

Review

Solute Reactive Tracers for Hydrogeological Applications: A Short Review and Future Prospects

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Abstract: Tracer testing is a mature technology used for characterizing aquatic flow systems. To gain more insights from tracer tests a combination of conservative (non-reactive) tracers together with at least one reactive tracer is commonly applied. The reactive tracers can provide unique information about physical, chemical, and/or biological properties of aquatic systems. Although, previous review papers provide a wide coverage on conservative tracer compounds there is no systematic review on reactive tracers yet, despite their extensive development during the past decades. This review paper summarizes the recent development in compounds and compound classes that are exploitable and/or have been used as reactive tracers, including their systematization based on the underlying process types to be investigated. Reactive tracers can generally be categorized into three groups: (1) partitioning tracers, (2) kinetic tracers, and (3) reactive tracers for partitioning. The work also highlights the potential for future research directions. The recent advances from the development of new tailor-made tracers might overcome existing limitations.

Keywords: reactive tracers; tailor-made tracer design; hydrogeological tracer test; kinetics; partitioning

1. Introduction

Tracer tests are one of the most well established techniques for site and process characterizations in the aquatic environment (i.e., in hydrology or hydrogeology). Various additives (e.g., particles, solids, solutes, and gases) and physical quantities (e.g., temperature and pressure) can be applied as tracers for interpreting hydraulic transport properties and/or reactive processes in the aquatic environment [1–4]. Some basic hydraulic properties, such as flow velocity or porosity, can be obtained by tracer tests using conservative (non-reactive) tracer compounds. The combination of a conservative tracer with at least one reactive tracer is commonly applied in order to assess additional system parameters, such as residual saturation [5,6], microbial activity [7,8], or temperature distribution [9,10]. The unique features of reactive tracers could provide valuable information on physical, chemical, and/or biological properties of the hydrological system which surpasses the capability of conservative tracers.

The application potential for tracers within the scope of advanced reservoir management, such as geothermal power generation or carbon capture and storage, has triggered the development of new tracers and tracer techniques in the past decades [11,12]. Reactive tracers used to detect specific

properties and processes in the aquatic environment must generally either have distinctive physicochemical properties (e.g., sorption) or undergo specific reactions such as hydrolysis. To identify the most suitable tracer compounds for a specific system or problem, a thorough understanding of the physicochemical properties and their chemically reactive behavior in the probed system is a prerequisite.

The main objective of this overview article is to present a systematic review of existing and proposed reactive solute tracers based on current research advances conducted in different scientific fields. The focus of this work is on chemical/artificial tracers which are intentionally introduced in the tracer tests. For each subclass of tracer, the underlying process, their key properties, and possible target parameters/applications are described. Furthermore, the potential areas for the future development and exploitation of new reactive tracers are elaborated. Hereby, the new approach of producing tailor-made reactive tracers may break down currently existing limitations on the investigation potential of commercially available compounds.

2. Definition and Theoretical Background

2.1. Definition

A tracer is defined herein as a distinguishable chemical compound which is deliberately added to an aquatic system having a temporally and spatially well-known input function (e.g., pulse injection). The respective system property or information of interest is derived based on the relation of the input function to the observed response function (breakthrough curve) within the investigated system.

Two general tracer types can be defined based on the degree of interaction with the systems. First, conservative tracers show virtually no interaction with the reservoir materials, and thus they flow passively with the carrier fluids at their velocity. Furthermore, they do not suffer any chemical or biological processes. This implies that these tracers are inert under reservoir conditions. The second type of tracers can be summarized as reactive tracers. The interpretation of reactive tracers relies on their known properties, physicochemical or chemical behavior during the transport. Reactive tracers are compounds that undergo a chemical reaction or physicochemical interaction processes in a predictable way under specific boundary conditions existing in the investigated system. Consequently, using the particular features of reactive tracers could provide unique information on physicochemical properties and/or water chemistry of the hydrological system far beyond the capability of conservative tracers.

Traditionally, tracer tests were conducted using conservative tracers. These tracers can provide general physical and hydraulic parameters of the system (e.g., porosity, dispersivity, or arrival time). In order to derive these parameters with great accuracy, the compounds are desired to behave ideally. The properties of an ideal tracer are well established [2]; they (1) behave conservatively (e.g., are transported with water velocity, not degradable), (2) have a low background concentration in the system, (3) are detectable in very low concentrations, and (4) have low or no toxicological environmental impact. Nevertheless, all solute tracers are influenced to some degree by physical, chemical, and/or biological processes. This means that completely ideal tracers do not exist in reality. Therefore, some knowledge of the investigated system is required beforehand to verify the practicality of the tracer behavior and thus to avoid test failure.

