

Review

A Critical Review of the Modelling Tools for the Reactive Transport of Organic Contaminants

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Featured Application: This paper helps to summarize the most relevant information on reactive transport models used to simulate the transport of hydrocarbons. The authors hope that this paper will be very useful for future modelers, stakeholders, and scientists, and will help them to select the most appropriate tools or to create new models.

Abstract: The pollution of groundwater and soil by hydrocarbons is a significant and growing global problem. Efforts to mitigate and minimise pollution risks are often based on modelling. Modelling-based solutions for prediction and control play a critical role in preserving dwindling water resources and facilitating remediation. The objectives of this article are to: (i) to provide a concise overview of the mechanisms that influence the migration of hydrocarbons in groundwater and to improve the understanding of the processes that affect contamination levels, (ii) to compile the most commonly used models to simulate the migration and fate of hydrocarbons in the subsurface; and (iii) to evaluate these solutions in terms of their functionality, limitations, and requirements. The aim of this article is to enable potential users to make an informed decision regarding the modelling approaches (deterministic, stochastic, and hybrid) and to match their expectations with the characteristics of the models. The review of 11 1D screening models, 18 deterministic models, 7 stochastic tools, and machine learning experiments aimed at modelling hydrocarbon migration in the subsurface should provide a solid basis for understanding the capabilities of each method and their potential applications.

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Keywords: quality assessment; machine learning; remediation; reactive transport; groundwater contamination; risk analysis; deterministic models; probabilistic models

1. Introduction

Contamination of soil and groundwater by organic pollutants is a global problem that needs to be addressed, especially at historically contaminated industrial areas, such as brownfields or abandoned sites. Despite their tainted past, these areas, often located in urban industrial regions and low-income communities, hold potential for revitalization through remediation efforts. In 2016, 1.38 million potentially contaminated sites were registered, 98% of them in 11 countries [1]. According to projections, this number is likely to increase, as potentially polluting activities took place at a total of 2.8 million sites [2–4]. Mineral oils and heavy metals are the main contaminants, accounting for about 60% of soil pollution.

In the EEA countries, around 235,000 contaminated sites have been remediated [4], which corresponds to 17% of the potentially contaminated sites currently registered. The cost of managing contaminated soils in Europe amounts to around 6.5 billion euros per year [5]. The cost of a site investigation is usually between EUR 5000 and EUR 50,000 (60% of reported cases), while the cost of remediation projects is usually between EUR 50,000 and EUR 500,000 (40% of reported cases) [3]. The cost of remediation and restoration can be even higher, ranging from EUR 150,000 to EUR 2 billion, as it is difficult to separate

these measures [6]. As hydrocarbon pollution is a widespread problem, many spatial planners and decision-makers are faced with the problem of rapid and cost-effective remediation. Decisions on remediation strategies require tools and guidelines that provide a reliable estimate of the time and labour required to reduce the plume and source of contamination [7,8]. Numerical modelling can be an important method to study the fate of hydrocarbons in the aquatic environment [9–11]. It can precede any on-site action, estimate the extent of contamination, and help select the most effective and economical remediation methods. They can therefore help scientists, engineers, and decision makers to significantly improve their knowledge and optimize site management. Numerical models can also help to reduce the costs associated with long-term monitoring programs and sampling campaigns by identifying biogeochemical processes and quantifying their long-term effects.

One of the first applications of computer modelling to estimate groundwater flow dates back to the 1960s when Remson, together with Appel and Webster, proposed the use of finite differences and digital computers to track water flow [12], but very few involved hydrocarbon seeps. Since the 1970s, however, the number of journal articles describing models for the transport of hydrocarbons in water has increased (Figure 1), with an abrupt increase in recent years. There have been several breakthroughs in knowledge during these decades, e.g., the involvement of microorganisms in oil spills was described in detail as early as the 1970s [13], and in the same year a fundamental theoretical concept of the chemical and biological processes associated with the presence of hydrocarbons in soil and groundwater was formulated [14]. The theoretical and numerical definition and realisation of multiphase transport of hydrocarbons can also be regarded as a fundamental advance in knowledge in the 1980s [15,16].

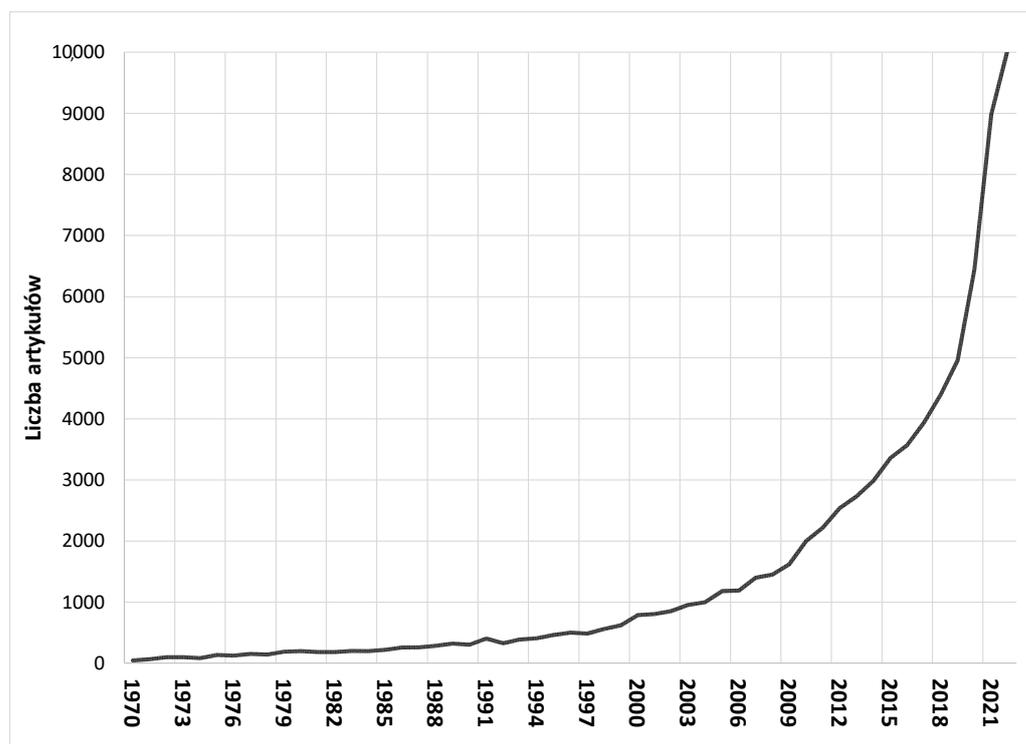


Figure 1. Number of articles in which the following keywords are mentioned: hydrocarbon, transport, model, and water in scientific journals; data from Google Scholar.

The first numerical models were based on a single organic pollutant whose degradation was simulated either by a single electron acceptor [17,18] or by several electron acceptors [19]. In the 1990s, the groundwater flow model—MODFLOW—was coupled with the reaction modules, and since then the term multispecies reactive transport has become established [20,21]. An important part of the hydrocarbon studies has also been

the development of standards for soil and water remediation based on the models and their uncertainty and sensitivity analyses [22–25], timeframes for remediation [26–28], and health risk assessments related to indoor and outdoor exposure [29–31]. These parameters are of critical importance to practitioners and environmental engineers whose goal is to revitalise polluted sites or return them to their natural state. The main turning points in hydrocarbon research have been the introduction of new remediation methods such as the use of nanoparticles [32,33], new devices/methods to measure pollutant concentrations [34–36], detailed monitoring [37–41], or the coupling of other techniques such as isotope measurements [42–44].

Remediation of hydrocarbon contaminated sites is an emerging field of research [45]. It has been reported that the number of papers published annually on this topic is increasing at an average annual growth rate of 9.22% [46]. Despite this large number of publications, only a few of them mention the need for further progress, which still needs to be improved, as hydrocarbons are among the most hazardous pollutants, posing a high risk to health and the aquatic environment.

So what does the future of hydrocarbon research look like? Looking at the articles from the last decades, one might conclude that some studies will continue to be site-specific, focusing on high-risk sites [47,48], large-scale sites [48–52], or areas with extreme conditions [53–57]. Certainly, some articles will refer to laboratory experiments and the dynamics of reactions affecting the attenuation of hydrocarbons in soils and water [58–60]. When it comes to studying the fate of hydrocarbons in the subsurface, there is still room for mesoscale laboratory studies [61–63] or field experiments [64–67], as these types of studies better reflect the ongoing processes in heterogeneous soils and the growth of bacterial communities in the quasi-real environment. It is likely that new studies will be required to address the remaining unresolved challenges in remediating hydrocarbon-contaminated soils, such as heterogeneity [68,69], realistic representation of volatile compound transport [70,71], accurate injection of oxidants or reductants [72,73], and modelling of these processes with new modelling tools [74,75] or with models that are well known but applied in novel ways [76,77]. Overviews of the fate and transport of organic pollutants and their bioremediation with updated knowledge of the mechanisms, the dynamics of the processes, and new modelling tools will also play an important role for future researchers to keep up with the trends [45,78–80].

Stochastic models are particularly interesting and can be used to construct probable scenarios, policy rules, guidelines, and risk assessments. They seem to be good solutions for complex systems where heterogeneity and randomness play a crucial role in the distribution of pollutants. These tools are described in the following sections together with examples of their application. A brief description of the application of machine learning methods in hydrogeological modelling is also included. This method, which offers high accuracy, is dynamically integrated into hydrological and hydrogeological modelling [56,81,82].

The aim of this article is to provide a comprehensive overview of existing solutions for modelling the transport and removal of hydrocarbons from the subsurface. This is facilitated by several objectives: the description of the processes controlling hydrocarbon migration and remediation required to build the conceptual model, the presentation of the most common mathematical models with their characteristics and limitations, and the presentation of the theoretical background of the different modelling approaches and their weaknesses and strengths.

This article is aimed at several groups: practitioners and experts in the field who opt for simpler solutions that are intuitive, have a user interface, and allow for a rich visualisation that can be presented to stakeholders and decision makers. For this reason, the deterministic 1D and 3D models are described in detail. In addition, this paper may be useful for scientists and developers who need a strong theoretical background and are interested in more sophisticated tools based on probability theory and machine learning algorithms. The paper could also be useful for future users and modelers. Therefore, the audience that can gain insights from reading this paper is broad, and the paper should help

in selecting the optimal modelling tool or combination of different models when assessing contaminated sites.

To summarize, this paper provides a roadmap for navigating between different approaches and models for predicting the fate of hydrocarbons in the subsurface. In addition to a brief overview of the history of discoveries in the field of hydrocarbon migration and removal from soils and groundwater, the paper provides insights into current and future trends in modelling and research. The novelty of this paper lies in the wealth of information to help future users make informed decisions and in the comparison of different approaches, including the application of machine learning algorithms to reactive transport. In addition, to the best of the authors' knowledge, it provides the most detailed description of stochastic models used to reproduce hydrocarbon migration in the subsurface.

2. Processes

As early as the 1970s, the fate of oil spills was described in terms of various processes, including advection, spreading and dispersion, dissolution, biodegradation, evaporation, and emulsification. However, due to the limited or lack of knowledge of analytical expressions for many of these processes and associated factors, the mathematical models were often simplified, resulting in several important processes being omitted [83]. In the early 1980s, the understanding of the fate and behaviour of spilled crude oil was extended to nine processes: advection, dispersion, evaporation, dissolution, emulsification, auto-oxidation, biodegradation, and sinking/sedimentation [84]. In the mathematical models, however, the focus remained on advection, dispersion, and evaporation.

However, stochastic reactive 3D flow transport was developed as early as 1985, taking into account first-order kinetics for degradation, adsorption, dispersion, spreading and retardation through a doubly porous medium [85]. This method proved to be sophisticated, cost-effective, and robust and enabled accurate calculations of pollutant concentrations in the plume of chlorinated hydrocarbons. Almost simultaneously, the BIOPLUME model [17,86] was developed, an early attempt to link 2D transport of dissolved hydrocarbons and biodegradation under low-oxygen conditions. This model was applied in aerobic aquifers to predict the release of organic pollutants by various processes such as convection, dispersion, mixing, and biodegradation.

In the 1980s, when computing power was still relatively modest, two parallel branches of modelling (deterministic and stochastic) were successfully formulated and implemented (Figure 2). At that time, however, modelling was primarily the preserve of engineers, scientists, and professionals who had the necessary knowledge and tools. After almost a decade, in response to the needs of practitioners, screening tools were developed to facilitate the use of these models in a user-friendly spreadsheet environment [87–89]. Another significant advance was the introduction of the modular open-source 3D groundwater flow model MODFLOW, together with MT3D and RT3D, which enabled the simulation of the transport of multiple species in water.

In the following sections, the processes controlling the migration of hydrocarbons are described in detail to improve the understanding of the underlying theory behind the algorithms incorporated into the mathematical models. While most models had to account for transport in the saturated zone, a few also can consider infiltration through the vadose zone. In addition, key processes such as dispersion, sorption, and biodegradation, which play a central role in controlling the concentrations of solutes in the subsurface, are explained in detail. Furthermore, lesser-known processes pertaining to the removal of contaminants, such as biodegradation or chemical oxidation, which are modelled by the included tools, are also discussed. Some additional processes that are not explicitly considered in the models but are important for the natural attenuation, leakage, and transport of hydrocarbons can be found in the cited literature [46,90–93].

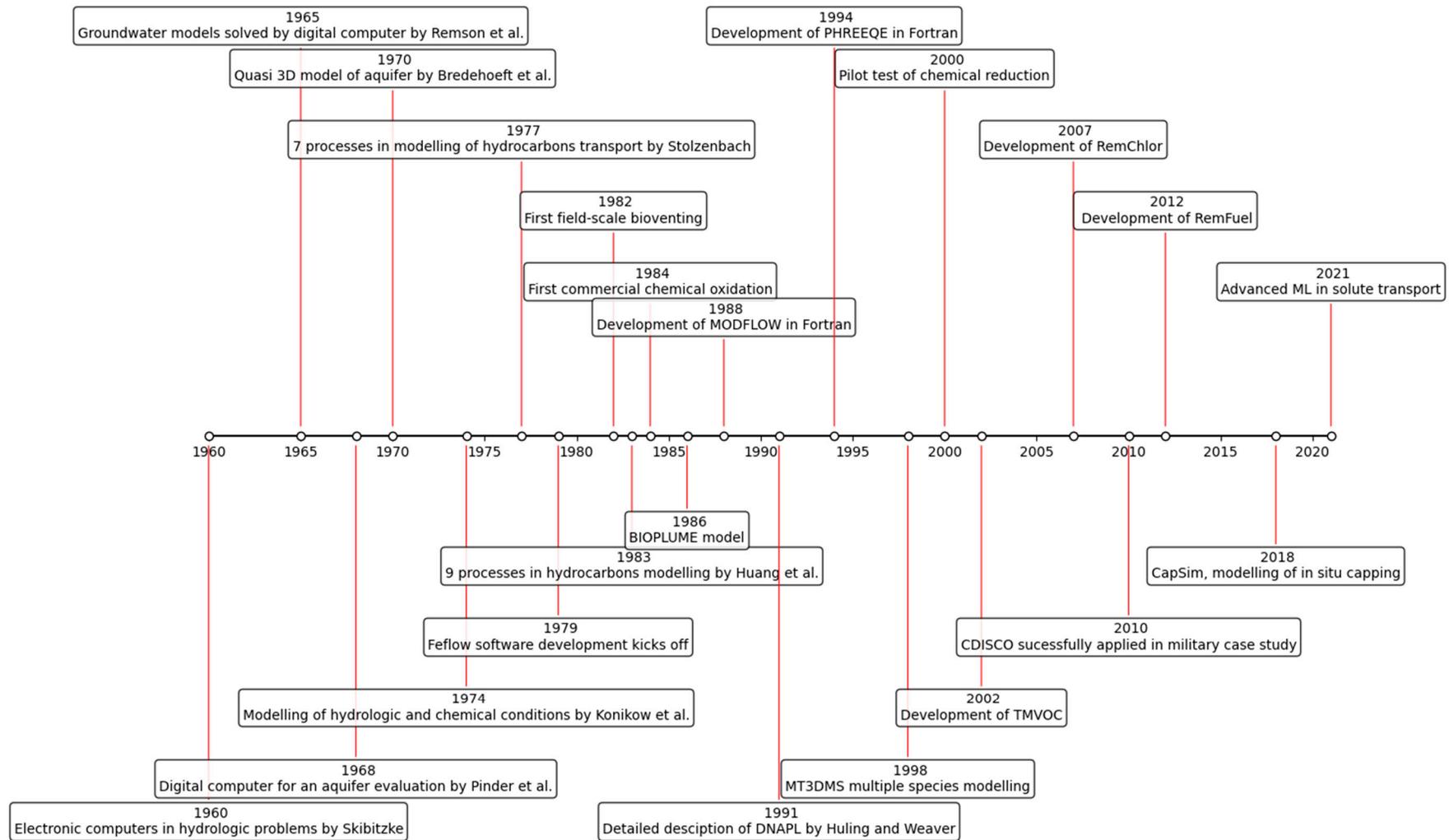


Figure 2. Timeline of key knowledge breakthroughs and models for the transport of hydrocarbon, references: [12,83,84,94–98].

