably the National Water Act (Act 36 of 1998) and the Water Services Act (Act 108 of 1997), form the cornerstone of the legal framework for water resource management. However, these acts may not sufficiently address the regulation of tracer testing, a method involving the introduction of specific substances into water systems for research purposes. The absence of explicit provisions for tracer testing in current legislation can lead to uncertainties regarding its implementation, monitoring, and potential environmental risks. While acts such as the Environmental Conservation Act (Act 73 of 1989) and the National Environmental Management Act (Act 107 of 1998) provide a broader context for environmental protection, including water quality standards, they may not specifically address the intricacies of tracer testing.

South Africa actively engages in scientific research involving tracer tests, but the overarching objective should extend beyond scientific inquiry. It is crucial to bridge the gap between scientific findings and policy or regulation development. Recognising tracer test's pivotal role in managing and preserving water resources, as well as upholding environmental and public health standards, there is a pressing need to address this regulatory deficiency. To achieve this, clear and comprehensive guidelines and reporting procedures should be established to facilitate compliance and effective oversight of tracer tests in South Africa. By incorporating sound scientific knowledge into well-defined policies and regulations, the country can ensure the responsible and sustainable use of tracers, aligning with broader goals of environmental protection and resource management. Building upon the foundation laid by Wolkersdorfer and LeBlanc (2012), it becomes evident that Section 37(1)(e) serves as the 'catch-all' clause, necessitating only the declaration of an activity, such as artificial tracer testing, as a controlled activity by the Minister for it to fall under potential regulation.

This proposed guidance document should provide clear and unambiguous directives, stipulating the requisite procedures when conducting a tracer test. It should specify which tracer classes meet safety standards and those that conform to accepted ecotoxicity levels. Furthermore, the document should explicitly define the appropriate governmental level, whether national, provincial, or local municipality, at which notification must occur—a process subject to variation depending on the specific regulatory framework and the scope of the tracer test. Beyond regulatory compliance, it is important to recognise that the data generated through tracer tests can serve as invaluable resources in the development of comprehensive databases. These databases, in turn, play a pivotal role in the characterisation and exploration of water resources within a specific region.

In light of the current absence of tracer test guidelines or regulations in South Africa, it is crucial to explore international models that can serve as templates for the creation of a standardised regulatory framework. These international examples illustrate diverse approaches to tracer test regulations, offering insights into both commendable practices and potential bureaucratic challenges. By examining such international experiences, stakeholders in South Africa can draw upon global expertise to develop a regulatory framework that aligns with their unique context and requirements, ultimately ensuring the responsible and sustainable use of artificial tracers while protecting water resources, the environment, and public health. For an in-depth exploration of international tracer test regulations, readers are encouraged to consult the comprehensive work of Wolkersdorfer and LeBlanc (2012), which offers a wealth of insights into regulatory approaches from around the world.

Internationally the regulation of tracer tests varies substantially across different countries, with the United States and Canada offering distinct approaches and frameworks for oversight. In the United States, comprehensive regulations are in place, with the Environmental Protection Agency (EPA) taking a lead role in ensuring the responsible use of tracers (US Environmental Protection Agency, 1999; 2017). (US Environmental Protection Agency, 1999; 2017). This oversight is facilitated through various regulatory frameworks such as the Safe Drinking Water Act and the Clean Water Act, which provide specific directives for conducting tracer tests in water supply and environmental preservation contexts. Crucially, the EPA places a strong emphasis on ensuring that tracers used are non-toxic and pose no risks to human health or the environment. An interesting note is that despite its toxic nature, rhodamine WT is permitted for use in both the United States and Canada Holmbeck-Pelham et al. (2000), (Holmbeck-Pelham et al., 2000), highlighting the need for a nuanced understanding of its regulatory status.

A key federal-level program in the United States is the Underground Injection Control (UIC) program, operating under the umbrella of the Safe Drinking Water Act and administered by regional offices of the U.S. Environmental Protection Agency (EPA). The UIC program specifically covers tracer injections into Class V wells (injection wells), with minimum inventory requirements outlined in 40 CFR 144.26. However, the implementation of these regulations can vary substantially among states, with only 24 out of 50 states having met or exceeded federal UIC requirements. Some states have parallel programs alongside EPA regional programs, while others rely on EPA regional UIC programs for enforcement. Additionally, some states may require detailed proposals for tracer usage, involving local departments or EPA offices in the review process, and may even involve toxicologists, epidemiologists, or health divisions for comprehensive tracer request reviews.