2.2. Conservative Tracer Transport versus Reactive Tracer Transport

The transport behavior of a tracer compound in the aquatic environment is affected by several physical and chemical processes. These processes result in spatial and/or temporal concentration changes of the introduced tracer during its transport, which are reflected in the system response function (e.g., breakthrough curve $c(t)$). Tracer transport is commonly described based on the principle of mass conservation by means of the advection-dispersion-reaction model in the three-dimensional form as follows:



$$R \frac{\partial c}{\partial t} = -\bar{V} \cdot \nabla c + \nabla(D_H \nabla c) + S, \quad (1)$$

where R is the retardation factor, c is the tracer concentration, t is the time, \bar{V} is the average pore water velocity, D_H is the hydrodynamic dispersion tensor (including mechanical dispersion and molecular diffusion), and S is the source/sink term accounting for the tracer transformation (degradation/generation).

As described above, tracer transport in water can be classified as conservative or reactive according to its interaction within the system to be studied. A conservative tracer does not interact or alter during the transport, and thus the concentration is not changed by processes other than dilution, dispersion, and partial redirection. As such, conservative tracers are expected to mimic the transport of water without retardation and transformation. They underlie only the purely hydrodynamic transport processes: advection, diffusion, and dispersion (as terms 2 and 3 in Equation (1)). It should be noted that various types of mixing always exist which should be interpreted with caution as the mixing or other dilution processes may influence the results of tracer experiments [13–16]. Therefore, conservative tracers are generally used to investigate hydraulic properties (e.g., tracking connectivities, flow pathways), analyzing travel times and flow velocities, determining recharge and discharge, and estimating hydromechanical properties (e.g., dispersivity, porosity). Common examples of conservative tracers under ambient temperatures are major anions such as bromide [17,18], stable isotopes such as ^2H and ^{18}O [4,19], dye tracers such as uranine [20–22], and rhodamine WT [23–27].

Apart from hydrodynamic transport processes, reactive tracers additionally underlie physical, chemical, and/or biological processes during their transport (terms 1 and 4 in Equation (1)). The implementation of reactive tracers with identical and well understood interactions or reactions could implicitly provide unique information on physicochemical aquifer properties (e.g., sorption capacity), water chemistry (e.g., redox condition, pH, ion concentrations), and other influencing parameters (e.g., temperatures, microbial activity) [28–30].

In order to benefit from the selective and process specific nature of reactive tracers, it is a prerequisite to combine them with at least one conservative reference tracer by performing a multitracer experiment to account for the purely hydrodynamic transport processes that affect both tracer types in the same way. Consequently, the reactive processes can be identified and quantified. The intended information from the tracers is gained by comparing the concentration versus time curves (breakthrough curves) of the reactive tracers with the conservative tracers (reference). This can be illustrated by the schematic breakthrough curves for a simulated tracer test having a pulse input function (Figure 1). The time shift and/or the reduction of the peak area (tracer mass) of the breakthrough curves indicate retardation and/or degradation, respectively. Measured breakthrough curves can be inversely interpreted using analytical or numerical models to estimate the values of controlling parameters, such as the distribution coefficient for the sorption process, the decay rate for the sorption process, or the decay rate for the biodegradation process.

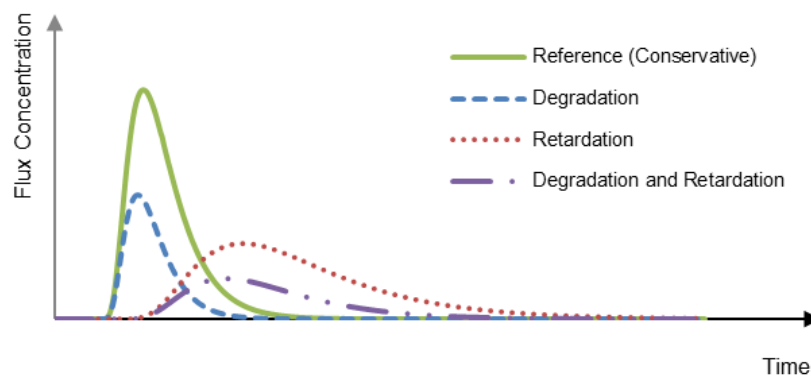


Figure 1. Schematic breakthrough curves for conservative tracer and reactive tracers after a pulse injection.

3. Types of Reactive Tracers

A generalized classification of currently existing reactive tracers and proposed reactive tracer concepts, including their required properties, possible applications, and processes is provided. Depending on their physical, chemical, and/or biological behavior, three major subgroups are distinguished (Table 1):

- Partitioning tracers: These types are based on the partitioning equilibrium between two immiscible phases or at their interfaces (fluid–solid, fluid–fluid) leading to a retardation relative to the conservative tracer remaining in (one) fluid phase.
- Kinetic tracers: These types are non-equilibrium tracers in which only the reaction kinetics are used for the parameter determination. As a result of the tracer reaction, the tracer signals are decreasing (parent compound) or increasing (daughter compound) with time (degradation). These tracers usually do not show retardation (no partitioning).
- Reactive tracers for partitioning: These tracers are a hybrid form of the preceding tracers, containing features of both: chemical reaction (degradation) of the parent compound and subsequent partitioning (retardation) of the daughter products.