2.1. Transport

Despite numerous studies and years of research into hydrocarbon migration, the process remains in the discovery phase. When hydrocarbons enter an aquifer, they move downward under gravity through a vadose zone and partition into subsequent phases [99–102]:

- mobile fluid—the mobile free product, mobile non-aqueous liquid phase (NAPL);
- residual liquid—an immobile, trapped portion of the hydrocarbons that occurs above and/or below the water table and is an additional, persistent source of contamination;
- aqueous—dissolved in groundwater and soil moisture;
- sorbed—adsorbed to soil particles;
- volatile—hydrocarbons in the gaseous state, which have evaporated (depending on Henry's constant) from the free product layer and/or dissolved phase and occur mainly in the unsaturated zone.

Once NAPLs reach the water table, they can form a visible free-product layer that floats on the surface of the groundwater—LNAPLs (Figure 3). The soluble compounds are dissolved while they are denser than water. DNAPLs migrate vertically downwards into the saturated zone.

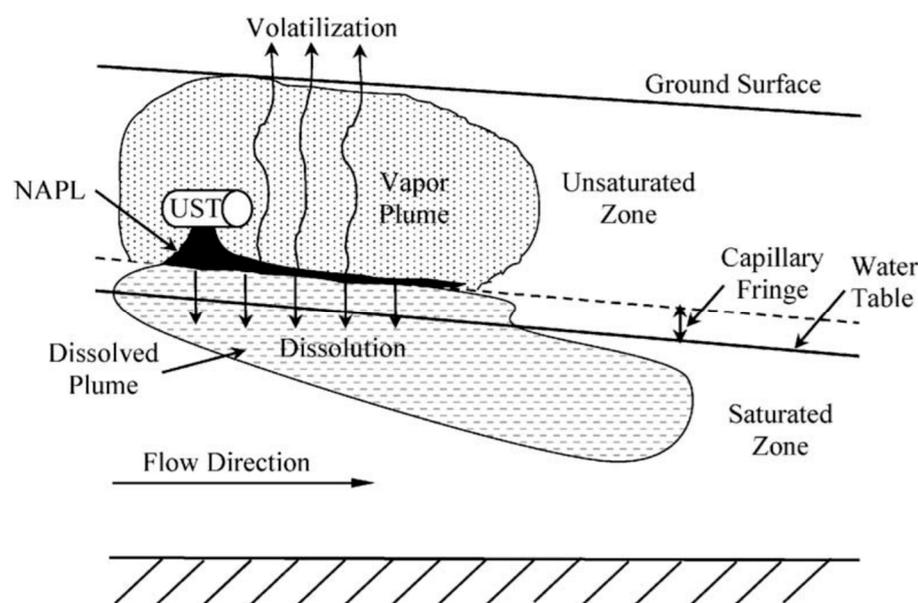


Figure 3. The concept of LNAPL migration with the decisive processes, source: [99].

Both phases, the dissolved and the free, migrate or spread laterally in the direction of the decreasing hydraulic gradient [103]. Long-term studies of the free-product plume have shown that it is not a continuous phase of hydrocarbons, its content rarely reaches 50%, and the remaining pore space is filled with water and air; this phenomenon is called partitioning [101]. In addition, recent studies have suggested replacing the image of an elongated contaminant plume with a characteristic oval smooth redox zone with the concept of a plume fringe, where the shape of the contaminated zone is sharp and pointed [104]. The mobility and transport of NAPL are controlled by several parameters, including water abstraction near the leak, groundwater fluctuations, properties of the liquid phase (density, viscosity, solubility, vapor pressure, volatility, and interfacial tension), properties of the soil in which it spreads (pore size distribution, initial moisture content), structural and geological conditions, and saturation functions (residual saturation and relative permeability) [105,106]. The fate of a contaminant plume is also determined by the nature of the medium. The transport of dissolved substances in karstified fractured environments usually occurs through favourable tectonic structures and fracture networks [107].

The forces that drive DNAPL movement are in turn dependent on the density and viscosity of the DNAPLs (Figure 4), the permeability of the aquifer, i.e., the heterogeneity, the groundwater velocity, and the DNAPL saturation and distribution [108].

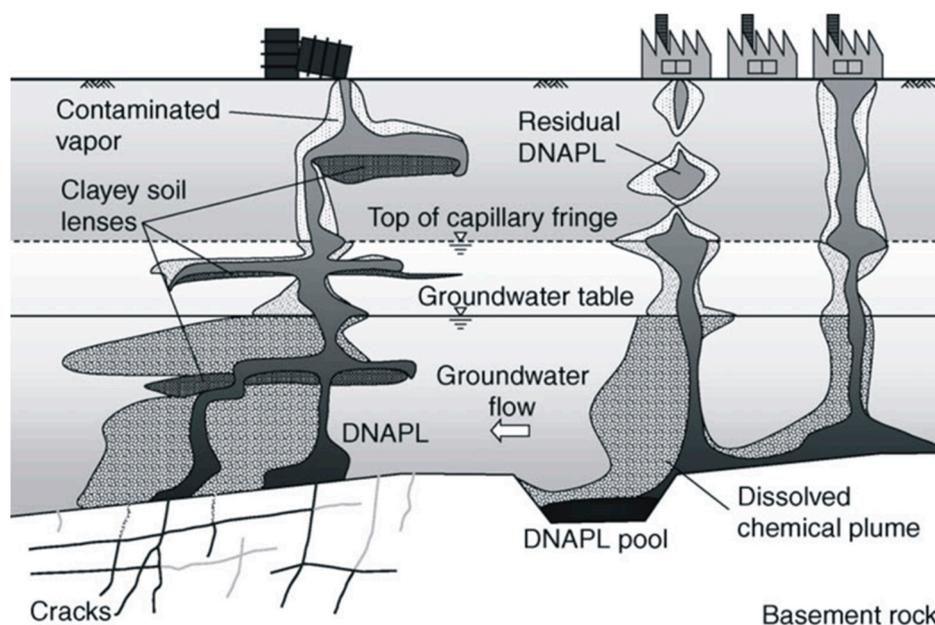


Figure 4. The concept of DNAPL migration through vadose and saturated zones according to [109].

Both low flow velocities and the likelihood of DNAPLs becoming trapped in pore spaces lead to the formation of residual bubbles and ganglia [109,110]. When the degree of DNAPL saturation in the soil is greater than the residual DNAPL saturation, the DNAPL plume is referred to as a pool [111]. The distribution of DNAPL sources among pools and ganglia leads to the use of the simple metric of the ratio of ganglia to-pool to quantify mass distribution (GTP) [112]. This parameter has been used in many environmental studies to determine the relationship between source zone geometry, dissolution rate, release time, and mass recovery [113,114]. In a homogeneous porous medium, mass transfer from a pool is expected to be proportional to the flow rate through the DNAPL and to the interface between the DNAPL and the aqueous phase. The low saturation of the DNAPL in the pool caused the groundwater to circulate through the pool, allowing the contaminants to escape at an early stage of contamination. The transfer of contaminants from a pool zone is again mainly due to the dispersive component. Since the advective flow through the pool is suppressed by the high DNAPL saturation, it is responsible for the accumulation of contaminants in the mature contamination phase [113,115,116].

Even within macroscopically homogeneous porous media, migrating hydrocarbons are presumed to follow narrow and irregular pathways. The movement along these favoured flow paths is dictated by competing driving and drag forces. When the driving force is relatively weak, hydrocarbons will migrate along paths where the hydraulic conductivity is relatively high [117]. Moreover, the transition of heavy hydrocarbons into the aqueous phase and subsequent transport with the flow is severely limited due to low solubility, high retardation, and a propensity for sorption and precipitation [118,119]. Consequently, heavy hydrocarbons are unlikely to migrate over long distances, except perhaps in karstic or fractured media.

2.2. Dissolution

When a hydrocarbon is mixed with water, it theoretically dissolves up to its solubility limit, and the excess is present as a free product. Solubility is also related to a parameter known as the soil saturation limit. This is the pollutant concentration at which the pore air and water in the soil are saturated with the chemical and the adsorption limits of the soil

particles are reached. Above this limit, the pollutant can be present in the free phase. If the hydrocarbon concentration is below the saturation limit, all pollutants present in the subsoil are distributed in three phases: dissolved, in vapor, and sorbed. The saturation limit in the soil depends on the water solubility, the dry bulk density of the soil, the soil-water partition coefficient, the porosity, and the Henry constant [120]. Understanding the dissolution processes in the source zone is crucial for a valid assessment of the mass balance for solvent transport models and for what follows after the lifetime of the pollutant source.

Ideally, equilibrium dissolution is expressed by Raoult's law of mass transfer in porous media [121], where the aqueous equilibrium concentration of a component in a mixture of NAPL is the result of phase mole fraction and solubility. In a non-ideal multicomponent mixture, which is usually the NAPL source at a heterogeneous contaminated site, Raoult's law may not be valid because the transfer to the aqueous phase depends on the abundance and intermolecular interactions between the components in the non-aqueous and aqueous phases [122,123]. These interactions are computed using a thermodynamic approach and parameterized by an activity coefficient, which factors in the non-ideal distribution [124,125].

The activity coefficient and molar fraction undergo variation as the dissolution process unfolds, influenced by changes in the composition of the remaining NAPL and the solubility of individual components within the mixture [126,127]. Approximations for the activity coefficients can be made using the universal quasi-chemical functional group activity coefficient (UNIFAC) method, which has demonstrated strong agreement with experimentally derived ternary phase diagrams [128,129].

The rate-limited, or non-equilibrium, mass transfer of NAPL becomes more realistic for multicomponent mixtures, particularly when the compounds are thermodynamically distinct. This process unfolds in three phases: initially, there are constant concentrations at or near equilibrium; then, this is followed by a rapid decline from the equilibrium concentration to levels three orders of magnitude below; and finally, tailing occurs when only about 0.5% of the original charge remains [130–132]. The non-ideal dissolution of NAPL residues and the dilution of effluent have been the subjects of numerous fundamental studies [131,133–143].

The solubility of hydrocarbons decreases with higher molecular weight, attributed to factors such as longer chain length (>C20) or an increase in aromatic rings (more than three aromatic rings) [144,145]. Generally, hydrocarbons with higher molecular weights are less prone to volatilization or dissolution. Instead, they tend to disperse into NAPL and soils, where they can be adsorbed by organic material or minerals [78,146]. This process results in the depletion of more soluble compounds and the enrichment of residues with less soluble ones, potentially leading to their precipitation as solids—a phenomenon known as solidification [147]. Additionally, the solubility of hydrocarbons is influenced by factors such as the temperature of the medium and the salinity of the groundwater [78,148,149]. The size of a plume (dissolved phase) is typically determined by the transfer of hydrocarbon-soluble compounds from the free product and/or residual phase, along with the hydrogeological properties of the aquifer [150].

2.3. Dispersion

The elimination of pollutants in soil and groundwater is the result of several processes in which dispersion plays an important role. In groundwater, two processes are associated with dispersion: molecular diffusion, and mechanical dispersion. Mechanical dispersion is defined as the spreading of a plume of contaminants as dissolved substances move through porous media. This process has long been recognised as a component of monitored natural attenuation (MNA) of contaminant plumes [151,152]. Mechanical dispersion, as defined by Domenico and Schwartz (1990) [153], is the mixing/spreading (depending on scale) of solutes caused by local displacements about the mean velocity. The differences in flow directions and velocities are naturally caused by the heterogeneity of a porous aquifer and the pore-scale bifurcation of groundwater flow lines consisting of clean and contaminated groundwater. This phenomenon occurs at all scales, from the microscopic (pore to pore) to

the megascopic (aquifer, catchment). On the small scale, three factors can influence the flow velocity: different pore sizes, tortuosity, and friction. On the large scale, the flow velocity is influenced by stratification, folds, faults, etc. Dispersion is therefore scale-dependent, but even at a given scale, the data published by Gelhar [154,155] show considerable differences with scale length (more than three orders of magnitude) (Figure 5). Dispersion reduces the concentration of the pollutant in groundwater, but not the total mass of the pollutant in the aquifer. The process in which molecular diffusion and mechanical dispersion come together is referred to as hydrodynamic dispersion [156–158].

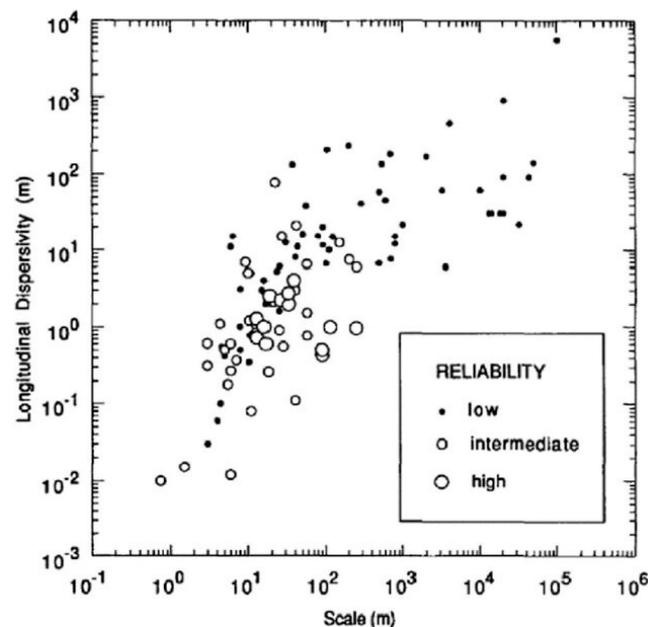


Figure 5. Relation between longitudinal dispersivity and scale after [155].