In Canada, there is a concerted effort to regulate and provide guidelines for the safe use of tracers, primarily in the context of environmental monitoring and assessment. The Canadian Council of Ministers of the Environment (CCME) plays a central role in developing national guidelines for tracer usage, with a strong focus on minimising environmental effects and safeguarding human health. However, it's important to note that specific regulations and guidelines for tracer tests are currently only in place in the province of Alberta. The Environmental Code of Practice for Hydrologic Tracing Analysis Studies, published by the Government of Alberta (1996), outlines mandatory requirements for conducting tracer tests within the province. These regulations provide the legal basis for tracer testing and water resource protection in Alberta. Additionally, guidelines from organizations like the CCME offer valuable recommendations for tracer selection, dosing, monitoring, data analysis, and reporting. Adhering to these regulations and guidelines is of paramount importance in ensuring the responsible use of tracers and the validity of tracer test results while safeguarding water resources.

Indeed, an integral aspect of tracer tests, particularly when conducted in proximity to areas where potable water is produced, is careful selection of tracers. This consideration is based on the authors' first-hand experience in Beaufort West, a Karoo town in South Africa (van Wyk and Witthueser, 2011). In this specific case, uranine was chosen as the tracer to estimate flow paths and travel times associated with uranium exploration activities in the south, which had the potential to affect the town's water supply. Fortunately, uranine was a sensible choice as it is non-toxic and readily degradable by sunlight, thus posing no substantial risk to human health. However, this experience highlights the critical importance of thoughtful and thorough tracer selection, ensuring compatibility with the environmental and health aspects of the specific location. The establishment of a regulatory framework in South Africa becomes imperative to effectively oversee the use of safe and non-toxic tracers in groundwater testing.

The implementation of guidelines within the framework of existing environmental protection acts, in collaboration with regional authorities, and with expert input, can help ensure the responsible and effective use of tracers in South Africa's groundwater management efforts. This framework should encompass various critical components, including conducting a comparative analysis of tracer test regulations to identify strengths, weaknesses, and potential improvements. It should also involve the adaptation of international guidelines to the local hydrogeological and environmental context, thereby ensuring the relevance and appropriateness of the regulatory framework. Furthermore, exploring best practices for test design, implementation, and data analysis is vital to enhance the quality and reliability of tracer test results.

Given the evolving nature of contaminants and environmental challenges, investigating the application of tracers for emerging contaminants should be an ongoing priority. Additionally, stakeholder engagement in the design and implementation of tracer tests can lead to more inclusive and effective groundwater management strategies. Lastly, conducting comprehensive risk assessments to evaluate the environmental and health effects of tracer tests is essential to safeguarding the well-being of both ecosystems and communities. In conclusion, these considerations logically build upon the importance of tracer test regulations discussed earlier, highlighting the need for a comprehensive regulatory framework that encompasses tracer selection, test design, risk assessment, and stakeholder engagement, all while aligning with the unique hydrogeological and environmental context of South Africa.

5. Flow and contaminant transport modelling in the vadose zone

While the introduction suggests a scarcity of available models, it's noteworthy that important strides have been made in the development of subsurface flow and transport models, particularly within the vadose zone, since the late 1970s (Nielsen et al., 1986; Nützmann et al., 2001; Šimůnek et al., 2003; Russo et al., 2014; Filipović et al., 2020; Zhou et al., 2021). These models involve solving the continuity equation and the advection-dispersion equation (Eq. (1)) to describe the movement of solutes in the vadose zone, considering appropriate initial and boundary conditions. Additionally, approximations are required for the time derivatives of both the flow and solute transport equations (Šimůnek and van Genuchten, 2016).

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \frac{B_d}{\theta}\frac{\partial C^*}{\partial t} + \left(\frac{\partial C}{\partial t}\right)_{rxn} \qquad (1)$$

where C = concentration of solute in liquid phase, t = time, D_L = longitudinal dispersion coefficient, v_x = average linear velocity, B_d = bulk density, θ = volumetric moisture content, C^* = amount of solute sorbed per unit weight of solid, rxn = subscript for biological or chemical reaction of the solute (other than sorption).