Table 1. Classification of reactive tracers.

| Reactive Tracer Type | Equilibrium tracers (partitioning tracers) | | | | Reactive tracer for partitioning (volume or interface sensitive after degradation) | Kinetic tracers (decaying tracers) | | |
|---|---|---|--|---|--|---|---|--|
| | Fluid–Solid | | Fluid–Fluid | | | One phase | | Two phases |
| | Sensitive for uncharged surfaces | Sensitive for charged surfaces | Volume sensitive | Interface sensitive | | Degradation sensitive | Thermo-sensitive | Interface- sensitive |
| Determining properties of tracer molecules | Uncharged but still soluble (moderately polar) organic compounds | Organic and inorganic ions with opposite charge compared to the surface | Compounds with quantifiable partitioning between two phases (soluble in both phases) | Amphiphilic compounds (surface active agents- surfactants) | Hydrophilic compounds, susceptible to decay leading to daughter compounds with different partitioning properties (coefficients) | Degradable compounds under applied conditions | Hydrolysable and hydrophilic compounds with known kinetic parameters and decay mechanisms | Hydrophobic and hydrolysable compounds |
| Possible target parameters/Application | Organic carbon content, surface area to volume ratio A/V (of uncharged surfaces) | Surface charge (surface charge density, exchange capacity), Surface area to volume ratio A/V (of charged surface) | Residual saturation | Residual distribution, contact area | Residual saturation or residual distribution, contact area | Attenuation capacity, other reaction relevant boundary conditions (e.g., redox conditions, pH) | Temperature and temperature distribution (cooling fractions) | Interfacial area (development with time) |
| Underlying (reactive) process | Sorption due to hydrophobic interactions | Sorption due to electrostatic interactions (e.g., ion exchange, hydrogen bonding) | Phase partitioning | Interfacial adsorption (partitioning between bulk phase and interface) | In-situ decay with subsequent partitioning | Chemical and biological reactions | Hydrolysis reaction, substitution | Hydrolysis reaction leading to inter-phase mass transfer |

3.1. Equilibrium Tracers

3.1.1. Fluid–Solid (Sorbing Tracers)

Sensitive for Uncharged Surfaces

A tracer compound sensitive for uncharged surfaces undergoes hydrophobic sorption onto uncharged sites of the sorbent (e.g., soil, aquifer material), particularly organic matter. Hydrophobic sorption is the result from a weak solute-solvent interaction coming from a decrease in entropy of the solution and can be explained by general interactions between sorbate and sorbent, e.g., van-der-Waals forces (dipole and/or induced-dipole interactions) [31]. The organic carbon content (f_{OC}) of the aquifer material generally correlates with the sorptivity and thus the retardation of a neutral (uncharged) organic compound [32–34]. Therefore, it is conceivable that substances, which are sensitive to uncharged surfaces, have the potential to determine the f_{OC} of a system from their observed retardation factor (R_{unc}) assuming a linear sorption isotherm:

$$R_{unc} = 1 + \frac{\rho}{n_e} K_{unc}, \quad (2)$$

where ρ is bulk density, n_e is effective porosity, and K_{unc} is the sorption coefficient. K_{unc} depends primarily on the hydrophobicity of the tracer molecules, typically characterized by the *n*-octanol-water partition coefficient ($\log K_{OW}$) and the f_{OC} of the geological materials. From $\log K_{OW}$ of the tracer compound, K_{unc} for a particular system can be estimated. According to the literature [35–37] $\log K_{OW}$ can empirically be related to the organic carbon normalized sorption coefficient (K_{OC}) in the form:

$$\log K_{OC} = a \log K_{OW} + b, \quad (3)$$

$$K_{OC} = \frac{K_{unc}}{f_{OC}}, \quad (4)$$

where a and b are empirical parameters.

Thus, from known $\log K_{OW}$ and determined R_{unc} , the average f_{OC} between the injection and observation points can be estimated. By selecting non-ionic compounds with moderate $\log K_{OW}$ values between 1 and 3 (1H-benzotriazole, carbamazepine, diazepam, and isoproturon) from formerly published column experiments by Schaffer et al. [38,39] using correlation factors for non-hydrophobic compounds after Sabljic et al. (1995), the observed f_{OC} values of the columns agree very well with the independently measured ones from the bulk using total organic carbon measurements. Despite the relatively large uncertainty regarding the chosen $\log K_{OW}$ values, all deviations of the absolute values between the measured and calculated f_{OC} are within one order of magnitude (less than factor 5).