The hydrodynamic dispersion coefficient, a key parameter in solute transport, characterizes this process and is known to vary with the Peclet number. The Peclet number compares the timescales of diffusion and advection over an average pore length. Despite its significance, the hydrodynamic dispersion coefficient remains incompletely known and understood, yet it is indispensable for numerous solute transport investigations. The hydrodynamic dispersion coefficient is a parameter that is not yet fully known and understood, but is crucial for many solute transport studies. In general, there are two basic approaches to hydrodynamic dispersion: the Eulerian, and the Lagrangian [159]. The first method may not be entirely efficient, since hydrodynamic dispersion is also a parameter at the pore scale, and Euler's approach is tied to the macroscale and an advection-diffusion equation [160–162]. The curve obtained is fitted to the analytical solution of Ogata–Banks [163] to obtain the dispersion value [164–168]. The Lagrangian approach adjusts the conservation of mass as the movement of the deformable fluid volume along the streamline according to the local velocity so that only the local dispersion and reaction are responsible for the instantaneous change in concentration [169]. In this way, global conservation of mass is guaranteed, while local conservation depends on the accuracy of the velocity estimation method. The most common Lagrangian methods are Random Walk Particle Tracking (RWPT) and Smoothed Particle Hydrodynamics (SPH). The first group of algorithms captures the motion and dispersion of a large set of particles representing a plume of fluid in an advancing flow field, while the element of Brownian motion is added to reproduce the effect of local dispersion [170–172]. Smoothed particle hydrodynamics is a mesh-free method that uses interpolation to obtain smooth field variables. The fluid is represented by particles, which in turn carry all the physical properties associated with the forces (gravity, rotation, and pressure) of the system to be reproduced. By interpolation, these properties are estimated

from all neighbouring particles within the range of this function, the so-called smoothing kernel. The collective motion of all particles then describes the flow pattern [173–175].

Hydrodynamic propagation has been and continues to be the focus of numerous studies across various levels. Among the unresolved questions are anomalies such as anomalous dispersion [176–178], negative dispersion, and solute dispersion under initial conditions [179], as well as issues regarding the apparent dispersion coefficient [180,181] and the challenging problem of the non-existent hydrodynamic dispersion coefficient [182,183]. Alongside laboratory investigations and theoretical considerations, there is a growing field of practical solutions for meso- and macro-scale remediation sites, aiming for accurate prediction of the plume fate [184,185].

2.4. Sorption

Adsorption is a mass transfer process where substances accumulate at the interface of two phases, such as liquid–liquid or liquid–solid (aquifer matrix). Adsorbents play a vital role in immobilizing certain pollutants from groundwater [186]. The sorption of organic chemicals in soils is a highly intricate process influenced by both matrix properties and contaminant characteristics, which dictate interactions between the sorbed contaminant and the solid surface. Binding to the solid is contingent upon factors like reactive groups, specific surface area, electrostatic charge, hydration sphere, ionic radius, steric effects, hydrophobicity, and more [187]. Various forces attract solute molecules to the solid surface, with electrostatic binding predominating in physical or chemical sorption scenarios [188]. Despite numerous studies on pollutant adsorption across various materials, including within remediation frameworks, there remains a need for deeper understanding of these complex mechanisms, often overlooked in favour of remediation efficacy [189].

There are several interactions that are responsible for the removal of pollutants from water by sorption, such as physical absorption, surface adsorption, ion exchange, complexation, chelation, acid–base interactions, proton displacement, precipitation, pore filling, van der Waals forces, electrostatic attraction, hydrogen bonding, hydrophobic interactions (π – π interactions, Yoshida interactions), inclusion complexes, diffusion into the network of the material, and covalent bonds [190,191].

Physisorption is inherently non-specific and involves interactive forces that are relatively weak. This process has been studied with regard to the immobilisation of organic pollutants on activated carbon [192]. Adsorption of organic compounds on porous materials, i.e., pore filling, is a recognised mechanism [193–195] and the maximum sorption by this process is explicitly related to the volume of micropores of the sorbent and is expressed by the Dubinin–Polanyi equations [196]. Van der Waals forces, also known as London dispersion forces, refer to the interactions between two neutral atoms, molecules or particles separated by a distance greater than their dimensions. Despite the weakness of the bond, these forces play a crucial role in understanding the mechanism of adsorption and the transformation processes of hydrocarbon molecules [197,198]. The mechanism of electrostatic attraction involves the interactions between the adsorbed substance (e.g., an organic pollutant) and the sorbent based on their electrical charges. Sorption by electrostatic interaction depends on the pH of the solution and the point of zero charge (PZC) of the sorbent [199]. Modelling studies have shown that π – π interactions and H-bonding interactions play an important role in the sorption of PAHs (polycyclic aromatic hydrocarbons) [200–203]. π – π interactions are weak non-covalent interactions that influence the chemical structure by providing significant stabilisation and strengthening of the bonds. In general, hydrogen bonds can form A–H–B type complexes, where A is any atom that is more electronegative than H because it removes an electron from H, making the hydrogen electron-deficient, and atom B is another electronegative atom, such as oxygen, nitrogen, halogens, etc. [204]. Sorption is a recognised effective technique for the removal of organic pollutants using activated carbon [205], resins [206], nanomaterials [207–209], zeolites [210,211], goethite [212], and stable organic substances [213].

The sorption and retardation of pollutants can be estimated by laboratory experiments in which contaminated water is mixed with aquifer materials containing different amounts of adsorbents. The sorption capacity of these materials is analysed by equilibrating known quantities of a solid with solutions of the compound in question. A diagram showing the relationship between the amount of sorbed compound per unit mass of solid and the concentration in the solution phase under equilibrium conditions is called an isotherm [188]. Sorption isotherms often exhibit non-linear behaviours (Figure 6). A comprehensive classification is provided in the works of Giles et al. [214,215] and Voice and Weber [188]. Some models, such as Langmuir [216], BET (Brunauer–Emmett–Teller [217]), and Gibbs, may not be suitable for describing sorption in the water phase. Therefore, only Freundlich and linear models appear suitable for characterizing pollutant reabsorption in the aqueous environment [218,219]. Given that the sorption process can also immobilize microorganisms (forming biofilms), isotherms can also be utilized to simulate the movement and attachment of microbes to soil particles. For simplicity, microorganism sorption is assumed to be linear. Detailed findings regarding microorganism sorption in porous media are available in the works of Mills [220], Aal et al. [221], and related references. Conversely, organic pollutants may be sorbed by various biological materials in a process termed biosorption [222,223].

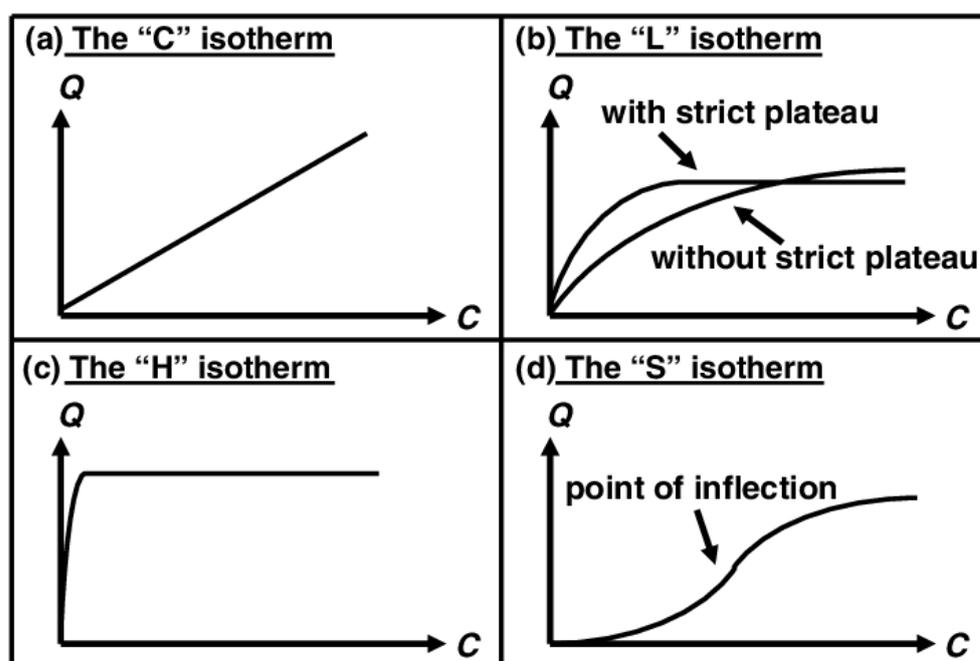


Figure 6. Four main types of isotherms after Giles et al. [214].

2.5. Volatilisation

Volatilisation is the transition from a liquid to a gaseous state and is crucial for the fate of organic compounds in the water–soil environment [224,225]. This process dominates the removal of low molecular weight aliphatics and is the most significant change in petroleum, leading to an enrichment of the high molecular weight fraction of residual hydrocarbons [79].

A comprehensive understanding of the factors governing the evaporative transport of organic compounds is crucial for estimating the quantity and composition of chemicals entering and exiting soils and water bodies. The transport of organic compounds from water to the atmosphere is influenced by several factors, including the chemical and physical properties of the pollutant (such as solubility, molecular weight, vapor pressure, Henry’s law constant, and Raoult’s law parameter), the presence of other pollutants and their physical properties, water body turbulence, and air–water interface conditions, as well as soil properties and environmental factors such as temperature [226,227]. Hydrocarbons

volatilize from residues bound to soil grains and the free phase, resulting in a depletion of lighter fractions from the remaining pool of organic chemicals, making it less mobile. Consequently, the vapor phase can travel long distances along preferred flow paths [228]. Vapor phase constituents in the soil may undergo biodegradation by microorganisms or re-volatilization into the atmosphere due to lower atmospheric concentrations, a characteristic feature of PCBs [229]. The release of volatile compounds into the atmosphere or soil gases follows a diffusion process. Two methods can be employed to calculate diffusion fluxes: the Stefan–Maxwell equations, which merge gas fluxes and express concentration gradients of each component in terms of the fluxes of other components; and the less stringent but less accurate first Fick equation, which posits that the diffusion flux density of a gas is proportionate to its concentration gradient and independent of other gases [230,231].

2.6. Biodegradation/Bioremediation

When organic pollutants enter the groundwater, they are subject to various processes that change their composition and physical properties. One of these is biodegradation, a process carried out mainly by fungi and bacteria, which is also an important process controlling the fate of organic pollutants in the subsurface [232–236].

The ability of bacteria to degrade even recalcitrant petroleum hydrocarbons has been known for many years [237–239]. The reasons why some organic pollutants are not bioavailable to organisms include their high hydrophobicity and their tendency to bind to soil particles in heterogeneous aquifers, the ageing of pollutant sources that are more solidified (amorphous forms are favoured for enhanced microbial degradation), aerobic or anaerobic conditions, pH, etc. [240,241]. The effects of biodegradation also depend on the types of microbial strains, as different microorganisms react differently to pollution, and also on the level of pollution, as this process is dose-dependent [242,243].

This adaptation could be achieved by selecting the most efficient strains [244–246], entrapment [247,248] or encapsulation [249–251], genetic modification or engineering of microorganisms by spontaneous or induced mutation, gene cloning, the removal of cell walls, or the insertion of genes from other species [252]. It should be emphasised that both dead and living bacteria can be used to remove pollutants. In the case of dead biomass, the target pollutants can be immobilised by biosorption [253] (Section 2.4).

The ultimate outcome of biodegradation/bioremediation processes is the conversion of organic pollutants into either simpler organic structures or into environmentally benign inorganic compounds such as carbon dioxide, water, and salts [254]. However, the biodegradation of certain organic substances, such as crude oil, can result in the formation of toxic carboxylic acids [255]. Bioremediation is widely regarded as a safe and relatively cost-effective method for removing pollutants from soil and groundwater. It is a versatile field technology that can be implemented either *in situ* or *ex situ*, characterized by rapid progress and a propensity for innovation [77,256,257].

Monitoring the effectiveness of bioremediation is critical to the successful treatment of contaminated sites, *i.e.*, assessing when and how target concentrations are reached. It is also crucial from an economic and management perspective, as it enables authorities to make informed decisions about the management of contaminated sites. Ongoing bioremediation monitoring includes chemical measurements of contaminant degradation in soil and/or groundwater, including at the contaminant plume, but may also include measurements of soil respiration and potential metabolites. Microbiological techniques can also be used for microbial enumeration and biomarker assessment, as it is important to monitor bacterial activity during microbially enhanced processes [258–260].

Biological degradation and bacterial activity can be simulated with analytical and numeric models [75,261]. The biokinetic models of biodegradation should include several processes, such as bacterial growth, decay, and respiration. The biokinetic parameters are usually derived from laboratory experiments, for example, from batch reactors. Since the biodegradation process is kinetic, it can be modelled as zero-order, first-order, instantaneous, Michaelis–Menten and Monod reactions. However, it is clear that the parameter

values determined at laboratory scale are not readily transferable to full-scale groundwater modelling, as bacterial growth in reactors is rapid and limited by substrate depletion, and in full-scale models, other factors such as temperature, pH, substrate quality, toxicity, electron acceptor availability, and biosorption influence microbial growth [103,262–264]. A novel approach to modelling biological processes is the use of artificial intelligence, such as neural networks. For example, replacing Monod kinetics with gene regulatory network kinetics agreed very well with experimentally observed biomass production [265,266].

2.7. Isotope Fractionation

As early as the late 1960s, Lebedev et al. [267] demonstrated that the oxidation of hydrocarbons leads to an accumulation of $\delta^{13}\text{C}$ in the remaining substrate. Stahl [268] investigated the biodegradation of crude oil and observed a similar trend, indicating significant isotope fractionation during the degradation of the aliphatic fraction. Additionally, maturation processes can influence the isotopic composition of organic compounds [269,270]. In recent years, isotope fractionation has been the focus of numerous studies aimed at monitoring and quantifying the outcomes of biodegradation processes under both aerobic and anaerobic conditions [271,272]. Findings from these studies have indicated that even in laboratory settings, different isotope fractionation factors can be obtained for the same substrates but with different enzymes, suggesting that predicting this process is challenging [273]. Furthermore, while the isotopic fractionation of aromatic hydrocarbons is relatively well understood, similar bond cleavage reactions in the degradation of volatile alkane chains present more complexities [274–276].

In general, the isotopic signature undergoes kinetic and equilibrium fractionation. While both processes can impact the isotopic fingerprint of hydrocarbons, kinetic fractionation tends to have a more pronounced effect on residues, resulting in an enrichment of substrates with heavier isotopes and products with lighter isotopes (known as kinetic isotope effect—KIE) [277]. The most significant isotope effects are associated with substitutions that influence reaction rates [278,279]. Determining KIE has become a standard measurement, with a wealth of KIE data available in the literature [280]. The disparity between theoretical and observed KIE aids in confirming or rejecting reaction pathways, including their rates, mechanisms, and intermediates [281]. However, in many cases, neither theoretical nor observed KIE is conclusive enough to support or refute hypotheses regarding reaction mechanisms. In such instances, complementary calculations with density functional theory (DFT) are necessary [280,282].

The extent of fractionation depends on geological conditions, including species, geochemical background, temperature, nutrients, and electron acceptors [272,283]. Isotope fractionation also depends on the nature of the chemical reaction, the mass of the respective isotopes, and molecular factors such as uptake of the reactant into the cell, transport of the reactant to the enzyme, or binding to the enzyme [42].

2.8. In Situ Chemical Oxidation (ISCO)

In situ chemical oxidation (ISCO) involves the injection of chemical oxidants into the subsurface to oxidise contaminants of emerging concern (COECs) such as chlorinated hydrocarbons, fuels, phenols, etc. This dynamic and aggressive process can be applied to both sorbed and dissolved hydrocarbons [284]. Several oxidants are being used or tested in practice today, such as Fenton, activated persulphate, permanganate, hydrogen peroxide, calcium peroxide, percarbonate, ozone, and peroxene. ISCO laboratory tests and field trials began in the 1990s. The results have been published in numerous articles, reports, and books, e.g., [59,285–291]. Most ISCO studies focused on the use of ozone in the vadose zone [292–295], permanganate, Fenton, and persulphate in the saturation zone [296–305]. ISCO is a flexible cost-effective method that can be applied to light and dense recalcitrant hydrocarbons such as aromatic hydrocarbons [306,307]. As with other remediation techniques, there are several challenges with ISCO, including optimal estimation of dose rate [290,308], accurate injection [309,310], ensuring safety [311,312], and

modelling, as few modelling tools are currently available [299,313,314]. ISCO was modelled using the computer code ISCO3D, which was adapted to simulate the oxidation of chlorinated hydrocarbons by permanganate [296], MITSU3D, and modified MIN3P to mimic the movement of permanganate in the 3D domain and under variable flux density [315]; DNAPL3D-RX simulated reactions between potassium permanganate and chlorinated ethenes [316], CDISCO, and CORT3D, and was developed as a decision support tool for permanganate oxidation planning [297,299,317].

