

SOLUTE REACTIVE TRACERS FOR HYDROGEOLOGICAL APPLICATIONS: STARTING AN OVERDUE PROGRESS IN KNOWLEDGE

Viet Cao^{1,*}, Tobias Licha²

¹Faculty of Natural Sciences, Hung Vuong University, Phu Tho, Vietnam

²Institute for Geology, Mineralogy and Geophysics, Ruhr-Universität Bochum, Bochum, Germany

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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) equilibrium 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: Hydrogeological tracer test, Kinetics, Partitioning, Reactive tracers, Tailor-made tracer design.

1. Introduction

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 [1,2]. 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 article is to present a systematic review of existing and proposed reactive solute tracers based on current research advances conducted in different scientific fields. For each subclass of tracer, the underlying process, their key properties, and possible target parameters/

*Email: caoviet@hvu.edu.vn

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. 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):

- Equilibrium 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.

2.1. Equilibrium tracers

2.1.1. 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) [3]. 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 [4]. 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:

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

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 [5,6] $\log K_{OW}$ can empirically be related to the organic carbon normalized sorption coefficient (KOC) in the form:

$$\log K_{OC} = a \log K_{OW} + b \quad (2)$$

Table 1. Classification of reactive tracers

	Reactive tracers (non-conservative tracers)					
	Equilibrium tracers (partitioning tracers)		Kinetic tracers (decaying tracers)			
	Fluid-Solid	Fluid-Fluid	Reactive tracer for partitioning (volume or inter-face sensitive after degradation)	One phase	Two phases	
	Sensitive for uncharged 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	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	Hydrolyzable and hydrophilic compounds with known kinetic parameters and decay mechanisms
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 saturation or residual distribution, contact area	Attenuation capacity, other reaction relevant boundary conditions (e.g., redox conditions, pH)	Temperature and temperature distribution (cooling reactions)
Underlying (reactive) process	Sorption due to hydrophobic interactions	Sorption due to electrostatic interactions (e.g., ion exchange, hydrogen bonding)	Phase partitioning	Intertacial adsorption (partitioning between bulk phase and interface)	Chemical and biological reactions	Hydrolysis reaction leading to inter-phase mass transfer

$$K_{OC} = \frac{K_{unc}}{f_{OC}} \quad (3)$$

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.* [4,7] 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 [8], short-chained alkyl phenols [9], or pharmaceutical compounds [10,11].

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 (Eq. 1) or to its surface sensitivity to the surface area (A) to volume (V) ratio if the sorption coefficient (K_c) is known:

$$R_c = 1 + \frac{A}{V} K_c \quad (4)$$

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 [12]; 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 [13], lithium [14,15], and monoamines [16]. A couple of field tests have also demonstrated the potential use of charged surface tracers for investigating the surface area, e.g., using safranin [17] and caesium [18,19]. Furthermore, this tracer type has the potential to estimate the ion exchange capacity of sediments [20].

2.1.2. 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:

$$R_{vs} = 1 + \frac{S_r}{(1 - S_r)} K_{vs} \tag{5}$$

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 1990's. The most commonly applied volume sensitive tracers are alcohols of varying chain length, such as 1-hexanol [21,22], substituted benzyl alcohols [23] and fluorotelomer alcohols

[24]. Additionally, sulfur hexafluoride (SF_6) [25,26], perfluorocarbons [27,28], radon-222 [29,30], and fluorescent dyes (e.g., rhodamine WT, sulforhodamine B, and eosin) [31] 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 [32,33].

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_{if}) and the interfacial adsorption coefficient (K_{if}). The retardation factor (R_{if}) defined through porous media follows:

$$R_{if} = 1 + \frac{a_{if}}{\theta_w} K_{if} \tag{6}$$

$$K_{if} = \frac{G_{eq}}{C_{eq}} \tag{7}$$

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 [34–36]. Further potential arises for other ionic and non-ionic surfactants (e.g., marlinat [37], 1-tetradecanol [38, 39], sodium dihexylsulfosuccinate [40]) and for cosurfactants (e.g., n-octanol and n-nonanol [41]).

2.2. Kinetic tracers

2.2.1. 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 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-}) [42–44], organic electron donors (e.g., low-molecular weight alcohols and sugars [45] and benzoate [46,47]), or the organic electron acceptor resazurin [48,49].

Thermo-sensitive tracers

Thermo-sensitive tracers are compounds undergoing chemical reactions that are well-defined and temperature driven, such as hydrolysis [50,51] or thermal decay [52,53]. 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:

$$k_{TS} = A e^{-\frac{E_a}{RT}} \quad (8)$$

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 (c) can be obtained [54]. T_{eq} references the thermal state of a probed reservoir relative to an equivalent system having isothermal

conditions, whereas c 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 [55, 56]. 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 [57] and in the field [58]. Other studies using classical tracers like fluorescein [59] or Amino G [53] 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 [51, 54, 60].