In Eq. (1), the first term on the right-hand side represents the dispersion of the solute, the second term represents advection, the third term accounts for the transfer of the solute from the liquid phase to solid particles through sorption, and the last term indicates changes in solute concentration over time due to biological or chemical reactions or radioactive decay.

To numerically solve the governing flow and transport equations, Galerkin-type finite element schemes are commonly employed. It is key to understand the relationship between soil water pressure, volumetric water content, and hydraulic conductivity, as elucidated by van Genuchten et al. (2014). This understanding forms the basis for effectively modelling the retention and movement of water and chemicals in the vadose zone. Various models for water retention function and unsaturated hydraulic conductivity are documented in the literature, with the van Genuchten model (Eq. (2)) being the most widely recognised.

$$S_e = \left[\frac{1}{1+|\alpha\psi|^n}\right]^m \qquad (2)$$

where α and n are parameters and m is generally assumed to equal 1-1/n, so that Eqn. (2) can easily be integrated with respect to ψ (soil water capillarity).

A plethora of numerical codes, differing in complexity and dimensionality, are available for the exploration of vadose zone flow and transport processes. These codes encompass both analytical and numerical models, capable of simulating variably saturated flow and

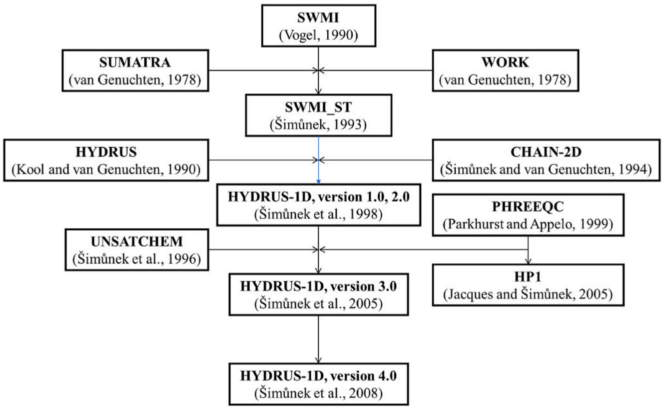

Fig. 4. HYDRUS-1D and related software packages (after Simunek et al., 2013).

transport in one-dimensional or multi-dimensional scenarios (Fig. 4). Notable references in this domain include works by (Van and Simunek, 2005; Bear and Cheng, 2010; Diersch, 2013; Simunek et al., 2013).

The Richards equation, originally formulated by Richards in 1931, serves as a fundamental framework for modelling saturated-unsaturated water flow. In modern practice, numerous finite element programs proficiently solve this equation to simulate the intricacies of water movement in porous media. Simultaneously, advection-dispersion type equations find application in modelling solute transport within the same context. For water flow, these finite element programs efficiently address the Richards Coxon and Ryan (2005) equation, offering insights into both saturated and unsaturated flow dynamics. The area of solute transport, on the other hand, often relies on advection-dispersion type equations for comprehensive analysis. Noteworthy references in this field include the works of (Helmig, 1997; Šimůnek and van Genuchten, 2016), who have contributed considerably to the understanding and implementation of these modelling techniques.

$$\frac{\partial \theta h}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\frac{\partial h}{\partial z} + K(h)\right] - S(h) \tag{3}$$

where θ is the volumetric soil water content (L^3/L^3), h is the soil water pressure head (L), K is the unsaturated hydraulic conductivity (L/T), often given as a product of the relative hydraulic conductivity K_r (dimensionless), and the saturated hydraulic conductivity K_s (L/T), z is the vertical coordinate (positive upward) (L), t is time (T), and S is a sink term representing root water uptake or some other source or sink (T^{-1}).

Nevertheless, a comprehensive discussion of the diverse analytical methods, including the Laplace transform, Fourier transform, and the method of moments, as well as in-depth exploration of the numerical codes mentioned earlier, lies beyond the confines of this review. Extensive summaries of these methods can be found in other papers (Šimůnek et al., 2003; Zha et al., 2019). Instead, this section will centre its attention on key aspects associated with flow and transport in the vadose zone. It will briefly outline the numerical challenges entailed and propose potential solutions, all within the context of vadose zone flow processes.