2.9. In Situ Chemical Reduction (ISCR)

Similar to ISCO, In Situ Chemical Reduction (ISCR) has been developed since the 1990s. This is a technique involving the targeted liquid injection or placement of solid and chemically reducing reagents in the path of the contaminant plume or near the contaminant source. By adding ISCR reagents to the subsurface environment, a sequence of different processes can create very strong (e.g., $E_h < -550$ mV) reducing conditions that stimulate the reduction of contaminant concentrations of interest to a desired level [318]. In general, the process is equivalent to In Situ Chemical Oxidation (ISCO), although this method has only been applied to the treatment of contaminant plumes, particularly through the use of permeable reactive barriers [319–321]. Injections upstream of the contaminant source have also been developed in the last decade [322]. Today, three types of natural and abiotic reducing agents are most commonly studied and used: minerals derived from a reducing form of iron [323–325], minerals that are composed of a reducing form of iron and sulphur [326,327], and molecules derived from organic material, quinones, or self-made soybean oil emulsion [328,329].

2.10. Air Sparging

Air sparging is an innovative and successful remediation technique that uses physical stripping (volatilisation) to remove volatile organic compounds (VOCs) and promote aerobic biodegradation in groundwater and soil by pumping a gas, usually air, into an area below the water table via injection wells [330–332]. The process of volatilisation is intensified by diffusion and mixing with aerated water [333,334]. The use of air sparging has grown rapidly since its testing in the mid-1990s under the auspices of the U.S. Air Force Research Laboratory, Airbase and Environmental Technology Division, and Tyndall AFB. These entities funded a project that encompassed both laboratory and field testing to refine the concept of air sparging [335].

Since its introduction, it has been the most widely used method for hydrocarbon contaminated sites, and is still popular today. However, there are still unresolved issues that pose challenges and affect performance, such as the accurate distribution of air in the target treatment zone and the relationship between the size of the contaminant source and air distribution, as well as reducing the risk associated with working with compressed air, which can have serious consequences if not handled properly. Normally, macro-bubbles are used for air purification, but the use of micro- and nano-bubbles (MNB) opens a new chapter in improving the effectiveness of air purification and leads to higher concentrations of dissolved oxygen [336,337]. Incorporating short pulses of high air pressure also improves the overall treatment by increasing the zone of influence and air permeability [338]. A number of mathematical models can be found in the literature that simulate the transport of air and pollutants by air sparging [339–345].

2.11. Bioslurping

Bioslurping is a combination of two in situ remediation processes: bioventing, and the recovery of free-floating products using vacuum pumps. It enables the removal of contaminants from capillary zones, vadose zones, and groundwater by promoting aerobic bioremediation [346,347]. It is a good method to remove both volatile organic compounds from the vadose zone and light non-aqueous phase liquids (LNAPLs), which are insoluble in water and float on the water table [348,349]. The system is composed of one or more small

diameter boreholes, a slurp pipe, and a vacuum pump. It should only be installed where the contaminants are close to the surface, at a maximum depth of 7 m, as the vacuum pump is inefficient in sucking up LNAPLs at greater depths. Bioslurping is also not recommended for the treatment of soils with low permeability [350].

2.12. Capping/Isolation

In situ capping involves covering the contaminated soil volume with one or more layers of sand, gravel, silt, or even geomembranes [351] to chemically or physically isolate and immobilise the contaminants and eliminate the risk of their dispersion into the aquatic environment [352]. If the cover does not fulfil the remediation objectives, certain additives can be added to the cover material. These additives reduce water infiltration through the cap, increase the sorption capacity, and improve the removal of contaminants. Reactive components added between the layers include apatite [353], zeolites [354], organophilic clays [355], and activated carbon [356], which also leads to improved stability [357]. Numerical simulations of contaminant transport through confining materials have been carried out since the 1980s [358–363]. These models consider both common processes of contaminant transport, such as advection and dispersion, as well as less common processes such as bioturbation, consolidation, or ion exchange.

3. Modelling

The fundamental equations governing flow and solute transport were pivotal for the advancement of modelling tools [364]. However, accurately modelling the fate of solutes presents significant challenges, as classical equations often fail to represent reality at the field scale [365]. Factors such as variable water velocity, soil heterogeneity (including double porosity), and variations in the transport equation arising from the predominance of advection or hydrodynamic dispersion contribute to substantial uncertainty in the initial deterministic solute models.

At this stage, the modelling of solute transport, particularly reactive transport, starts to diverge from expectations and needs. One approach is to simplify the process to make it more accessible for modelers and users. 1D screening models with intuitive user interfaces have been developed based on highly simplified site conditions. These tools have aided in comprehending the fundamental processes influencing hydrocarbon transport. While they may not precisely replicate all contaminant concentrations, these models offer practitioners a rough understanding of contamination extent and timing with minimal computational effort.

In cases requiring more intricate models, modular 3D flow models with reaction modules have been employed. These models offer greater accuracy in describing the plume, and account for the variability of parameters affecting flow and reactivity across space and time. Another method that effectively captures the sub-surface's randomness distribution is stochastic modelling. Initially, this approach was reserved for modelers with a profound understanding of the mathematical intricacies of solute transport. However, it is now gaining recognition for its high predictive accuracy. Between these approaches—simple 1D screening tools, complex deterministic models, and stochastic models—there exists an opportunity for hybrid models that leverage and integrate the best attributes of each approach.

3.1. Screening Models

A screening process can be broadly defined as a decision-making step to either proceed with a comprehensive environmental assessment or to conclude with no further action [366]. During this initial screening phase, information regarding the contaminated site, sensitive environmental receptors, presence and concentrations of hazardous pollutants, and their potential migration pathways is gathered. When a detailed quantitative risk assessment (DQRA) is warranted, modelling tools are often utilized to replicate the fate of contaminants in media such as groundwater, as well as exposure parameters [367–369]. Hence, screening

models should furnish a framework for a detailed description (including quantity and size) of chemical sources in the environment and the probable migration pathways.

Screening models can take into account different processes that take place either in the vadose or in the saturated zone. However, the potential user should be aware that these tools are often based on a simplification of the local flow conditions and do not take into account, for example, the heterogeneity of the soil. Most of the simple models use the advection-dispersion equation (ADE1) and assume steady-state transport conditions [367]. Simplification of some processes and properties may be intentional and desirable, as models used in the initial environmental assessment and regulatory process should not be overly complicated [370,371]. Most screening models are analytical, so they do not require much computational power and the calculations are usually fast. The small and well-structured input data, embedded functions, and a very intuitive user interface ensure that these models are easy to use and check.

The use of mathematical modelling provides the scientific basis for regulation and policy and can support both early decisions on risk reduction and further remedial action [119,370,372,373]. The utility and validation of some screening models are reviewed by the Council for Regulatory of Environmental Modelling (CREM). In addition, the National Research Council (NRC) established the Committee on Models in the Decision Process in 2005 to address all scientific and technical issues related to the selection and use of computational and statistical models in EPA's decision-making processes.

Additional efforts to disseminate knowledge about environmental assessment models and the behaviour of chemicals in the subsurface include initiatives such as the US EPA Chemistry Dashboard. This platform offers data from numerous external databases and predictive models. Another resource is SMaRT Search (EPA Science Models and Research Tools), a searchable database of environmental modelling tools. Furthermore, the advancement and utilization of environmental fate models have been promoted in recent decades through collaborative efforts between model developers and users in working groups, as well as through the organization of workshops and knowledge-exchange platforms.

In summary, the simple screening tools are used for a number of listed reasons:

- Limited data requirements that do not compromise the accuracy of the mathematical representation. Screening models require little data per se, and the representation of even large systems is accurate in simple models, as the statistical relationships required to assess uncertainty can often be expressed more realistically at the aggregate level [374].
- Lower implementation costs. Simpler models are more cost-effective in terms of time and resources [375].
- Computational simplicity. Simplicity is favoured by some practitioners and decision makers who need an approximate time frame for remediation and the mass to be relocated. Screening models are parsimonious, i.e., these models achieve the expected level of explanation or prediction with as few parameters as possible [376].
- Transparency makes it easy to understand the relationships between the parameters because the assumptions are made from the outset and are encapsulated in a few mathematical formulae rather than buried in the complex computer codes. This rule can lead to the development of simple and effective strategies [377].
- The instructive nature of these tools. The simple and intuitive interface, the technical support, the visualisation, and the availability of manuals make them the first choice for beginners [378].
- The ease of development and modification, advances in understanding the mechanisms of mass transfer, and access to open source codes are leading these modelling tools to be created and shared with potential users [76,379].
- Screening models are excellent for minimising risk and are favoured by practitioners and stakeholders. Involving these two groups in the risk mitigation process can lead to better feedback. In addition, these models are less likely to produce catastrophic errors and can serve as an early warning system [380].

The routine use of screening tools in remediating contaminated sites may not foster innovation. Moreover, the fragmented information and limited overviews of various models highlight the urgent need for a detailed analysis of existing contaminant transport screening models. Such an analysis would aid future users in making informed choices and identifying areas for further development by model developers. The selection of a screening tool depends on various factors including availability, constraints, and input data. Figure 7 provides a simple flowchart to assist in making an optimal choice, considering factors such as in situ treatment or natural attenuation, model characteristics, and recent applications.

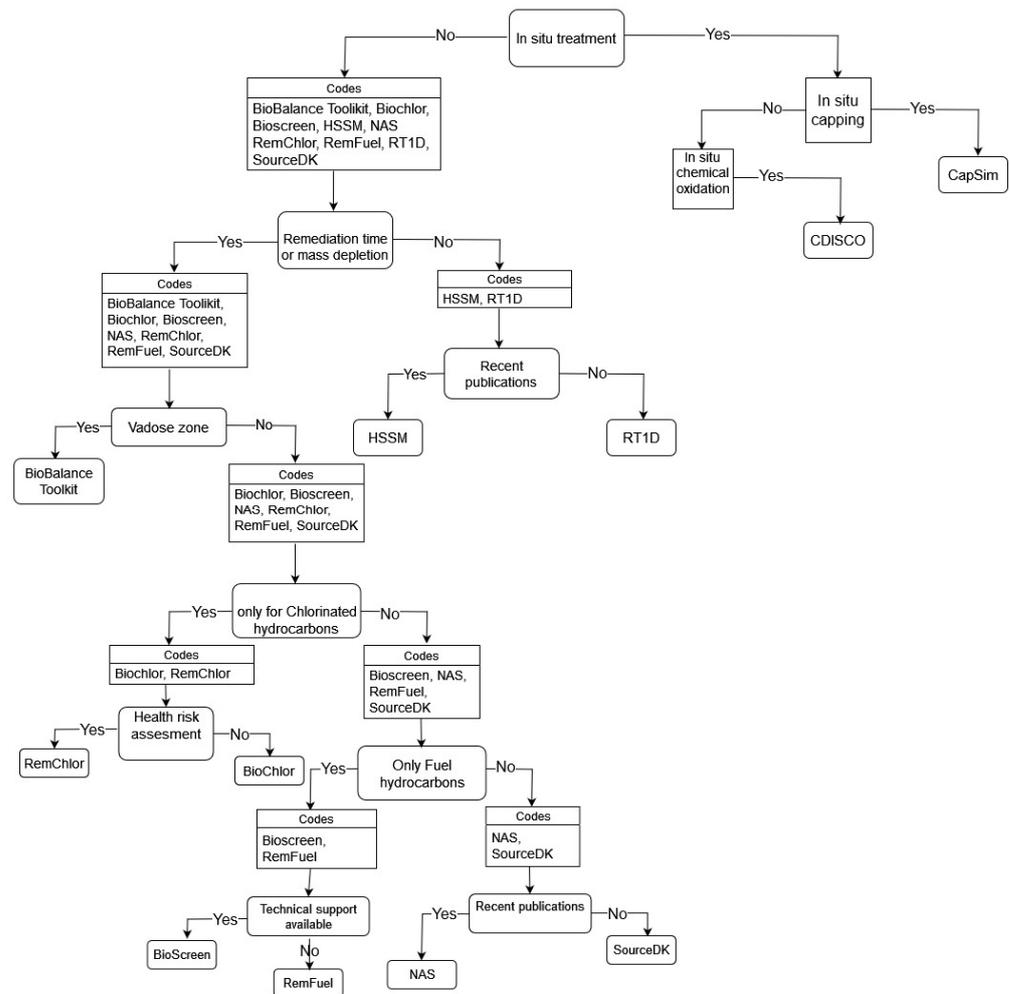


Figure 7. The simple flow chart on screening tools, their features, available support, and recent novel applications.

Below are the most commonly used screening tools for modelling the distribution and removal of hydrocarbons in variable saturated media. These solutions are briefly described to avoid copying their manuals. Their properties are listed in Table 1. The limitations, as well as input and output data for the models, can be found in the Supplementary Materials (Tables S2 and S3).

Table 1. Screening tools and modelled processes.

Model	Dimension	Flow	Transport	Biodegradation	Kinetics	Sorption	Cost
BioBalance Toolkit	1D flow	Vad, S, S-S	3D dispersion	+(AN)	F-O	+	Free
BIOCHLOR	1D flow, 2D transport	S, S-S	1D advection, 3D dispersion	+ (AN)	F-O	+	Free
BIOSCREEN	1D flow, 2D transport	S, S-S	1D advection, 3D dispersion	+ (AN, AE)	F-O, I	+	Free
CapSim	1D flow	S, S-S, T	1D transport	+	F-O	+	Free
CDISCO	1D transport	S, S-S,	1D transport,	-	F-O	+	Free
HSSM	1D flow, 1D transport in vadose zone, 2D transport in saturated zone	Vad, S, S-S, T	1D transport in Vad. zone, and 2D in saturated zone	-	-	-	Free
NAS	1D flow, combined transport	S, S-S, T	2D analytical 3D numerical	+ (AN, AE)	F-O	+	Free
REMChlor	1D flow, 2D transport	S, S-S	1D advection, 3D dispersion	+ (AN, AE)	F-O	+	Free
REMFuel	1D flow, 2D transport	S, S-S	1D advection, 3D dispersion	+ (AN, AE)	Zero-O; F-O, M	+	Free
RT1D	1D flow, 1D transport	S, S-S	1D transport	+ (AN, AE)	F-O, M, or other user-defined	+	Free
SourceDK	1D	S, S-S	1D advection and dispersion	+	F-O	+	Free

Vad—vadose zone, S—saturated zone, S-S—steady state condition, T—transient condition, AN—anaerobic biodegradation, AE—Aerobic biodegradation, F-O—first order, I—instantaneous, M—Monod, M—Michelis–Menten.

3.1.1. BioBalance Tool Kit

The Biobalance Toolkit is designed as a user-friendly Excel spreadsheet, incorporating a series of analytical solutions and routines implemented through Visual Basic code. It facilitates the calculation of electron donor and acceptor mass balances in chlorinated solvent plumes emanating from the source [381]. For more detailed information on this model, refer to the article by Kamath et al. [382].

3.1.2. BIOCHLOR

This tool operates within the environment of a Microsoft Excel spreadsheet. It utilizes calculations derived from Domenico's analytical solvent transport model (equation) to simulate various processes including 1D advection, 3D dispersion, linear adsorption, and biotransformation through reductive de-chlorination, the primary biotransformation process observed at most chlorinated solvent sites [88,383].