To the extent of our knowledge, this tracer type has not yet been explicitly proposed, and therefore their potential could be further investigated. Some promising examples include 8:2 fluorotelomer alcohol [40], short-chained alkyl phenols [41], or pharmaceutical compounds [42–44].

Sensitive for Charged and Hydrophilic Surfaces

A tracer compound sensitive for charged surfaces undergoes ionic sorption between a charged moiety of a tracer molecule and an oppositely charged surface of the sorbent (e.g., soil, aquifer material). In this case, there is a strong electrostatic interaction (e.g., ion exchange, hydrogen bonding, or surface complexation) between tracer sorbate and sorbent.

Retardation of a solute due to ion sorption on natural solids (R_c) can be related either to a sorbent mass (Equation (2)) or to its surface sensitivity to the surface area (A) to volume (V) ratio if the sorption coefficient (K_c) is known [45]:

$$R_c = 1 + \frac{A}{V} K_c, \quad (5)$$

These tracers are required to be water soluble, ionized (electrically charged), and can be organic or inorganic substances. The selection of tracers for this application is based on the surface charge of the sorbents. Further, the pH condition strongly influences the charge states of organic compounds (e.g., bases, acids, and ampholytes) and the sorbent's surface [33]; thus, pH and the point of zero charge of the surface should be considered before selecting a tracer compound.

Many laboratory tests have been conducted to demonstrate the feasibility of charged surface tracers to interrogate the surface area, e.g., using safranin [46], lithium [47–49], and monoamines [50]. A couple of field tests have also demonstrated the potential use of charged surface tracers for investigating the surface area, e.g., using safranin [51] and caesium [52,53]. Furthermore, this tracer type has the potential to estimate the ion exchange capacity of sediments [54].

3.1.2. Fluid–Fluid

The fluid-fluid tracers summarize liquid–liquid tracers and liquid–gas tracers due to the similarity in the underlying processes and applications.

Volume Sensitive Tracers

A volume sensitive tracer is a compound that partitions between two immiscible fluid phases (liquid–liquid or liquid–gas). A different solubility in the two fluid phases leads to the specific phase distribution and results in a retardation of the tracer. Volume sensitive tracers are very useful in estimating the volume of the immobile phase (residual saturation). For example, one common application of this type of tracer is to characterize the source zone of non-aqueous phase liquids (NAPLs) for contaminated sites. Another popular use is to evaluate the effectiveness of treatment techniques before and after the remediation of NAPLs, thereby obtaining independent estimates on the performance of the cleanup. This tracer can also be used to identify residual gas or supercritical fluid phases, such as in carbon capture and storage applications. When sorption onto solids is negligible, the retardation factor (R_{vs}) is a function of the average residual saturation (S_r) within the tracer flow field [55,56]:

$$R_{vs} = 1 + \frac{S_r}{(1-S_r)} K_{vs} \quad (6)$$

where K_{vs} is the partition coefficient between two fluid phases.

A large number of laboratory experiments and field-scale tests have been conducted to detect NAPL contaminations since the 1990s. The most commonly applied volume sensitive tracers are alcohols of varying chain length, such as 1-hexanol [57–60], 1-pentanol and 1-heptanol [61–63], 2-ethyl-1-butanol [5,61,64], 6-methyl-2-heptanol [65,66], 2,2-dimethyl-3-pentanol [56,65,66], 2,4-dimethyl-3-pentanol [57,63,64,67–70], substituted benzyl alcohols [6,71] and fluorotelomer alcohols [72]. Additionally, sulfur hexafluoride (SF_6) [73–77], perfluorocarbons [61,78], radon-222 [79–81], and fluorescent dyes (e.g., rhodamine WT, sulforhodamine B, and eosin) [82] have also been suggested for use as volume sensitive tracers. Recently, the noble gases krypton and xenon were applied successfully in the determination of the residual CO_2 saturation [83–87].

Interface Sensitive Tracers

An interface sensitive tracer is a compound that undergoes the accumulation (adsorption) at the interface between two immiscible fluids, typically liquid–liquid or liquid–gas, leading to the retardation of the tracer. The magnitude of adsorption at the interface is controlled by the physicochemical properties of tracer compounds and by the interfacial area, particularly the size of the specific fluid–fluid interfacial area (a_{nw}) and the interfacial adsorption coefficient (K_{if}). The retardation factor (R_{if}) defined through porous media follows [88,89]:

$$R_{if} = 1 + \frac{a_{if}}{\theta_w} K_{if} \quad (7)$$

$$K_{if} = \frac{G_{eq}}{C_{eq}} \quad (8)$$

where a_{if} is the specific interfacial area, θ_w is the volumetric water content, and K_{if} is the interfacial adsorption coefficient (ratio between the interfacial tracer concentration in the sorbed phase at the interface (G_{eq}) and the fluid (C_{eq}) at equilibrium).