Researchers, spanning from Richards Coxon and Ryan (2005) to van Genuchten et al. (2014), Delleur (2006), and Šimůnek and Bradford (2008), have put forth a myriad of models to characterise the flow of water in porous media. These models, such as single-porosity, dual-porosity, dual-permeability, multi-porosity, and multi-permeability models, aim to capture distinct flow behaviours in granular soils, macroporous soils, and fractured rocks. The Richards equation (Eqn. (3)) is a widely adopted formulation for describing uniform flow, conceiving the medium as a compilation of impermeable soil particles separated by pores or fractures that permit flow and transport Šimůnek and van Genuchten (2016).

In modelling, single-porosity models presuppose the presence of a single, fully accessible pore system for water and solutes. Conversely, dual-porosity and dual-permeability models delineate two discrete pore regions: one linked with macropores or fractures and the other encompassing micropores within soil aggregates or the soil matrix. Notably, dual-porosity models often assume stagnant water in the matrix, whereas dual-permeability models account for water flow within the soil or rock matrix. To enhance modelling precision in specific scenarios, multi-porosity and multi-permeability models incorporate multiple pore and permeability systems, offering refined representations of intricate flow dynamics in porous media. Looking at exploration of water flow in vadose zone media reveals a host of critical research areas. These encompass addressing scale effects and non-equilibrium processes, integrating coupled physical phenomena more effectively, accommodating intricate geometries and heterogeneity, exploring data-driven methodologies, and underlining the imperative of sustainable water resource management.

In addition to the foundational models governing water flow and solute transport, the complex interactions between contaminants and soil particles profoundly influence transport behaviour, with processes like adsorption, desorption, and chemical reactions serving as critical factors. Vadose zone hydrology is a key area, given its role in shaping the movement of water and solutes in unsaturated soils, influenced by parameters such as soil moisture content, hydraulic conductivity, and capillary pressure. Furthermore, the looming issue of climate variability introduces substantial uncertainties by bringing variability to precipitation patterns and temperature, thereby exerting profound effects on vadose zone dynamics. Emerging technologies, such as remote sensing and advanced modelling approaches, further enrich our understanding of these processes.

5.1. *Experimental investigations*

Due to issues of non-linearity, analytical solutions of unsaturated flow models are, generally, not feasible, even in the simple one-dimensional case. Nevertheless, there have been a number of attempts to develop analytical, semi-analytical, or approximate solutions, such as those based on the series expansion techniques and integral methods. Analytical solutions are normally used for simplified transport systems involving linearised governing equations, homogeneous conditions, simplified geometries of the domain, and simplified initial and boundary conditions. Nevertheless, these and other methods have been applied to derive approximate analytical solutions for unsaturated flow (Bear and Cheng, 2010; Szymkiewicz, 2013). Numerical models have proven to be superior to analytical methods when tackling the non-linear partial differential Richards equation governing unsaturated flow, as highlighted by Pollacco Fernández-Gálvez et al. (2022). This superiority often stems from the ability to partition time and spatial coordinates into smaller subsets, such as finite differences, finite elements, and finite volumes, effectively transforming the governing partial differential equations into systems of algebraic equations, a concept elaborated upon by Pollacco Fernández-Gálvez et al. (2022).

In the domain of numerical methods applied to solving the advection-dispersion solute transport equation (Eqn. (1)), these methods generally fall into three categories: (i) Eulerian; (ii) Lagrangian; and (iii) mixed Lagrangian-Eulerian methods. Eulerian methods, as discussed by Šimůnek and van Genuchten (2016), are associated with standard finite difference and Galerkin-type finite element methods, which have been instrumental in early solute transport problem-solving and remain popular choices. While these methods can introduce numerical oscillations, judicious choices of small space and time steps can almost entirely mitigate this issue. Alternatively, upwind finite difference methods have been employed to eliminate numerical oscillations in purely advective transport, and upstream weighting has been proposed for finite elements. Lagrangian methods, though adept at circumventing numerical oscillations, may introduce challenges such as artificial dispersion, non-conservative solutions, and difficulties in implementation in two or three dimensions. Instabilities arising from inappropriate spatial discretisation can also manifest during prolonged simulations, often due to the deformation of the stream function, as cautioned by (Van and Simunek, 2005).