BIOCHLOR can be successfully and reliably applied to sites for which general assumptions apply (e.g., steady groundwater flow, a vertical, planar source, and first-order decay). Examples of its application can be found in the work of Clement et al. [384] and Kuchovsky and Sracek [385]. The recently developed BIOCHLOR-ISO is an add-in to BIOCHLOR. This tool is based on an analytical solution, and is able to reproduce both the natural attenuation processes and the isotope fractionation that occurs in biological radiation [76]. BIOCHLOR-ISO is a dual isotope approach, which means that carbon and chlorine isotopes are included in the calculations [386].

3.1.3. BIOSCREEN

Similar to the tool mentioned above, BIOSCREEN is designed as a user-friendly Microsoft Excel spreadsheet. Based on Domenico's analytical model (equation), it can simulate aerobic and anaerobic reactions and processes along the flow path. This tool can simulate natural attenuation processes with three options: transport without decay, first-order decay, and solute transport with immediate biodegradation and multiple soluble electron acceptors [86]. Examples of its use can be found in the work of Khan and Husain [387] and Akins et al. [388]. An improved version of BIOSCREEN-AT, based on the exact analytical solution for reactive transport from a point source in three dimensions, is also available as an MS EXCEL-based spreadsheet [389]. This well-known and user-friendly latest version of BIOSCREEN has been extended to allow the analysis of two isotopes (e.g., ^{13}C and ^2H) in each compound. The dual isotope approach is sensitive to reaction mechanisms, and allows for the prediction of isotope ratios in groundwater as a function of time and space. This provides the user of BIOSCREEN-AT-ISO with information on the degradation and/or sorption of contaminants in the aquifer [379].

3.1.4. CapSim

CapSim was developed entirely in the Python programming language [390], utilizing additional libraries such as NumPy, SciPy, and Matplotlib for visualization purposes. It is a multi-layered 1D model designed to simulate processes occurring in heterogeneous soil materials during in situ capping. CapSim provides users with the flexibility to modify soil properties and layer thickness. Moreover, it encompasses common processes in porous environments including advection, diffusion, dispersion, sorption, and reaction. Additionally, CapSim enables more intricate simulations such as bioturbation, deposition, or water exchange [360].

3.1.5. CDISCO

CDISCO is a spreadsheet-based model that can be very helpful in the development of efficient and cost-effective in situ chemical oxidation (ISCO) remediation using permanganate [299,317]. In addition, one of the functions of CDISCO is an economic analysis that can help in estimating the preliminary cost of injection performance. This tool was extensively tested in the Massachusetts Military Reserve case study [391].

3.1.6. HSSM

The HSSM model was specifically crafted to simulate the transport of LNAPL through homogeneous mediums [392]. It is important to interpret the simulation results with a degree of caution, considering the model relies on numerous site-specific assumptions. The model encompasses the 1D vertical flow of LNAPL in the vadose zone, its movement to the water table, dispersion at the water surface, and the 2D vertically averaged flow of LNAPL through the aquifer towards various uptake points, such as in the groundwater. Although the model is available for download, it is no longer updated or supported. Despite its lack of ongoing technical support and aging, this model continues to be utilized and even customized to meet specific user needs. For instance, a modified version of HSSM has been adapted to accommodate the rectangular shape of a leak and simulate the infiltration and redistribution of NAPL from leaking tankers [393]. Present applications of this model include its integration with other models like MT3DMS [394], predicting pollutant concentration in surface waters [395], and tracking pollutants like benzene leaking from pipelines [396].

3.1.7. NAS

The Natural Attenuation Software (NAS) serves as a screening tool developed to assess the effectiveness of various remediation methods, complemented by supervised natural attenuation [397]. NAS enables the estimation of remediation timeframes for monitored natural attenuation (MNA) [398], during which pollutant levels decrease to

acceptable levels, processes addressed by NAS encompass sorption, NAPL dissolution, and biodegradation. The efficacy of NAS has been validated through successful testing at multiple sites, including NAES Lakehurst, NJ, USA (natural source degradation), Seneca Army Depot, NY, USA (source dredging), and NSB Kings Bay, GA, USA (chemical oxidation of the source zone) [399–402].

3.1.8. REMChlor

REMChlor is designed to simulate the transient effects of remediating contamination sources and plumes [403,404]. This model utilizes a power function relationship between source mass and source depletion, providing users with the flexibility to simulate partial source remediation. Users can choose to simulate three processes: complete or partial plume remediation, natural attenuation, and source decay. Applications of REMChlor can be found in studies by Tyre [405] and Henderson et al. [406]. Although this tool remains available to users, it is no longer updated or supported. A more recent development is the incorporation of diffusion through the matrix into this analytical tool, resulting in the REMChlor-MD model, which was employed for the attenuation of perfluoro-octane sulfonate. The model effectively replicated field data for concentration, mass release, and total mass. Furthermore, when used to analyse long-term transient effects over 40 years of groundwater transport, the REMChlor-MD model demonstrated that the majority of the measured contaminant mass leaving the source areas accumulates in downgradient zones with low permeability [407].

3.1.9. REMFuel

REMFuel is an analytical solution designed to simulate the remediation of hydrocarbon sources and plumes under dynamic transient conditions. Similar to REMChlor, REMFuel allows users to estimate the timeframe for remediation, specifically the time required to reach a target concentration at a site, while considering various methods of source removal. The release of pollutants is calculated based on a power function for multiple fuel constituents. These pollutants can be removed at any time post-release through natural attenuation and/or enhanced degradation. The model accommodates concentrations within the plume with up to three degradation zones and three degradation times, each with different degradation rates [408]. While this tool remains accessible to users, it is no longer updated or supported.

3.1.10. RT1D

RT1D is a comprehensive solution developed in Visual Basic, designed to operate directly within an Excel spreadsheet. It excels in simulating biochemical and geochemical reactive transport scenarios, making it particularly well suited for laboratory experiments [409]. Notably, RT1D stands out for its capability to tackle advanced biogeochemical challenges, including rate-limited sorption, bioaugmentation, microbial transport, denitrification, and sequential batch reactor dynamics. This model's sophistication and versatility set it apart from other screening tools.

3.1.11. SourceDK

The Microsoft Excel-based software SourceDK [410] offers three distinct methods for estimating pollutant mass within the source zone: the simple volume concentration calculation, detailed volume concentration calculation, and NAPL relation method. The simple volume concentration method relies on the average soil concentration within the saturated source zone. However, this approach may underestimate the total contamination mass, since it does not consider the mass of residual NAPL and dissolved phase. The accuracy of the soil concentration estimation technique directly impacts the final results. Conversely, the detailed volumetric concentration calculation utilizes actual average groundwater and soil concentration data in each phase (residual NAPL, dissolved mass based on the extent of the source zone, and adsorbed mass in the downgradient). The estimation method based

on NAPL relationships incorporates the residual NAPL mass, which is generally acceptable as it represents the majority of the contaminant mass in the source zone.

3.2. Stochastic Models

Stochastic hydrogeology operates on the concept of probability, which is inherently subjective and reflects the level of understanding or confidence in the actual state of affairs within a system that exhibits randomness [411–414]. Hence, stochastic hydrogeological models must address the probable distribution of input parameters and their associated uncertainties: theoretical uncertainties arising from limited knowledge about the processes impacting model outcomes; measurement uncertainties stemming from instrument accuracy; and uncertainties attributed to spatial and temporal non-uniformity or missing data [415,416].

The use of stochastic processes to visualise hydrological and subsurface processes is not a new concept. The first publications and reports on this topic appeared in the late 1960s and early 1970s [417–424]. In the early days of stochastic subsurface research, many efforts were made to realise mathematical equations for effective parameters such as effective conductivity and macrodispersivity in an elegant way, under the premise that these parameters could be used in large-scale flow and transport models.

Matheron [419], for instance, is renowned for developing the theory of regionalized variables, which elucidates the statistical relationships among sample points by considering not only their values, but also their spatial arrangement. Consequently, observed values are outcomes governed by specific probability density functions. The framework of linear geostatistics has served as a foundational framework for many geostatisticians and modelers [425,426]. Beran [420] and Todorovic [422] accurately forecasted and delineated the mathematical modelling of solute transport at the molecular level. Chow and Prasad [423] asserted that natural hydrological systems, such as watersheds, and hydrological processes inherently exhibit stochastic behaviour, implying that their dynamics vary over time in accordance with probabilistic occurrences. The modelling of stochastic processes at the watershed scale has been the focus of numerous investigations [427–429].

In recent decades, stochastic studies have addressed various topics due to environmental concerns and interest in subsurface contamination: the modelling of structures, unsaturated soil properties, the spatial propagation of fall heights and velocities, and the transport of reactive solutes [430]. It should be emphasized that, thanks to stochastic subsurface hydrology, many processes have been better understood, the most important mechanisms have been identified, and a new paradigm—heterogeneity—has been introduced in subsurface transport studies.

The theoretical progress and a deepening of the understanding of subsurface processes as stochastic has been greatly aided by the dynamic development of computers and programming, access to high-resolution data, and the performance of large-scale experiments [154,411,431–433].

Despite their extensive development history, a discrepancy persists between stochastic approaches to subsurface hydrology and practical application [434]. Stochastic models appear to be less favoured compared to the more prevalent deterministic models, possibly due to their inherently complex mathematical nature or, as some researchers suggest, an aura of esotericism and abstraction [415]. The reluctance to embrace stochastic methods more widely in routine site assessments may also stem from the increased economic burden associated with stochastic analyses and a shortage of professionals equipped with the requisite training and qualifications [435]. For instance, until 2016, university courses addressing stochastic methods in hydrogeology were notably absent [414].

Some problems related to the economic feasibility of stochastic methods have been solved by incorporating new innovative field techniques that allow for the tracking of changes in soil conductivity and the collection of large data sets. Meanwhile, the development of open-source stochastic tools, the addition of stochastic modules to common modelling tools, information platforms, webinars, and general advances in computer lan-

guages and machine learning have facilitated the training and education of experts in stochastic modelling methods.

The shortcomings that may hinder the broader application of stochastic models in reactive transport were extensively outlined in the work of Cirpka and Valocchi [436]. Among these, inadequate consideration of the processes and properties governing system behaviour stands out as a significant challenge. For instance, stochastic modelling of the plume tends to underestimate the mass in the tail by focusing solely on the arrival of contaminant peaks. This approach may seem unrealistic to many remediation practitioners and experts who are aware that pollutants are released over extended periods, resulting in the formation of elongated plumes. Moreover, models focusing on local pollution should also account for mixing and its dependence on small-scale heterogeneity [437]. However, incorporating this process into stochastic models poses a notable mathematical challenge. Additionally, stochastic tools, much like screening models, rely on simplified flow conditions, such as a uniform and steady mean flow and permeability characterized by a multi-Gaussian distribution with low variance. Consequently, this approach appears to fall short in accurately describing the intricate hydrogeological formations and modelling the long-term fate of pollutants.

But from another perspective, the advantages of stochastic approaches are the following:

- Dealing with large and small data sets. For large data sets, the law of large numbers and the central limit theorem state that a large number of samples converge to the expected value/mean and that this sample mean tends to the standard normal distribution. This justifies the use of the Gaussian normal distribution and the mean value in the stochastic models. Depending on the specific modelling approach, the type of data, and the research question, stochastic models can be applied to small data sets when the researcher is faced with the greatest uncertainty [438–441].
- Dealing with multiple uncertainties at different levels requires a complex approach and the involvement of experts from the fields of statistics, computer science, and domain-specific knowledge. This is an emerging and challenging field of research [415,442,443].
- The probabilistic approach offers a range of equally probable solutions instead of a single (approximate) solution, and can provide better information for risk managers and policy makers [428,444–446].
- Dealing with the plume is possible, but can be more difficult to calculate using travel time and breakthrough curves in a given plane at a given distance from the source. However, with increasing distance, the travel time moments become less sensitive to the variability of the parameters responsible for transport, and can be expressed by simple statistical moments such as mean, variance, and correlation function [447–449].
- Rapid progress is being made through the general development of computational methods, and this is likely to become increasingly important, supported by the recognition of population inference from big data and data validation [450,451].
- Simplifications are justified in stochastic models, as local heterogeneities have only limited long-range effects. Furthermore, simplifications can make the simulations more manageable and still capture the essential behaviour of the system [452–454].
- Conceptualisation: Since many stochastic models have a solid mathematical basis, it is common to start modelling on the basis of detailed mathematical and theoretical knowledge and then transfer the results of the conceptual work into one or more mathematical models. For deterministic models with GUI, it is easier to forget the initial modelling phase [455].

3.2.1. ART3D

ART3D v. 2.0 is an independent FORTRAN code that operates using straightforward text files and has the capability to address numerous coupled reactive transport equations. This versatile software offers three distinct modes of operation: forward mode, enabling the prediction of concentrations within a plume; backward mode, facilitating the estimation of parameter data from monitoring wells; and stochastic mode, allowing for the evaluation

of the probability of exceedances at specified locations within the plume [456,457]. The code incorporates modules designed for automatic parameter estimation and stochastic analysis, employing Monte Carlo methods. Additionally, the output file generated by ART3D can be converted into a 3D image for visualization using compatible software tools. The ART3D code encompasses a comprehensive set of equations, including those representing one-dimensional advection, three-dimensional dispersion, linear sorption, first-order biodegradation, and multiple chemical reactions [458]. Optimization within ART3D is facilitated through the utilization of the PORT library, originally developed by David M. Gay at Bell Laboratories [459]. The parameters subjected to optimization include the retardation factor, percolation rate, dispersion coefficients, decay constants, and concentrations in the source zone. In the Monte Carlo analysis, these parameters can be randomized, with options to specify either a uniform distribution or a normal distribution for each randomized parameter. The ART3D tool underwent testing at a Superfund site in Louisiana, where it was also compared to the results obtained from modelling with BIOCHLOR. This comparison allowed for a meaningful assessment of deterministic and probabilistic approaches [460]. During the testing phase, ART3D was executed over a simulation period spanning several hundred years, with a time step of 25 years. Both simulations with and without the natural attenuation option were conducted. The model provided insights into the declining concentrations of tetrachloroethene (PCE), trichloroethylene (TCE), dichloroethane (DCE), and vinyl chloride (VC). Notably, vinyl chloride emerged as the most problematic substance in the analysed area, presenting a contamination risk to the soil for the next 300 years. ART3D is integrated into the GMS software package and can be downloaded along with the source code as a standalone model.

3.2.2. Factorial-Design-Based Stochastic Approach

The Factorial Design-Based Stochastic Modeling System (FSMS) integrates a mass transfer model, factorial analysis, and Monte Carlo simulations to address single and multiple uncertainties within the mass transfer model. This system employs a factorial approach, which can be viewed as a specialized form of sensitivity analysis, allowing for the simultaneous assessment of multiple parameters' effects on the outcome [461]. In a study by Qin et al. [462], this approach was applied to a laboratory experiment involving a tank reactor filled with heterogeneous materials (clay, sand, and arable soil) contaminated with benzene. Four parameters were identified as uncertain: the mean and variance of permeability and porosity. Subsequently, the Monte Carlo method was employed to simulate the stochastic processes associated with groundwater flow and benzene transport within the heterogeneous medium. A physical model was created on a pilot scale to validate the stochastic method. It was found that the uncertainty of the input parameters, especially the mean porosity, has an influence on the outcome of the model. The results showed that simple statistics such as mean, standard deviation, and percentiles should be considered when analysing the risk of oil spills. Furthermore, factorial design and Monte Carlo simulations are integral parts of the hybrid stochastic design for modelling NAPL contaminated aquifers [463]. This approach is based on the deterministic numerical 3D model BioF&T, and uses stochastic methods for parameterisation.