The desired compounds for this tracer class are amphiphilic molecules (containing both hydrophobic and hydrophilic groups). Information on fluid-fluid interfacial areas, along with residual saturation (assessed by volume sensitive tracers) assists the understanding of the fate and transport of contamination in the systems.

One of the most popular interface sensitive tracers that have been successfully tested in laboratory and field scales is the anionic surfactant sodium dodecylbenzene sulfonate [67,69,88,90–100]. Further potential arises for other ionic and non-ionic surfactants (e.g., marlinat [101], 1-tetradecanol [102,103], sodium dihexylsulfosuccinate [104]) and for cosurfactants (e.g., *n*-octanol and *n*-nonanol [105]).

3.2. Kinetic Tracers

3.2.1. One Phase

Degradation Sensitive Tracers

Degradation sensitive tracers are compounds that undergo biotic and/or abiotic transformations. Depending upon the nature of the tracer specific (reaction controlling boundary conditions), chemical and/or biological characteristics of the flow system can be investigated. Information on the decay mechanism and the equivalent kinetic parameters is a prerequisite for their successful application. The decay mechanism is usually desired to follow a (pseudo) first order reaction to limit the number of required kinetic parameters and to avoid ambiguity. In addition, other influencing factors on kinetics should be considered before application (e.g., pH, light, and temperature). The reaction rate constant (k_{DS}) can be estimated by measuring the extent of tracer loss of the mother compound or the associated increase of a transformation product along the flow path.

This type of tracer has been studied and tested in field-scale experiments over the past 20 years. Their main purpose is to determine microbial metabolic activity (natural attenuation processes) and/or to assess redox conditions. Numerous redox-sensitive tracers have been applied for laboratory and field scale investigations, such as inorganic electron acceptors (e.g., O_2 , NO_3^- , SO_4^{2-} , CO_3^{2-}) [106–116], organic electron donors (e.g., low-molecular weight alcohols and sugars [117] and benzoate [118–120]), or the organic electron acceptor resazurin [8,121–128].

Thermo-Sensitive Tracers

Thermo-sensitive tracers are compounds undergoing chemical reactions that are well-defined and temperature driven, such as hydrolysis [129–131] or thermal decay [132,133]. Prior knowledge on their reaction mechanisms is required for each specific thermo-sensitive tracer. To avoid ambiguity, reactions following (pseudo) first order reaction are desired, and the reaction speed (expressed by the reaction rate constant (k_{TS})) is preferred to be solely controlled by temperature. For these reactions, the dependence of temperature (T) on k_{TS} is the essential factor for estimating the thermo-sensitivity expressed by Arrhenius law:

$$k_{TS} = Ae^{-\frac{E_a}{RT}}, \quad (9)$$

where A is the pre-exponential factor, E_a is the activation energy, and R is the ideal gas constant.

By knowing the corresponding kinetic parameters, the equivalent temperature (T_{eq}) and the cooling fraction (χ) can be obtained [134]. T_{eq} references the thermal state of a probed reservoir relative to an equivalent system having isothermal conditions, whereas χ has the potential to further estimate a spatial temperature distribution of the investigated system.

A typical application of these tracers is to investigate the temperature distribution of a georeservoir. The first field experiments using ester compounds (ethyl acetate and isopentyl acetate), however, were unable to determine a reservoir temperature [135–137]. The failure of the studies was

attributed to the poor determination of pH dependence and the lower boiling point of the tracer compounds compared to the reservoir temperature leading to vaporization. New attempts demonstrated the successful application in the laboratory [9] and in the field [138]. Other studies using classical tracers like fluorescein [139] or Amino G [132,133] were able to identify the reservoir temperatures. Currently, extensive research has been conducted to study structure-related kinetics of defined thermo-sensitive reactions with promising results [9,10,130,131,134].

3.2.2. Two Phases

Kinetic Interface Sensitive (KIS)

KIS tracers are intended to be dissolved or mixed with a non-aqueous carrier fluid (e.g., supercritical CO₂ [11]) and injected into the reservoir. The underlying process is an interface-sensitive hydrolysis reaction at the interface between the aqueous and the non-aqueous phase. Here, the tracer saturates the interface of the evolving plume due to interfacial adsorption and reacts irreversibly with water (hydrolysis with first-order kinetics). Due to the constant (adsorbed) concentration of the reactant at the interface, the reaction kinetics is simplified to (pseudo) zero order kinetics. The formed reaction products are monitored in the water phase.