However, numerical approaches are not without their own set of challenges, notably convergence and mass balance issues. Finite element techniques, as emphasised by Kumar (2016), offer a substantial advantage over standard finite difference methods by enabling a more precise representation of irregular system boundaries and the incorporation of non-homogeneous properties. When coupled with unstructured triangular and tetrahedral elements, finite element methods allow for a highly accurate description of complex transport domains, as expounded by (Šimůnek and van Genuchten, 2016). This versatility in handling intricate geometries and varying properties makes finite element methods a preferred choice in many vadose zone simulations, demonstrating their indispensability in modern computational modelling for unsaturated flow and solute transport.

Numerical solutions based on the standard *h*-based formulation of the Richards equation initially yielded subpar results, marked by considerable mass balance errors and inaccurate predictions of pressure head distribution in vadose zone profiles Celia et al. (1990). However, these issues were effectively addressed through the application of the Picard iteration method for spatial finite element approximations. Additionally, Kirkland et al. (1992) introduced a transformation method that combined θ-based and *h*-based models, making it applicable to variably saturated systems. This innovative approach involved a new dependent variable, a linear function of pressure head and water content in both saturated and vadose zones. While the Picard iteration is commonly applied to vadose zone models, it's worth noting that Newton-Raphson (NR) iterations, albeit more complex and potentially resulting in non-symmetric matrices, offer faster convergence (J. Pollacco Fernández-Gálvez et al., 2022). However, NR iterations increase algebraic complexity and computational costs due to the presence of derivative terms, leading to non-symmetric matrix systems (Paniconi and Putti (1994).

Furthermore, the numerical solution of the Richards equation is sensitive to convergence-control strategies and methods for adapting the timestep size during simulations. Adaptive time discretisation, ranging from heuristic to control-based-error methods, has proven to be more efficient (Kavetski et al., 2001; Belfort et al., 2007). The applicability of linearization techniques, specifically the Newton and Picard schemes, in solving the Richards equation for variably saturated-unsaturated flow problems has been investigated by Islam et al. (2017). Their research involved four one-dimensional numerical experiments using different soil characteristics to examine the effect of various nonlinearities, including the van Genuchten-Mualem and Brooks-Corey models, on the convergence behaviour of the Picard and Newton schemes. The results highlighted that the Newton method exhibited greater robustness and speed, particularly for highly nonlinear problems like simulating vertical drainage through layered soil from initially saturated conditions over a 12-day event. For the Newton method, it became evident that the total number of steps and CPU time increased substantially as the head tolerance was reduced. This phenomenon was primarily attributed to the pronounced infiltration front in space, which led to these observed trends.

Pollacco Fernández-Gálvez et al. (2022) showcased substantial progress in the management of non-reactive (NR) processes. This progress was achieved through the application of suggested criteria for physical smoothing, incorporating a dynamic smoothing approach denoted as Ω. This approach not only enhanced the overall performance of the model but also improved its accuracy compared to the conventional method of absolute convergence, which relied on HYDRUS for validating the Hydrological Pixel (HyPix) model. The study achieved excellent agreement by attaining root mean square error (RMSE) values close to zero RMSE $\leq 1.8 \cdot 10^{-2}$ and Nash-Sutcliffe efficiency (NSE) values close to 1 (NSE ≥ 0.93) when computing simulated θ-profiles. HyPix demonstrated superior performance compared to HYDRUS, especially in soils with a coarse texture. This was primarily due to the accuracy of its time-stepping-ψ method, which outperformed the time-stepping-θ method.

The time-stepping-ψ approach effectively reduces ΔT (time step) when the soil approaches saturation, resulting in improved accuracy. Furthermore, HyPix showcased the effectiveness of a multistep optimization algorithm in gradually upscaling soil hydraulic parameters. This approach introduced heterogeneity, as optimizing the hydraulic parameters of each layer individually yielded poor results. By considering the overall soil water dynamics across the vadose zone, HyPix achieved better representation and enhanced performance in simulating soil water behaviour. Multistep optimization serves as a valuable technique for transforming a detailed layered profile of soil hydraulic parameters into a model with a reduced number of layers. This process not only allows for upscaling but also provides an estimation of the uncertainty associated with the decrease in layer complexity J. Pollacco Fernández-Gálvez et al. (2022).