3.2.3. Fuzzy Stochastic Approach

A fuzzy stochastic approach offers a method to evaluate the risks associated with BTEX contamination of groundwater under various uncertainties. Li et al. [464] utilized a stochastic fuzzy approach, employing a modified fuzzy vertex method alongside a Monte Carlo simulation to forecast petroleum contamination in the subsurface. Their study, conducted using a 3D model of a petroleum-contaminated aquifer, underscored the significance of integrating uncertainties in critical hydrogeological parameters like permeability and porosity into the calculations to accurately depict the contamination extent. Maqsood [465] introduced this approach to quantify the relationships among uncertain hydrogeological parameters. Similarly, Zhang and Huang [466] adapted an integrated

3D multiphase and multicomponent model, UTCHEM, in conjunction with an interval fuzzy modelling system for the subsurface (IIFMS) to project benzene concentrations over a 20-year simulation period, incorporating uncertainties in variables such as porosity, longitudinal dispersivity, and permeability.

3.2.4. HPS-PROBAN

The HPS-PROBAN approach combines the semi-analytical transport model (Horizontal Source Model) with a probability analysis program—PROBAN. The HPS model was proposed by Galya [467]. It is a semi-analytical 3D model that solves the transport equations of advection and dispersion, and can simulate first-order decay and sorption. The numerical output of the model proposed by Galya is the concentration distribution at each point down gradient from the contamination source. PROBAN [468] is a software package developed to perform the complex probability analyses. The link between PROBAN and HPS is established via user-defined FORTRAN 77 subroutines. This approach was validated using data from the Environmental Protection Agency (EPA) [469] and findings from a review in the work of Newell et al. [470]. In this case study, the probability of not reaching target concentrations of o-xylene downstream of the spill was estimated. The random variables included the aquifer, the source, and the chemical parameters. The results, particularly the probability of not reaching the target contaminant concentration, were largely related to the velocity, length of the source, and the kinetic rate of biodegradation. The final results were compared with Monte Carlo simulations, and showed good agreement with relatively low computational effort.

3.2.5. Null Space Monte Carlo

In the realm of numerical groundwater modelling, outcomes are inherently approximate due to the inherent uncertainties. However, techniques exist to complement deterministic groundwater models by identifying and assessing these uncertainties. One such method is the Null Space Monte Carlo method (NSMC), which leverages the Monte Carlo approach and calibration-constrained parameters to compute parameter fields for model validation [471]. NSMC implementation can be facilitated through the PEST code [472], which is integrated into the GMS software. Consequently, users typically start by acquiring the deterministic groundwater model (e.g., MODFLOW) alongside flow-path delineation (particle tracking method). Subsequently, they employ PEST for parameter calibration and uncertainty evaluation. The method has been effectively used to identify areas potentially contaminated by chlorinated hydrocarbons, and to determine the most likely sources of contamination in the vicinity of water stations in Milan [473].

3.2.6. LaSAR-PHREEQC Approach

LaSAR (Lagrangian Stochastic Advection Reaction) is an analytical stochastic approach for modelling coupled transport and reaction processes in heterogeneous flow media [474,475]. According to the LaSAR approach, transport takes place between the injection layer, in which the solute (pollutant) enters the system, and the control layer. Several assumptions must be made along the flow path. The solute is injected uniformly, transport between the two layers occurs along single and independent flow paths (streamlines) that do not cross each other, water flow is assumed to be steady and unidirectional, advection is the dominant transport mechanism, and diffusion and dispersion in the pore space are generally neglected [431]. The heterogeneity of the soil means that moving particles have different probabilities of reaching the control plane. The variability of the flow is therefore reflected in the differences in travelling time along the individual streamlines, while the statistics of the residence time can be represented by a PDF (probability density function), which can follow one of the usual statistical distributions (e.g., lognormal or bimodal). Geochemical and biochemical processes take place along the streamlines, e.g., the dissolution or precipitation of minerals, the sorption or biodegradation of organic pollutants, or even radioactive decay. These reactions are simulated using the PHREEQC code [476] and the

one-dimensional transport option. This approach has been tested in environmental studies, including the modelling of acid mine drainage [477] and the transport and biodegradation of hydrocarbons [478].

3.2.7. PREMChlor

PREMChlor is a probabilistic model that accounts for uncertainties in all key parameters required to simulate the remediation of chlorinated solvents. This tool can support the optimal remediation strategy based on the results of source and plume treatment scenarios. PREMChlor is the result of coupling the analytical model REMChlor with the Monte Carlo modelling package GoldSim. All input parameters are considered stochastic and are represented by probability density functions (PDFs). With PREMChlor, source remediation is simulated as partial removal of a mass by dissolution, advection, and decay, while plume remediation is modelled by time- and distance-dependent decay using the first-order sequential decay chain [404]. The results of the model include concentrations, mass release, cancer risk, and remediation costs. Although PREMChlor is a relatively new tool, it has been successfully tested, with the results published in the papers of Liang et al. [479,480]. The PREMChlor model was evaluated for its ability to predict the impact of remediation on the TCE plume, taking into account uncertainties in seven key reactive transport parameters: initial source mass and concentration, correlation between source mass removal and concentration, source remediation effectiveness, groundwater velocity, background plume degradation rate, and plume treatment effectiveness.

It requires the installation of the GoldSim player, which can also be downloaded free of charge.

3.3. Machine Learning Paradigm

The machine learning paradigm is not inherently stochastic, but in many application areas, it relies on stochastic methods that deal with well-known and classical statistical problems, such as regression, classification, decision, clustering, etc. The difference is not in the problem itself, but in the approach, i.e., analysing huge amounts of sometimes complex and unstructured data and using a large number of algorithms and computational resources [481–483].

Recently, the ease of data acquisition and storage forces scientists to face the paradox of data abundance or the curse of dimensionality, i.e., the difficulty of finding a structure when there are too many variables [484,485]. Machine learning (ML) seems to be the perfect method for all ecological data mining problems, as it is able to find hidden patterns, relationships, and correlations in large amounts of data [486–489]. Machine learning also focuses on the development of algorithms and models that can learn from data and perform predictive analyses [490–493]. The primary limitations or failure to meet expectations in machine learning methods may result from poor data quality, e.g., missing values, mislabelling, duplicates, and interpretability of results. The researcher must have basic knowledge to explain the high or low accuracy of the model. The greatest challenge in model-based interpretability arises when models characterised by high predictive accuracy are so simple that they can be easily understood by modelers or reviewers [494,495].

Machine learning (ML) consists of two primary phases: the induction of the model, which involves processing vast amounts of data in various forms (structured, unstructured, semi-structured, metadata, or time series data), and the efficient representation of the model and inference. Stochasticity can manifest in the first phase during data generation, augmentation, or resampling [496,497]. The behaviour and performance of numerous machine learning algorithms are characterized as stochastic, as many optimization algorithms operate in stochastic domains, while others rely on randomness or probabilistic decisions.

Two processes should be considered in the context of stochastic methods and machine learning: optimization, and generalization. Many optimization algorithms must operate in stochastic domains, while others rely on randomness or probabilistic decisions. Although optimization has a complex computational background, its function is simple and practical:

to enhance functionality, and address real-world problems. Furthermore, optimization and machine learning can be examined from two perspectives: first, the contribution of optimization to enhancing the performance of machine learning [498–501]; and second, the optimization of processes facilitated by the outcomes of machine learning algorithms [502,503]. Another crucial aspect of machine learning is generalization: during generalization, we assume that the algorithm has identified the pattern and captured the regularity.

A common algorithm employed in optimization is stochastic gradient descent (SGD), where the gradient of a loss function is computed repeatedly and randomly for a single training sample or for mini-batches of samples, and the model parameters are updated accordingly [501,504]. Some other machine learning models, such as Gaussian Naive Bayes, Gaussian Mixture Models, and Bayesian Networks, are probabilistic and utilize stochastic principles to represent data and make predictions. Gaussian Naive Bayes, for instance, is among the best-performing probabilistic classifiers based on Bayes' theorem, and tends to perform very well even under unrealistic assumptions, particularly on small training datasets [505]. In summary, stochastic machine learning models find applications in pattern recognition, data mining, image analysis, and risk analysis [506–508].

Environmental studies, particularly those addressing the fate of pollutants, often rely on time-series data to make predictions based on observed trends. It is widely acknowledged among machine learning practitioners that accurate predictions derived from time-series data are immensely valuable. The reliability of these predictions hinges on factors such as the quality and size of the time series dataset, as well as the time horizon for which the prediction is needed; typically, short-term predictions entail lower uncertainties [509]. Deep learning techniques and time series analysis methods encompass Convolutional Neural Networks (CNN), Recurrent Neural Networks (RNN), and Long Short-Term Memory (LSTM) models [510–512].

In recent years, machine learning has also been adapted for water science studies, with many publications focusing on the applicability of algorithms for modelling water quality in different environments [513–520] and water treatment [521–526]. Machine learning methods have also been successfully applied in the identification, tracking, and removal of pollutants [527–533]. In the context of the numerous studies on water quality, machine learning can predict the amount and fate of pollutants, taking into account complex processes and interactions between different control parameters. Particular attention is paid to organic pollutants and the assessment of contaminated sites, including through the application of image recognition technology [533–539].

Sprocati and Rolle [534] focused on the electrokinetically assisted bioremediation (EK-Bio) of organic pollutants (chlorinated ethenes) in porous media with low permeability. They simulated the complex processes in a simplified horizontal 2D domain between a cathode-anode doublet. Reactive transport was simulated using the code NP-Phreeqc-EK [540], which combines the flow and transport software COMSOL Multiphysics with the geochemical code PHREEQCRM, which performs seven kinetically controlled reactions and six equilibrium reaction calculations. The surrogate model approach, a neural network utilising a stacked MLP (multilayer perceptron), was then adapted to investigate the response of the system for different input combinations.

Xia et al. [538] used Long Short-Term Memory (LSTM) and Extreme Gradient Boosting (XGBoost) to predict DCE degradation at the contaminated site. The variables from 3 months of data were used for training and prediction of DCE concentrations. This means that the input variables for the models were the data from one sampling process, and the prediction was made for the next sampling process. The performance of the model was evaluated using three common assessment measures: mean absolute error (MAE), mean absolute percentage error (MAPE), and root mean square error (RMSE). XGBoost was more accurate at high DCE concentrations, and reproduced DCE variations better.

Chen et al. [539] combined numerical models such as WOFOST, HYDRUS, and MODFLOW with a machine learning model. In this application example, the saturated zone flow model MODFLOW is replaced by a neural network with radial basis function, which re-

duces the computational cost, but does not reduce the accuracy. The paradigm is validated using an eco-hydrological model that couples WOFOST and an unsaturated flow model HYDRUS. This solution requires real data (meteorological, soil, and crop data), and the observed data can also be used as a training set for an RBF neural network. This paradigm could later be further developed by replacing two physically based numerical methods, i.e., WOFOST and HYDRUS, with machine learning models.

3.4. Deterministic Models

Deterministic approaches to the flow and transport of solutes assume that the parameters responsible for the movement of water and solutes are known and identifiable. If the parameters are known, their spatial distribution can be outlined and their heterogeneity can be captured. This is a classical extrapolation method that assumes that the heterogeneity can be deterministically captured by interpreting all field data. The main work that precedes deterministic modelling is therefore the identification of the parameters and the collection of all information about them from available sources and from experts in the field.

The collaboration of many experts from different disciplines and the approach that everything can be defined give the nice aspects of multidisciplinary and certainty. And it is only natural that people demand certainty. For example, probability predictions of rainfall were received with scepticism because people wanted to know if it was going to rain, not how likely it was to rain [541]. This could be one explanation for the widespread use of deterministic approaches.

Our society and science in general rely on deterministic technical systems. For example, the emails we receive are the emails that were sent, the files on our computers are the files we put there, and we can be sure it is nothing else. This is because we expect correct behaviour for a certain input pattern [542,543]. This certainty can be a blessing in a highly mechanised world where we rely on accurate responses. Surprisingly, determinism even exists in quantum physics [544] and in AI algorithms [545,546].

The deterministic paradigm of ordinary differential equations (ODEs) is undoubtedly highly valuable, as it adheres to the law of mass action and serves as a mathematical foundation for solute transport models. Employing a deterministic solution offers numerous benefits, foremost among them predictability and repeatability [543]. Advocates of deterministic models cite their user-friendly nature, richness, and the availability of graphical user interfaces, technical support, and detailed manuals as key advantages. Moreover, deterministic models are generally easier to comprehend and interpret, they boast efficiency, and have a proven track record in numerous environmental studies. Notably, the relationship between input and output parameters does not require governing equations [547]. The visualisation of results, often in the form of animations—a common feature in deterministic software—can also be more engaging for decision-makers and stakeholders compared to outcomes of probabilistic representations [548].

The use of deterministic models is not always possible or advisable, especially when unknown or unknowable parameters are crucial for the model [542]. Indeed, the main disadvantage of determinism is that it cannot deal with uncertainty, and additive uncertainty is analysed using probabilistic methods. Many deterministic codes are equipped with intuitive user interfaces, and the untrained modeler starts with the construction of the numerical form rather than the assumptions of the conceptual model. Furthermore, the mathematical core is hidden in the computer code, which is inaccessible or difficult to access for the average user.

There is no strict and fast scheme for building an accurate deterministic solute transport model. However, most should meet the following requirements and rules:

1. When collecting all available data, pay particular attention to the patterns of spatial variability of the controlling parameters (e.g., hydraulic conductivity and/or permeability) and the scarcity of the data, as this determines the complexity of the model. It is also important to assess the representativeness of the available samples.

- High-quality input data play a key role in ensuring the accuracy and reliability of predictions and effective decision-making [549–551].
2. Preprocessing, data may need to be pre-processed to ensure that the input is free of missing values and anomalies before it is included in a model [496,552,553].
 3. Conceptual design, any analytical or numerical modelling should start from a concept. The conceptual model (or models) is based on the generalisation of the site-specific conditions and the physico-chemical processes involved in solute transport. The main problem of a deterministic approach arises precisely at this stage of modelling when trying to represent reality, as it is well known that data rarely represent complete phenomena and trends [554]. Conceptual uncertainties, for example, those related to model structure or inappropriate simplifications, have been identified as one of the main causes of uncertainty in deterministic modelling of fluxes and reactive solute transport, and this problem is receiving increasing attention [555–558]. Ultimately, much is left to the creativity and experience of the modeler. This dependence on the human factor can be both a strength and a weakness of the model. Predictive or fate models are prone to immeasurable conceptual errors because the future is largely unknown and based on projections. However, predictive models can provide feedback and data that was not previously known [559] and can subsequently be used to create different (optimistic and pessimistic) scenarios [560]. In addition, predictive models contribute to continuous learning and adaptation, as models can be updated and improved over time as more data become available [561].
 4. When selecting or developing one or more numerical models, it is difficult to give guidelines due to the subjective nature of the conceptual model, but it should be possible to put the concept into a solvable, usually numerical, form. Once the expert has an overview of the processes and the desired level of accuracy or, as the modelers would say, model complexity, they need to decide which numerical tool is best suited to their needs. Model complexity is again a term for which there is no clear definition [562]. However, the study by Baartman et al. [563] agrees that model complexity takes into account the number of explicitly included processes and feedback loops. The size and completeness of the data set should also determine the level of complexity. It is also important to adhere to the principle of model parsimony, i.e., reflecting variability but not leading to overfitting, which is often the case with complex models. It is also recommended to start with a simple model and carefully increase the complexity [564–566]. However, users must be aware that oversimplification can also be a problem, as a very simple model can also have detrimental consequences for the prediction of future system behaviour [567]. Furthermore, adapting the cross-checking approach, i.e., constructing simple (surrogate, emulators) and complex models, could support future decisions [567–572];
 5. Discretisation, when choosing a numerical model, the user must consider the issue of discretisation of the domain. Numerical deterministic models of reactive transport must be discretised due to the principle of conservation of mass. For one-dimensional models, this is comparable to dividing the domain into a chain of tank reactors. There are two common methods of spatial discretisation: finite differences, and finite elements. Unstructured geometry (finite element method) should be used where the consideration of heterogeneity has the greatest impact on flow and mass transfer, as it allows the user to adjust the resolution if necessary without having to refine the entire model. However, the first choice for modelling reactive transport is usually structured, as it is easier to implement biogeochemical processes in the model and mass-conservative calculations are available [573]. In recent decades, advances in computing power (more powerful CPUs) and new modelling approaches have enabled the inclusion of more complex geometries for solute transport [573–578]. In any case, the quality or resolution of the mesh influences how fast the model runs and how accurate it will be. Poor mesh quality leads to further errors in the model [573,579,580]. To correct the discretisation of the model, the user should be