In order to have minimal partitioning into the polar water phase, the potential tracers have to be non-polar in conjunction with high $\log K_{OW}$ values. Furthermore, the KIS tracer reaction kinetics has to be adapted to the characteristics of the reservoir (T, pH) and the interfacial area dynamics in order to resolve the plume development. In contrast to the parent compound, at least one of the reaction products has to be highly water soluble resulting in low or even negative $\log K_{OW}$ values. Thus, back-partitioning into the non-aqueous phase can be avoided.

This class of reactive tracers was originally intended to characterize the fluid–fluid interfacial area (e.g., between supercritical CO₂ and formation brine during CO₂ storage experiments [140]). Currently, only limited laboratory experiments with the supercritical CO₂ analogue fluid *n*-octane are available [11].

3.3. Reactive Tracers for Partitioning

A reactive tracer for partitioning is a compound comprising the features of both partitioning tracers and kinetic tracers. This type of tracer undergoes in-situ decay of the parent tracer compounds with subsequent partitioning of the daughter compounds. The concentration of both parent and daughter compounds are determined. The separation of the arrival times of the two tracers indicates the residual saturation similar to volume sensitive tracers (see section 3.1.2). The tracer compounds are hydrophilic and must be susceptible to decay leading to daughter compounds with different partitioning coefficients. Kinetic parameters should be evaluated in order to acquire suitable compounds for specific conditions of tracer tests (e.g., types and time scales). In contrast to kinetic tracers, the kinetic parameters are not used in the evaluation of the breakthrough curves for these tracers.

The most common fields for the application of these types of tracers are oilfields and carbon capture and storage. Esters like ethyl acetate have been proposed to determine the residual oil saturation according to Cooke [141]. By 1990 they have been successfully applied to oilfields [142,143] and are continued to be implemented today [144,145]. Myers et al. (2012) demonstrate the feasibility of using reactive ester tracers (i.e. triacetin, propylene glycol diacetate and tripropionin) to quantify the amount of residually trapped CO₂ through an integrated program of laboratory experiments and computer simulations. Later, the research was also demonstrated successfully in field experiments [146].

4. Exploitation Potential and Further Challenges of Developing Reactive Tracers

4.1. The Necessity for New Tracers—Tracer Design Approach

The use of tracers for hydrogeological applications has a long history. The first reported tracer application was around 10 A.D. to track the connection between the spring source of the Jordan River and a nearby pond [147]. Since then, the development of technology and the advances of tracer testing with a wide selection of tracer compounds have brought effective tools for investigating different properties of the aquatic environment. In general, tracer tests could be applied to any kind of natural and engineered systems. It is especially advantageous for not directly accessible systems compared to other techniques. Nevertheless, there are still many systems in which the potential of using reactive tracers is not yet fully exploited and more attention should be paid to these, including:

- The hyporheic zone, a transition zone between surface water and subsurface water, has been recognized as a hotspot for biogeochemical reactions, making the exchange of water, nutrients, and organic matter important parameters. This zone is a mixing zone which has a complex hydrological situation and heterogeneity containing dissolved gasses, oxidized and reduced species, temperature patterns, flow rates, etc. Due to the large number of variables, the quantification of processes in the hyporheic zone is still a challenge [148,149].

- Hydraulic fracturing (fracking) in shale/tight gas reservoirs has gained growing interests in the oil and gas industry during the last decade [150]. However, fracking may pose environmental risks [151,152]. During the stimulation process, fracking fluid is injected into the reservoir to create additional flow paths for the transport of hydrocarbons. Hydraulically induced fractures may connect pre-existing natural fractures and faults leading to the creation of multiple permeable pathways which may cause groundwater contamination [153]. Therefore, there is a high demand for the application of tracers to predict the risk or to track the contamination (i.e. fracking fluid) [154].

- Other fields may include karst aquifer characterization (due to the strong system heterogeneity and variability), geothermal fluids and acid-mine-drainage (due to complex water chemistry and temperature).

The design of new innovative reactive tracers requires new strategies. Molecular design has been successfully established as a methodology for producing tailor-made molecules with desired properties or effects in several scientific disciplines, especially in life sciences, such as pharmacology, biochemistry, medicine [155], and material sciences [156]. The target-oriented combination of well-studied structural elements and molecular features (e.g., functional groups, substructures, homologues, etc.) allows the creation of novel compounds with desired structures and properties. Almost an unlimited number of compounds is imaginable and can be synthesized individually for a magnitude of applications. However, molecular target design of tracer substances for studying the aquatic environment has yet to be widely considered.