6. Conclusions and future directions

By considering the use of both artificial and environmental tracer techniques, this review offers insights into the various transport processes, residence times and flow paths in altered vadose zone settings. These insights have provided a clearer understanding of the factors influencing travel times, primarily driven by the complex structures of these altered vadose zones. By harnessing the power of both single and multiple hydrological tracers, a refinement of estimations of fluxes between the vadose zone and the water table can be achieved.

The exploration into stable isotope tracer data has shown that preferential flow paths persist regardless of the initial moisture content in the vadose zone. This phenomenon appears to be intricately linked to the duration and intensity of rainfall events, as corroborated by inorganic ions and fluorescent dyes. These precipitation events have effectively created piston flow conditions, flushing tracers through the vadose zone. Moreover, the critical role played by the vadose zone in governing water movement, alongside other vital contaminant transport processes such as advection, diffusion, hydrodynamic dispersion, and microbial contaminant interactions, has been highlighted. To accommodate the considerable spatiotemporal variability inherent in hydrological systems, the necessity of high-frequency measurements, including in situ fluorimetry coupled with field-scale sampling needs to be considered. The extent to which various tracers applied are stored (in the matrix) and released (preferential flow paths) under changing moisture contents is largely regulated by the altered vadose zone. This is also highlighted by the vadose zone thickness in its effects on residence times and hydrological behaviour. Studies employing tracers and modelling techniques have shown that a thicker vadose zone can lead to longer travel times for water and contaminants, enhancing the protective functionality of the groundwater system.

Moreover, the use of fluorescent dyes and natural tracers, particularly in karst aquifers, has allowed the capture of rapid and preferential flow dynamics inherent in these systems. While karst aquifers, with their specific geological characteristics and complex hydrological processes, offer valuable insights into vadose zone flow and serve as natural access points for studying the interplay between surface water and groundwater. It is essential to recognise that studying other aquifer types can be equally relevant and useful. The knowledge gained from studying karst systems and employing various tracers contributes to improving modelling techniques and advancing our understanding of hydrogeological processes in different aquifer types.

Overall, these findings emphasise the crucial role of the vadose zone thickness in modulating residence times and groundwater dynamics, with implications for contaminant transport and recharge processes. However, the presence of preferential pathways may alter the relative importance of thickness in these processes. In terms of translating science into policy regulations, tracer safety and regulation highlight the importance of considering the toxicity and ecotoxicity of tracers when conducting tests in subsurface environments, especially in areas where communities rely on borehole water for domestic use. While some tracers like uranine, eosin yellow, amidorhodamine G, pyranine, and tinopal CBS-X have shown no adverse effects, others such as rhodamine WT, B, and 6G have genotoxic and ecotoxic properties and should be avoided under all circumstances.

The absence of specific tracer test guidelines and regulations in South Africa, despite its progressive water legislation, creates a regulatory gap and lack of clarity on reporting requirements. To address this issue, it is key to establish a standardised regulatory framework or technical guidance document that includes requirements for conducting tracer tests, specifies safe tracer classes, and addresses appropriate notification processes at the government level. International examples from countries like the United States and Canada can serve as models for developing such regulations.

Furthermore, further research in the field, especially with a focus on addressing some of the environmental challenges associated with vadose zone alterations and contaminant transport, is imperative. Additionally, advancements in numerical models for flow and contaminant transport in the vadose zone need to address existing research gaps, such as scale effects, non-equilibrium processes, coupled physical processes, complex geometries, heterogeneity, and the application of data-driven approaches. Convergence and mass balance problems are common in numerical approaches, but techniques like Picard and Newton iterations, adaptive time discretisation, and multistep optimization have been developed to improve model accuracy and performance. These advancements provide valuable insights for sustainable water resource management and a better understanding of vadose zone processes.

CRediT authorship contribution statement

Yazeed van Wyk: Writing – original draft, Investigation. **Matthys Alois Dippenaar:** Writing – review & editing, Supervision. **Eunice Ubomba-Jaswa:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no conflict of interest.

Data availability

No data was used for the research described in the article.

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