- able to meet certain quality criteria [581,582]. Furthermore, if the reactive transport calculations include complex reactions such as precipitation, dissolution, oxidation, etc., the model needs a very accurate temporal resolution, i.e., many time steps.
6. The calibration of the numerical model is based on the many model parameters that control the processes that take place along the flow. The parameter set can be adjusted to maximise the fit of the model to a set of experimental data [583]. Therefore, the focus is often on the differences between observed and modelled values, i.e., the residuals. However, calibration must also consider whether the assigned parameters are appropriate (an experienced modeler is a great advantage here). It is therefore important not only to compare the model predictions with the observed data, but also to quantify and explain the uncertainty associated with the model and the data, as calibration and uncertainty analysis are closely linked, and no calibration results should be presented without quantifying the predictive uncertainty of the model [584]. Freyberg [585], for example, conducted an experiment with students who calibrated a groundwater model by trial and error using a series of observed heads. It was found that models with small residuals between simulated and observed data did not make better predictions than models with larger residuals. This problem is of great importance for highly parameterised models, as although they provide an excellent fit, they are also prone to overfitting as the parameter estimation lags behind the noise of the observations [586]. Furthermore, the worst predictions were made by models where the hydraulic conductivity was different in each cell of the model. Therefore, for groundwater flow models, the accuracy of the prediction must be weighed against the complexity of the model, especially the distribution of hydraulic conductivity/transmissivity [587]. The estimation of hydraulic conductivity is extremely important, as it is a key modelling parameter that controls water movement and usually only a fraction of the total investigated area is sampled [588]. The trial-and-error method is monotonous, time-consuming, and also judgmental, as the modeler is responsible for finding an acceptable level of agreement between simulated and observed data. To reduce the time required for calibration and to make this process more systematic and transparent, additional numerical tools can be used [589–591]. Recently, several calibration methods have been presented, including global optimisation methods [592], Bayesian-based calibration methods using Gaussian process error models [593], and pilot point calibration methods [594,595]. A promising alternative to the existing optimisation tools included in the modelling software are algorithms written in modern scientific languages such as R and Python, e.g., FloPy [596], ogs5py [597], RedModRPhree [598], toughie [599], and r2ogs5 [600]. It should be emphasised that model calibration can be even more challenging than model construction, as it requires an understanding of phenomena beyond hydrogeology and relies on disciplines such as algebra, geostatistics, geophysics and programming [472,601–603]. In addition to the choice of method, another important aspect is the data used in the calibration. A number of studies have concluded that calibration using observed hydraulic heads and surface water levels or discharges may not be sufficient, and that to improve the quality of the model it may be necessary to use a range of different data sources such as temperature, temporal information, exchange fluxes, and concentrations [604–606]. Another question that has been raised is whether steady state calibration is sufficient for predictive models and their accuracy for long-term decision support when it is known that hydrogeological processes never occur in steady states. This question also involves a trade-off between the time and labour required to run and calibrate complex transient models and the benefits of such predictive analysis [588,607]. During the calibration process, the modeler may fall into a non-uniqueness or equifinality trap, where different sets of fitted parameters lead to the same results. In general, this phenomenon is due to a lack of knowledge about the actual structure and the processes occurring in the subsurface. Equifinality can also be caused by a larger number of parameters than available observations or by correlations between parameters [586,608];

7. Analysing uncertainties, together with calibration and uncertainty reduction, is crucial for the accurate representation and prediction of systems. Some uncertainties can be removed, such as epistemic uncertainty, which arises from missing or imperfect knowledge [609–612]. Sources of uncertainty include: input data (from input data and external forces on the system), technical (related to codes, software constraints, etc.), structural (related to the conceptual model and simplification of the system), parameters (related to parameter distribution, parameter estimation, and constraint variables), prediction uncertainty, and calibration data uncertainty [613,614]. Uncertainty can be reduced by adding additional data on current and historical system behaviour (data assimilation, e.g., through high-resolution monitoring and hydrogeophysical screening [615]), by comparing different parameterisation methods and models, and by changing model resolution and other modelling measures based on experience. Statistical methods dedicated to the broad field of uncertainty analysis can be divided into six classes: Monte Carlo sampling, response surface-based methods including polynomial chaos expansion and machine learning, multi-model approaches, Bayesian statistics, multi-criteria analysis, and least-squares-based inverse modelling [614]. Methods successfully applied in water-related studies include generalised likelihood uncertainty estimation (GLUE) [616,617], differential adaptive evolution (DREAM) [532,618], parameter estimation code (PEST) [619,620], the Bayesian approach including total error analysis (BATEA) [621–625] and multi-objective analysis [626,627], machine learning methods [628], and the Null-Space Monte Carlo method (NSMC) [629,630]. Some helpful guidelines for successful calibration and uncertainty analysis, even under the pressure of climate change, can be found in the work of Mai [631].
8. Sensitivity analysis (SA) aims to examine how uncertainty in the results of a model or performance measure is distributed across different sources of uncertainty in the inputs [632–635]. Some researchers define SA as drawing a conclusion when/where uncertainty has an impact [636]. Therefore, sensitivity analysis helps to focus efforts on the most critical parameters when collecting additional data or refining parameter estimates. When conducting a SA, the objective should be defined first. Depending on this, samples for selected parameters/factors (probabilistic approach) or discrete values for the entire parameter range (global methods) are selected. Local methods investigate the effects of variability of the input data around the nominal values, while global methods aim to investigate the uncertainty of the results caused by changes in the input data over the entire range [637]. The model results are evaluated by examining, for example, the variance or distribution of the model results, which should allow the identification of the parameters that influence the results the most. The uncertainty analysis is not part of the sensitivity analysis, but both should be performed in parallel, as they are essential parts of the model development. In the best case, the uncertainty analysis should precede the sensitivity analysis, as the uncertainties should be estimated before linking to input data and parameters [638,639]. Reviews of SA methods in environmental and water modelling can be found in the following works: Saltelli et al. [640], Hall et al. [641], Perz et al. [642], Gao et al. [643], Pianosi et al. [644], Koo et al. [645], and Razavi et al. [646];
9. Maintenance and preservation: Knowledge is a resource, so if we consider models as a source of knowledge, we should use and protect them carefully [647]. Once a model exists and has been validated and verified, it can be used in the future for different purposes and for conditions that are now unknown and go beyond those for which the model was developed. Therefore, it is important to maintain it until it can be replaced or rewritten [648,649]. It should be noted that many of the models mentioned in this overview have been changed or overwritten over time. It is important to regularly check that the model is running, that it is still fit for purpose, that documentation is available and relevant, and that even modest technical support is provided to users. It is important to remember that the model must be available for future open-ended

access, which should not be dependent on institutional and technical factors. For this reason, many people, especially independent developers and researchers, choose to use open source platforms (GitHub, CoMESES, OpenModelica, PyDSTool, etc.) to disseminate and test models.

Below are brief descriptions of the most common numerical models with examples of their application in practice. Tables S4 and S5 of the Supplementary Material show the most important features of the most common deterministic models to help the reader make their choice. In some cases, price is a decisive factor in users' choices, so the prices of commercial solutions are also given.

3.4.1. BIOPLUME III

BIOPLUME III is a 2D model for simulating the sequential biodegradation of hydrocarbons in groundwater using a series of aerobic and anaerobic electron acceptors: oxygen, nitrate, iron (III), sulphate, and carbon dioxide. It was developed by modifying a two-dimensional transport model using the method of characteristics (MOC) [96]. The output of the model is the distribution of oxygen and pollutant concentrations. This tool has already been described and used in detail. For more information, see [150,387,650–654]. Raei et al. [653], for example, coupled BIOPLUME III and the Non-dominating Sorting Genetic Algorithm (NSGA-II) to optimise the remediation of groundwater contaminated by hydrocarbons, taking into account stakeholder feedback. The model and algorithm enabled the localisation of extraction and injection wells in the hypothetical BTEX-contaminated area. The optimisation function was used to minimise the fragmentation of the contaminant plume and increase the integration of the plume for the desired contaminant concentrations.

3.4.2. BIOREDOX-MT3DMS

Bioredox was developed in 1998 by Carey et al. [655] based on the public domain code of MT3D. This model can be used to predict the results of enhanced bioremediation of petroleum hydrocarbons and chlorinated solvents. Bioredox allows the simulation of by-product and halogen transformations and coupled oxidation-reduction reactions. It has been used to evaluate the natural attenuation of BTEX and chlorinated ethenes at a former fire training site at Plattsburgh Air Force Base in New York [655].

3.4.3. Bioslurp

Bioslurp is a finite element model for the simulation of three-phase flow (water, oil, and gas) and multi-component transport in heterogeneous porous and fractured media with varying saturation. This tool can be used to simulate the bioslurping process, which is a vacuum-enhanced recovery of NAPL. This tool has already been tested several times. Its application has been described by Lundy et al. [656], Tkaczyk and Pietrzak [657], and Sharmin and Gabr [658]. In the latter study, Bioslurp was combined with the MATLAB genetic algorithm toolbox to optimise remediation by achieving targets related to time, vacuum level, and placement of the extraction well.

3.4.4. Bioventingplus

Bioventingplus is a computer program that calculates the cost and effectiveness of remediation from the air, taking into account site-specific conditions and the type of pollutants [659]. Functions include airflow, mass recovery, and cost analysis. The airflow module aims to determine the air pressure, flow rate, pore volume turnover rate, and extraction efficiency. These parameters are calculated taking into account the injection conditions, i.e., pressure and soil properties. Mass removal is estimated based on the multicellular, multiphase, and multicomponent model. The model was successfully tested. The results can be found in Parker and Islam [660], Johnson and Parker [659], and Benner et al. [661]. The study by Benner et al. was conducted at the site of the former drum storage facility where several releases of LNAPL occurred, resulting in contamination of soils with a total mass of 4600 ± 2300 kg, of which about 350 ± 175 kg were identified as toluene,

ethylbenzene, and total xylenes (TEX). Using Bioventingplus simulations, it was estimated that in situ air sparging during the 1113-day remediation could result in the removal of 140 kg of petroleum hydrocarbons. If biodegradation is also taken into account, the mass of contaminants removed increases to 760 kg. The numerical modelling of the total pollutant removal using volatilisation and biodegradation agreed with the results on site.

3.4.5. Chain_2D

Chain_2D is a predecessor of HYDRUS-2D v. 2 [662]. Since the model uses chain reactions in reactive transport equations, it is possible to predict not only the concentration of the impurities—the parents—but also the concentration of the reaction products—the daughters [663]. The flow in porous media with different saturation, i.e., at the boundary between the vadose and the saturated zone, is simulated with the Richards equation, while the transport of solutes is calculated with the convection-dispersion approach. The software can handle flow in irregular heterogeneous aquifers. The flow and solute transport can take place in the vertical plane, in the horizontal plane, and in a three-dimensional domain characterised by radial symmetry about a vertical axis [662]. The CHAIN_2D code was applied to a heavily polluted site (chlorinated hydrocarbons) near the city of Tilburg in the Netherlands [663].

3.4.6. CORT3D

The CORT3D model helps to assess the impact of site-specific conditions on the effectiveness of chemical oxidation and to make decisions and plan injection (site, oxidant concentration) [297]. This tool is based on the widely used and well-tested code RT3D version 2.5 [20,384,664]. CORT3D simulates the dissolution of NAPLs using the stagnant film model [665], equilibrium or rate-limited sorption, second-order kinetic contaminant oxidation, kinetic oxidation of NOD considering a fast and a slow kinetic part, and diffusion simulated using different effective diffusion coefficients for each mobile species. The code simulates three aqueous mobile components (contaminant, aqueous chloride, and aqueous oxidant) and five immobile components (NAPL, sorbed contaminant, manganese oxide, fast NOD, and slow NOD). The CORT3D calculations account for velocity changes caused by time-varying permeability due to the dissolution of NAPL and the precipitation of manganese dioxide due to permanganate consumption. This code has been tested at the Navy Training Centre site in Florida [666].

3.4.7. Feflow

Feflow is an intuitive and complementary model for the flow and transport of fluids. It can simulate many phenomena related to fluid flow, groundwater ageing, contaminant and heat transport, and density-driven processes in differently saturated porous and fractured media at different spatial scales (from local to regional). Feflow uses the finite element method to solve many problems related to groundwater management, e.g., the impact of hydromechanical infrastructure, tunnelling, creation of retention zones, seepage through dams and dykes, remediation scenarios, etc. Feflow is widely used in practice and in science. Examples of its application to the reactive transport of organic material can be found in the work of Blake and Taffet [667], Kühlers et al. [668], Söderberg [669], Innocenti et al. [301], Kouamé et al. [670], and Praseeja and Sajikumar [671]. Kouamé et al. investigated the flow of a hypothetical release of benzene through the simulated Abidjan aquifer. The initial concentrations of dissolved benzene of 43.12 mg/L and 14.37 mg/L were simulated to enter the aquifer injected at the Shell petrol stations. Adding the results of the vertical and horizontal transport time gives a global transport time of 38 to 47 years. The results show that there is a risk of pollution for 14 wells, and that possible air entrapment can allow the formation of pollution pools that represent a secondary source of hydrocarbons.

3.4.8. Hydrus

Hydrus is a Windows-based 2D/3D finite element model for simulating the flow and transport of multiple species in differently saturated, heterogeneous, porous media. The model enables the optimisation of soil and hydrogeological parameters. One of the functions of Hydrus is to define good agricultural practice in relation to water management. Other environmental applications include risk assessment of contaminant plumes from landfills, infiltration of wastewater, and the interaction between groundwater and surface water. Since many environmental problems cannot be solved without insightful analyses of the fate of pollutants and their interactions, the hydrogeochemical model PHREEQC has been integrated into the basic version of Hydrus. The coupling of PHREEQC with Hydrus leads to a considerable extension of the functionality with regard to reactive transport, and enables the simulation of surface complexation, sorption, precipitation, and dissolution, as well as other mixed equilibrium and kinetic biogeochemical reactions. For the application of Hydrus in hydrocarbon transport studies, we refer to the work of Casey and Šimůnek [672], Ngo et al. [673], Mallants et al. [674]. The latter study reproduced the fate and transport of biocides in soil as a result of their accidental release. The simulation included the degradation chain of the biocide bronopol, the delay, and the convective-dispersive transport of the biocide bronopol and its degradation products.

3.4.9. MT3D/MT3DMS

MT3D is a modular 3D model for simulating the transport of pollutants in groundwater [675]. MT3D is capable of simulating flow in both unconfined and confined aquifers, including variable layer thicknesses and different hydraulic and chemical boundary conditions. The MT3D code has been used extensively for contaminant transport modelling and remedial assessment studies. Some examples can be found in the articles [676–680]. The next generation product, MT3DMS [681], improves several aspects of the transport model. The adaptation of a structure that allows the addition of user-defined reactions could be useful in modelling complex biological and geochemical processes. MT3DMS, like its predecessor MT3D, has been tested in a number of environmental studies. Recent examples can be found in references [682–685]. MT3D and MT3DMS can be downloaded for free, with the latter embedded in other software such as Visual Modflow and GMS. Gao et al. [685] simulated the migration of organic pollutants from a trench filled with a tank of liquid waste with a volume of 600 m³. The numerical simulation includes fluctuations in the groundwater level, which were crucial for the migration of pollutants, adsorption in the soil, and biodegradation.