4.2. Strategy for Designing Novel Reactive Tracers

Creating tracer molecules, which react in a predictable way under given physicochemical conditions, is a relatively new and very innovative concept. By knowing exactly how certain reservoir conditions drive the tracer reaction, new insights into the controlling variables may be gained. In the following, the exemplary molecular target design of thermo-sensitive and interface-sensitive tracers is described. The prerequisite for the design (selection and modification) of molecules that are able to act as thermo-sensitive and interface-sensitive tracers in reservoir studies, respectively, is a thorough understanding of their reactive behavior. In particular, it is vital to understand the role and influence of each structural element in the molecule on its reaction kinetics and its physicochemical tracer properties (e.g., detection, acidity, solubility, sorption, etc.). In Figure 2, the main steps for a successful theoretical and practical molecular target tracer design are shown schematically.

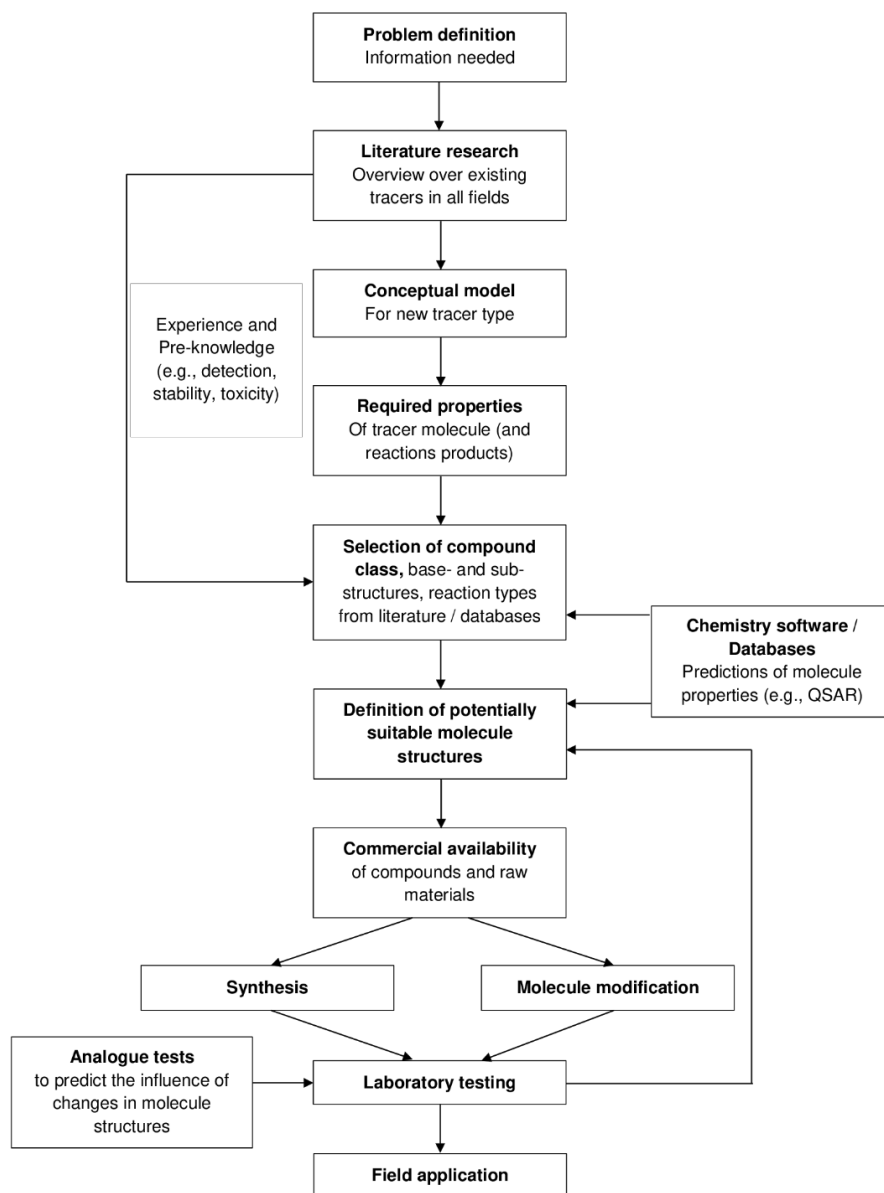


Figure 2. Schematic overview for the design of reservoir tracers.