2.2.2. Two phases

Kinetic interface sensitive (KIS)

KIS tracers are intended to be dissolved or mixed with a non-aqueous carrier fluid (e.g., supercritical CO_2 [1]) 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 CO_2 and formation brine during CO_2 storage experiments [61]). Currently, only limited laboratory experiments with the supercritical CO_2 analogue fluid n-octane are available [1].

2.3. Reactive tracers for partitioning

A reactive tracer for partitioning is a compound comprising the features of both equilibrium 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 [62]. By 1990 they have been successfully applied to oilfields [63,64] and are continued to be implemented today [65,66]. 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 [67].

3. Exploitation potential and further challenges of developing reactive tracers

3.1. The necessity for new tracers -Tracer design approach

In general, tracer tests could be applied to any kind of natural and engineered systems. It is especially advantageous for systems that are not directly accessible 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, for example:

- The hyporheic 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 a large number of variables, the quantification of processes in the hyporheic zone is still a challenge [68,69]. Currently, resazurin is the only tracer being investigated in which promising results are obtained for accessing the hyporheic processes and exchanges [48,49].

- Hydraulic fracturing (fracking) in shale/tight gas reservoirs has gained growing interests in the oil and gas industry during the last decade, but fracking may pose environmental risks [70]. 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 [71]. Therefore, there is a high demand for the application of tracers to predict the risk or to track the contamination (i.e. fracking fluid) [72].

The design of 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, such as pharmacology, biochemistry, medicine [73]. 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.

3.2. 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 Fig. 1 the main steps for a successful theoretical and practical molecular target tracer design are shown schematically.

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 (Fig. 2). Several physicochemical attributes make them convenient for the selection as the backbone structure. Naphthalenesulfonates are strong acids with corresponding low logarithmic acidity constants (pKa) 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/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°C [74,75]. 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 [76,77]. 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 [78], their use in groundwater studies is administratively non-restricted, and they are established conservative tracers for the characterization of geothermal reservoirs [76,79].