3.4.10. PFLOTRAN

The PFLOTRAN computer code [603,686] solves the mass and energy conservation equations for a range of aqueous phases, supercritical carbon dioxide, black oil, and a gaseous phase in variably saturated porous media in one, two, or three dimensions. It couples two modules, PFLOW and PTRAN, which represent flow and reactive transport. The PFLOW module solves the mass conservation equations for water and carbon dioxide and an energy balance equation, while the PTRAN module solves mass conservation equations for a multi-species reaction system. The latter includes homogeneous aqueous speciation reactions, heterogeneous gaseous speciation, mineral precipitation, dissolution reactions, ion exchange, and sorption reactions. PFLOTRAN was tested to simulate the movement of LNAPL through the vadose zone [687] and to identify factors influencing the migration of methane near oil and gas wells [688].

3.4.11. PHREEQC

PHREEQC [476,689] is a computer program for the simulation of reactions and transport processes in pristine and polluted waters. The calculations include reactions with minerals, gases, solid solutions, and exchangers. Advanced users can use specialised modules to simulate more complex processes defined in the BASIC language. 1D transport,

which includes diffusion, advection, and dispersion, also allows for the diffusion into stagnant zones, known as double porosity. Recently, new tools have been released that add Python programming and plotting capabilities [690,691]. Due to its availability and flexibility, PHREEQC is widely used. It is not only popular, but also reliable. Its modelling results have been compared with those of other codes several times [692–695]. PHREEQC has also been used to model the migration and biodegradation of hydrocarbons [478,696–698]. For example, Bailey et al. modelled the migration of hydrocarbons through sandstone formations at Rainbow Rocks in the USA. The presence of bitumen changed the colours of the sandstone and led to changes in trace elements and mineral assemblage.

3.4.12. PHT3D

PHT3D is a 3D multicomponent code for reactive transport in saturated porous media [699]. The reactive transport equation is solved with MT3DMS using the sequential operator splitting technique [700–704] with a slight modification described by Walter et al. [705]. All concentration changes of aqueous components and immobile species resulting from reactive processes are calculated using PHREEQC. PHT3D has been integrated into the PMWIN package and Visual Modflow since version 4.1. PHT3D has been successfully used in various fields: controlled groundwater recharge, water quality in catchment areas of water abstraction points, fate of oxidisable organic compounds, fate of brominated/chlorinated compounds, dispersion-controlled transport, reactive transport under different density conditions, and the transport of pesticides. This tool has been used by both experts and beginners. Recent examples can be found in references [706–711]. Ng et al. [711] investigated the fate of a historical hydrocarbon plume at the Bemidji site, where the secondary effects were the subject of simulations. In addition to the anaerobic biodegradation of BTEX, the outgassing of carbon, the input of dissolved inorganic carbon (DIC), pH buffering, and the immobilisation of Fe(II) were also included in the calculations.

3.4.13. RT3D

RT3D (Reactive Transport in 3-Dimensions) simulates the reactive flow and transport of various mobile and/or immobile species in aquifers [664]. RT3D is based on the code MT3D, but has considerably extended the possibilities for reaction modelling. RT3D offers an operator splitting strategy [20,712] for the contaminant transport equation. RT3D is equipped with several pre-programmed reaction modules and one user-defined reaction module. The list of ready-to-use modules includes: aerobic instantaneous degradation of BTEX, kinetically limited degradation of BTEX, a double-monod model, sequential degradation reactions, an aerobic/anaerobic model for the degradation of PCE/TCE, natural and enhanced attenuation of chloroethanes, chloroethenes, chloromethanes, and daughter products [713,714]. Similar to MT3D, RT3D uses a separate model, usually Modflow [715], to determine the velocity and groundwater pressure distribution. As the RT3D code can be customised to simulate various processes, including microbially mediated responses, it has been used in several laboratory and pilot bioremediation experiments [716]. It can, and has, been used in many regional environmental studies on the fate of pollutants [23,717–721]. Joo et al. [721] tested the RT3D model in a lumped approach to simulate the transport of 12 organic compounds in mixtures through a column filled with sands containing different proportions of organic carbon, generating new breakthrough curves and evaluating sorption capacity. RT3D is also integrated into the Visual Modflow program, the GMS package, and the Groundwater Vistas tool.

3.4.14. SEAM3D

The concept behind the SEAM3D (Sequential Electron Acceptor Model 3-Dimensional) model is biodegradation by sequential electron acceptors and solute transport in a three-dimensional heterogeneous system [722]. A key feature of the code is its compatibility with the MODFLOW model. The reactively transported solutes can be biodegradable substrates, nutrients, and electron acceptors for microbial growth, products of biodegra-

dation, daughter products of the substrates, or non-reactive tracers. In general, SEAM3D is equipped with four chemical packages: biodegradation, NAPL dissolution, reductive de-chlorination, and co-metabolism. SEAM3D has been used to predict the dispersion of chlorinated solvents at Little Creek Naval Amphibious Base in Virginia Beach for the US Navy, to simulate a controlled release of jet fuel at an air force base in Mississippi, and to model simulations of a gasoline-contaminated site near Beaufort, South Carolina, to explain why natural attenuation was ineffective [723]. More recently, SEAM3D has been used to study benzene transport in shallow coastal groundwater [724] and the dissolution of DNAPL [725].

3.4.15. SUTRA

SUTRA uses both finite element and finite difference methods to simulate density-dependent groundwater flow in variable saturated media and reactive solute transport, including sorption and decay reactions. SUTRA also allows the simulation of heat transport in liquid and solid media (aquifer and its matrix). SUTRA can be used for areal and cross-sectional modelling, and reactive simulations can be used for pristine areas and brownfields. The latter makes Sutra useful for solving contaminant transport problems and remediation scenarios. Examples of the use of Sutra in reactive transport studies can be found in the works of Koch and Zhang [726], Beneš and Eliáš [727], Rashid and Kaluarachchi [728], El-Kadi [729], and Plampin and Provost [730].

3.4.16. TMVOC

TMVOC is a FORTRAN model developed for simulating and analysing VOC flows [731]. This tool can simulate the flow from one to three dimensions in porous or fissured media with different saturation. It can therefore be used to study the fate of NAPLs in the vadose zone and in groundwater. In addition, the model can simulate the formation of oil lenses at the groundwater surface, the dissolution and transport of VOCs into the groundwater, the evaporation and migration of VOCs in the interstitial air of the unsaturated zone, and the reversible sorption of VOCs on the rock matrix. The main application of TMVOC could be NAPL outfall sites and remediation alternatives in the vadose zone and below the water table. It has been tested and the results have been published by Batistelli [732], Erning et al. [733], MacKenzie [734], and Guo et al. [55]. The latter study was related to the assessment and prediction of the effects of bioremediation on chlorinated hydrocarbons in a very large fractured karst aquifer in Zibo City, China. In the modelling study, the effects of hydrocarbon compounds on the chemical status of groundwater were reproduced using ions: NO_3^- , SO_4^{2-} , HCO_3^- , Cl^- , and an isotope $\delta^{13}\text{C}(\text{DIC})$.

3.4.17. TOUGH

TOUGH is basically a series of programs that can be used to simulate flows in fissured and porous media. TOUGH2 is a basic program for multiphase flows and heat transport. The flow takes into account the transitions between liquid and vapour states and various forces that influence the fluid movement (gravity, pressure, and viscosity). Several modules from the Tough software family can be used for the reactive transport of hydrocarbons, T2VOC, TMVOC, and TOUGHREACT. The first two modules are designed for three-phase flows (water, air, and VOCs) in heterogeneous porous media. The last module is more suitable for reactive transport studies where chemical interactions between solutes need to be considered. These chemical transformations include kinetic processes such as precipitation or dissolution reactions. There are many papers dealing with the transport of hydrocarbons using TOUGH or one of its modules. Many of these have been published in TOUGH conference proceedings and articles, for example Hodges et al. [735], Fagerlund and Niemi [736], Falta [737], Fagerlund et al. [738], Yang et al. [739], and Zhou et al. [740]. The latter combined two models, HYDRUS-1D and TOUGH, to simulate the influence of the freeze–thaw process in the soil on the water flow and the redistribution of NAPL (toluene in this study) with the water fluctuations.

3.4.18. UTCHEM

UTCHEM is a 3D model for multiphase flow and reactive transport of multiple compounds that can simulate a variety of processes in differently saturated media [741]. Accordingly, this multidisciplinary approach can be applied to many applications, especially surfactant enhanced aquifer remediation (SEAR). In addition, physical, chemical, and biological processes associated with the fate and transport of NAPLs were included in the model. These processes include the dissolution and/or mobilisation of NAPLs by undiluted remediation fluids, chemical and microbiological transformations, and changes in fluid properties during site remediation. UTCHEM enables the simulation of remediation fluids with variable density, temperature, and viscosity. The GMS software can provide the interface to UTCHEM. Some recent applications relate to oil/water partitioning (Huynh et al. [742]) and transport of DNAPL in deep aquifers (Wenyi et al. [743]).

4. Discussion and Conclusions

The decision-making process at the outset of modelling involves choosing between a deterministic or stochastic approach. Traditionally, these approaches were viewed as competing strategies [744], but contemporary practice recognizes their potential as complementary tools across various stages of a remediation project. This acknowledgment stems from the understanding that reality falls between complete determinism and total randomness [745]. Thus, selecting a modelling framework becomes an exercise in compromise, even among scientific circles. Deciding whether to adopt a simpler model, grounded in expert knowledge, or opting for a more intricate approach involving multiple models presents a challenge. Some experts advocate for simpler solutions due to their accessibility to end-users, who may lack hydrological or programming expertise [564], while others advocate for more complex models [746]. A relatively recent framework gaining traction is the hybrid approach, which combines surrogate emulators with more intricate models [572]. It is crucial for potential users to recognize that even simple screening models can be potent and suitable for practitioners [747]. Moreover, the pivotal step of conceptual modelling and prioritizing remediation objectives is often overlooked by newcomers, leading to potentially unrealistic outcomes.

In the decision-making process regarding the choice of modelling approach, a boundary between science and practice undoubtedly emerges. The modeler must consider the preferences of decision-makers, who often favour simple and transparent tools. They may only resort to more complex and inherently costlier models when supported by experts capable of ensuring credibility and quality assurance. In theory, the expectations of policy makers and environmental managers may be lower compared to those of scientists. However, this dynamic could shift if science uncovers difficult problems or unexpected phenomena that are challenging to address [748].

This underscores the importance of collaborative efforts in assessing contaminated sites and their subsequent remediation using numerical tools. Dialogue between stakeholders and modelers is essential to establish a systematic framework supporting management decisions [749,750]. An enhanced understanding of the processes underlying the conceptual model and the code is crucial for achieving better results. Therefore, users and beneficiaries of environmental modelling should be actively engaged throughout the modelling process from conception to validation. Selecting appropriate modelling tools demands experience, creativity, knowledge, and, at times, intuition. To meet the expectations of stakeholders, a modeler must possess not only a deep understanding of the model itself, but also the methodologies for its validation.

Paradoxically, forecasting the future of modelling reactive transport presents challenges. Simple models are expected to remain essential due to their usefulness and the ease with which their elegant analytical solutions can describe extensive systems. Additionally, they can be readily adjusted for new tasks and integrated with more advanced tools, such as machine learning models [751]. Deterministic models, still predominant, are likely to persist, particularly in situations requiring process-based understanding and consideration

of complexity [752]. However, stochastic approaches may offer greater reliability for long-term solute fate predictions, particularly in heterogeneous media with varying saturations. Consequently, stochastic models or their hybrid variants are anticipated to gain traction. In many instances, stakeholders versed in pollution risk assessment will prefer a range of probable values with an acceptable level of confidence. The accessibility of data and open-source solutions will undoubtedly facilitate the development of new models, with machine learning techniques and emulators increasingly applied in pollution transport studies at the operational and field levels.

This article aims to provide an overview of the various approaches used for simulating hydrocarbon migration in groundwater. It covers simple screening models, stochastic methods, and common deterministic models, along with a brief discussion of machine learning and its relevance to hydrocarbon migration. Additionally, the authors outline the advantages and limitations associated with each modelling approach. For deterministic modelling, basic guidelines for model construction are provided to aid in selecting appropriate tools, particularly for sensitivity or uncertainty analyses. Mathematical formulations are omitted, as they are not essential for this overview. Furthermore, the availability of these models and their applications in experimental and field studies are also discussed.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app14093675/s1>, Table S1: Summary of the models used for the transport of hydrocarbons; Table S2: Screening tools and their limitations; Table S3: Screening tools with their input and output data; Table S4: Deterministic models, area of usage, processes and method of modelling; Table S5: Deterministic models, their availability and reactions that can be modelled.

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Abbreviations

3DFATMIC	3-Dimensional Subsurface Flow and Fate and Transport of Microbes and Chemicals model
ART3D	Analytical Model for Simulating Reactive Multi-species Transport in 3-Dimensional Groundwater Systems
BIOREDOX-MT3DMS	A Coupled Biodegradation-Redox Model with Modular Transport 3 Dimensional Model Simulator
CDISCO	Conceptual Design for In Situ Chemical Oxidation
COEC	Contamination Of Emerging Concern
CORT3D	Chemical Oxidation Reactive Transport in 3 Dimensions
DFT	Density Functional Theory
DNAPL	Dense Non-Aqueous Phase Liquid
EEA	European Environment Agency
EPA	Environmental Protection Agency
ES&T	Environmental Services & Technologies
ESTCP	Environmental Security Technology Certification Program
FEFLOW	Finite Element subsurface Flow system
FEHM	Finite Element Heat and Mass Transfer Code
GMS	Groundwater Modelling System
HPS-PROBAN	Horizontal Plane Source—Probabilistic Analysis

HSSM	Hydrocarbon Spill Screening Model
ISCO	In Situ Chemical Oxidation
ISCR	In Situ Chemical Reduction
KIE	Kinetic Isotope Effect
LaSAR	Lagrangian Stochastic Advection Reaction
LNAPL	Light Non-Aqueous Phase Liquid
ML	Machine Learning
MNA	Monitored Natural Attenuation
MNB	micro and nanobubbles
MOC/MOC3D	Method of Characteristics
MT3D	Modular Transport in 3 Dimensions
MT3DMS	Modular Transport 3 Dimensional Model Simulator
NAPL	Non-Aqueous Phase Liquid
NAS	Natural Attenuation Software
NOD	Natural Oxygen Demand
NSMC	null space Monte Carlo
PAH	polycyclic aromatic hydrocarbons
Pdf	Probability Density Function
PHREEQC	pH-Redox-Equilibrium C programming language
PREMChlor	Probabilistic Remediation Evaluation Model for Chlorinated solvents
REMChlor	Remediation Evaluation Model for Chlorinated solvents
REMFuel	Remediation Evaluation Model for Fuels
ROI	Radius of Influence
RT1D	Reactive Multispecies Transport in 1-Dimensional groundwater systems
RT3D	Reactive Multispecies Transport in 3-Dimensional groundwater systems
RTF	Remediation Time Frame
RWPT	Random Walk Particle Tracking
SEAM3D	A Sequential Electron Acceptors Model for 3-Dimensional Solute Transport
SERDP	Strategic Environmental Research and Development Program
SPH	Smoothed Particle Hydrodynamics
SUTRA	Saturated and Unsaturated Transport Model
SWMS 3D	Simulator of Water flow and Movement of Solute in 3-D variably saturated media
TMVOC	Transport of Multicomponent VOCs model
TOUGH	Transport Of Unsaturated Groundwater and Heat
UTCHEM	University of Texas Chemical Compositional Simulator
VOCs	Volatile Organic Compounds

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