Based on available literature and experiences from laboratory and field tests, a promising base molecule for both tracer types is believed to be the class of naphthalenesulfonates, into which thermo- and interface-sensitive groups can be incorporated (Figure 3). Several physicochemical attributes make them convenient for the selection as the backbone structure. Naphthalenesulfonates are strong acids with corresponding low logarithmic acidity constants (pK_a) of <1 . Therefore, this compound class forms anions even at very low pH values and is highly water-soluble ($>1000 \text{ g L}^{-1}$). The resulting pH-dependent $\log K_{OW}$ of -2.87 at $\text{pH} > 5$ (SciFinder, ACD (Advanced Chemistry Development)/Labs) is also very low, which implies a non-sorptive behavior and, thus, a high mobility in aquatic systems. Additionally, naphthalenesulfonates are stable under oxygen-free conditions and temperatures up to $250 \text{ }^\circ\text{C}$ [129,157]. The molecule's good fluorescence with a direct detection limit in the low $\mu\text{g L}^{-1}$ range is another important feature of naphthalenesulfonates. Hence, their detection in field tests by online determination simplifies the experimental effort needed. Furthermore, (high-pressure liquid) ion pair chromatography combined with solid phase extraction and fluorescence detection (SPE-IPC-FLD) lowers the detection limit by around one order of magnitude ($<1 \mu\text{g L}^{-1}$) even in highly saline matrices, such as brines from deep reservoirs [158,159].

The chromatographic separation even allows the simultaneous analysis of several compounds and, therefore, the use of different isomers, derivatives, and homologues. Finally, naphthalenesulfonates are non-toxic [160], their use in groundwater studies is administratively non-restricted, and they are established conservative tracers for the characterization of geothermal reservoirs [158,161].

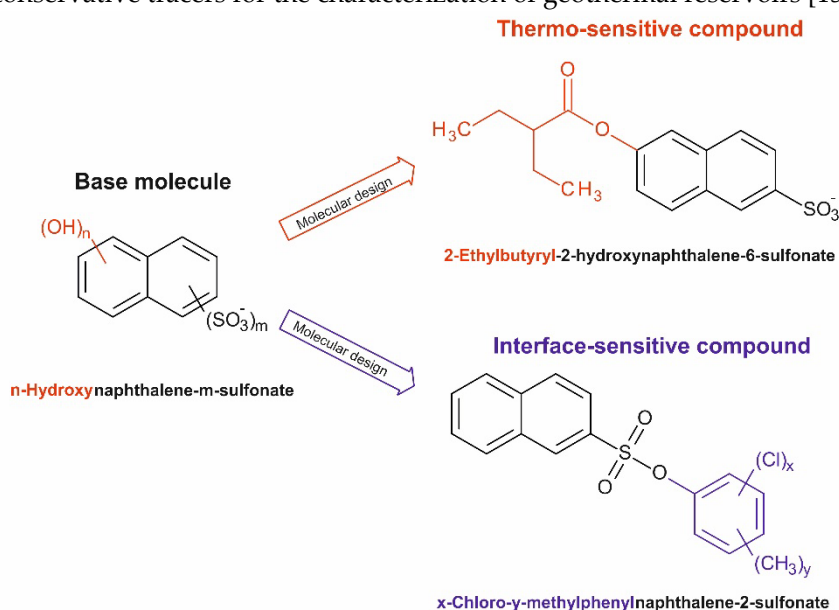


Figure 3. Design of two different types of potential reservoir tracers based on naphthalenesulfonate as common structural element.

5. Summary and Conclusions

The selection of optimal reactive tracer compounds is main challenge that needs to be considered before conducting a tracer test. For instance, when designing a thermo-sensitive tracer test, a tracer that decays too slowly under a system's temperature lengthens test duration needlessly and thus makes observing the differences in mean residence times difficult; too fast decay makes it challenging for the test implementation. Moreover, new reactive tracer compounds have been extensively developed in the past decades due to the demand in new advanced technologies. Therefore, a complete understanding of the physicochemical properties of reactive tracers and their occurring processes is essential. Depending on the biophysicochemical behavior, three types of reactive tracers can be distinguished, namely: equilibrium tracers, kinetic tracers and reactive tracer for partitioning. Equilibrium tracers are based on the partitioning equilibrium between two immiscible phases or at their interfaces. Kinetic tracers are non-equilibrium tracers in which only the reaction kinetics are used for the parameter determination. Reactive tracers for partitioning are a hybrid form of equilibrium tracers and kinetic tracers.

The complexities of natural systems, along with the large number of requirements for the tracers, make the selection and use of reactive tracers not a simple task, but an art. Based on the knowledge of tracer properties, tailor-made tracer compounds are being developed with the required properties or effects in hydrogeology. The target-oriented combination of well-studied structural elements and molecular features (e.g., functional groups, substructures, homologues) allows for the creation of novel compounds with desired structures and properties. Nearly an unlimited number of compounds can be synthesized individually for specific applications. This innovative concept can expand the potential application of tracers in different fields (e.g., quantification of processes in the hyporheic zone, prediction of environmental risks of hydraulic fracturing). Molecular design assists the preselected properties (e.g., fluorescence) of both reactants and products. This allows a mass balance, and thereby opens the opportunity of a tracer test design without an additional conservative tracer.

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