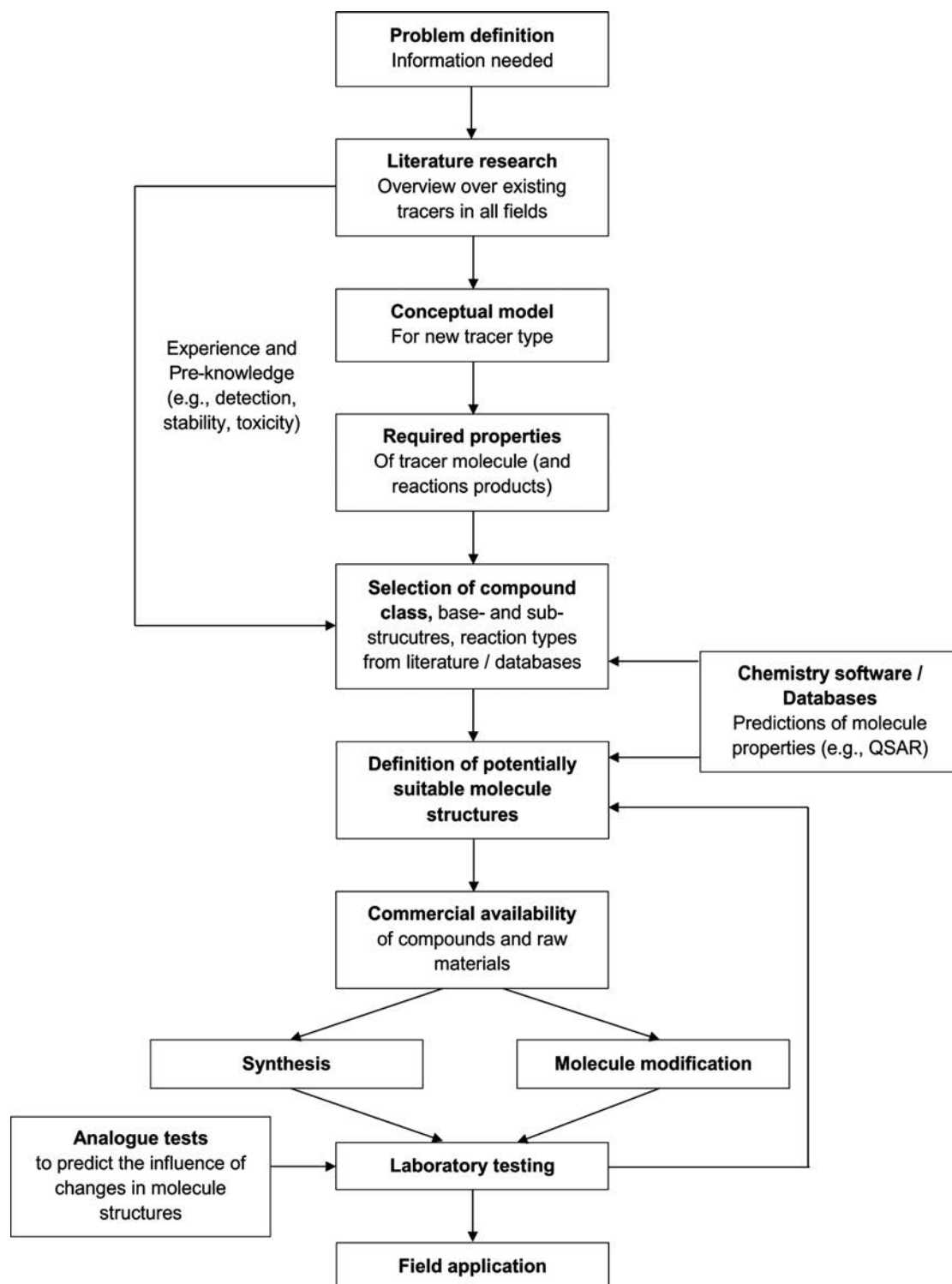


FIG. 1. Schematic overview for the design of reservoir tracers

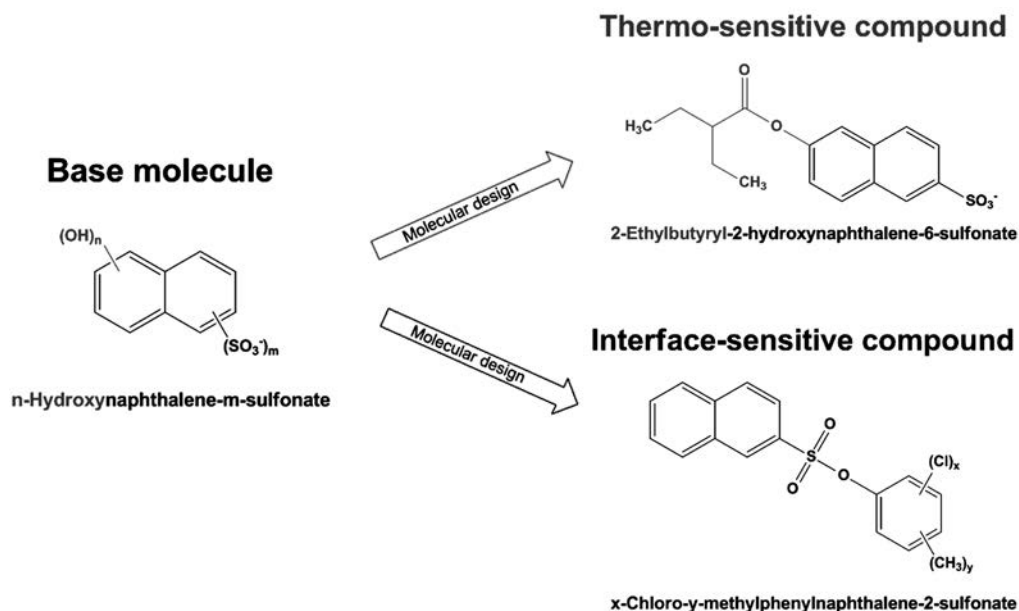


FIG. 2. Design of two different types of potential reservoir tracers based on naphthalenesulfonate as common structural element.

4. 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 decay too slowly under 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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CHẤT THĂM DÒ HOẠT ĐỘNG TRONG NGHIÊN CỨU ĐỊA THỦY VĂN

Cao Việt^{1,*}, Tobias Licha²

¹ Khoa Khoa học Tự nhiên, Trường Đại học Hùng Vương, Phú Thọ

² Viện Địa chất, Khoáng vật và Địa vật lý, Trường Đại học Ruhr-Bochum, CHLB Đức

TÓM TẮT

Phương pháp sử dụng chất thăm dò là một trong những phương pháp phổ biến để nghiên cứu môi trường nước và các quá trình trong địa chất thủy văn. Việc kết hợp chất thăm dò bảo toàn với ít nhất một chất thăm dò hoạt động được sử dụng rộng rãi để xác định thêm những thông số đặc trưng của hệ như nhiệt độ, hoạt động của vi sinh vật, những đặc điểm mà không thể đo đạc một cách trực tiếp.

Hiện nay, mặc dù được ngày càng có nhiều chất thăm dò hoạt động mới được nghiên cứu, phát triển và ứng dụng, nhưng chưa có nghiên cứu tổng quan và hệ thống hóa các chất thăm dò hoạt động. Mỗi chất thăm dò hoạt động đều có ưu và nhược điểm riêng. Lựa chọn áp dụng chất thăm dò dựa trên điều kiện thực tiễn và mục tiêu nghiên cứu. Bài báo phân loại chất thăm dò theo tính chất hóa học của chúng theo 3 nhóm: (1) chất thăm dò cân bằng, (2) chất thăm dò động học, và (3) chất thăm dò hoạt động theo sự phân bố. Đồng thời cũng đề xuất các hướng nghiên cứu mới tiềm năng và hướng tới việc chế tạo các chất thăm dò theo từng đối tượng, mục đích cụ thể.

Keywords: *Chất thăm dò hoạt động, Chế tạo chất thăm dò hoạt động theo nhu cầu, Hoạt động thăm dò hóa học.*