DYES AS TRACERS FOR VADOSE ZONE HYDROLOGY

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[1] Dyes are important tracers to investigate subsurface water movement. For more than a century, dye tracers have provided clues about the hydrological cycle as well as flow and transport processes in the subsurface. Groundwater contamination often originates in the vadose zone. Agrochemicals applied to the soil surface, toxic compounds accidentally spilled by human activities, and contaminants released from waste repositories leach through the vadose zone and can ultimately pollute groundwater resources. Dyes are an important tool to assess flow pathways of such contaminants. This review compiles information on dyes used as hydrological tracers, with particular emphasis on vadose zone hydrology. We summarize briefly different human-applied tracers, including nondye tracers. We then provide a historical sketch of the use of dyes as tracers and describe newer developments in visualization and quantification of tracer experiments. Relevant chemical properties of dyes used as tracers are discussed and illustrated with dye intermediates and selected dye tracers. The types of dyes used as tracers in subsurface hydrology are summarized, and recommendations are made regarding the use of dye tracers. The review concludes with a toxicological assessment of dyes used as hydrological tracers. Many different dyes have been proposed as tracers for water movement in the subsurface. All of these compounds, however, are to some degree retarded by the subsurface medium. Nevertheless, dyes are useful tracers to visualize flow pathways.
Index Terms: 1875 Unsaturated zone; 1829 Groundwater hydrology; 1832 Groundwater transport; *Keywords:* dyes, tracers, vadose zone, visualization, unsaturated zone
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1. INTRODUCTION

[2] Tracers play an essential role in the experimental investigation of chemical, physical, and biological systems. In general, a tracer is a substance or entity

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that is experimentally measured in a system of interest for the purpose of deducing process information from the tracer signal. Tracers are used when the system of interest is inaccessible by direct measurements. Such systems are ample, for example, the human body, a chemical reactor, or the subsurface environment. To be detected by a measuring device, a tracer must be distinctively different from other substances or entities within the system of study. Various forms of tracers are used, including chemicals, solid particles, or energy (e.g., temperature).

[3] In hydrology, and specifically in subsurface hydrology, tracers have played a significant role in elucidating our current understanding of the hydrological cycle and of subsurface flow and transport processes. Determinations of flow connections, flow velocities, and hydrodynamic dispersion are the most common uses of tracers. Although a wide variety of tracers are used, dyes have been, and remain, among the most prominent subsurface water tracers. The popularity of dyes is attributable to their low detection limits, visualization potential, and ease of quantification by chemical analysis.

[4] The vadose zone is the unsaturated subsurface region between the soil surface and the groundwater table, and it plays an important role in protecting groundwater resources from contamination. The vadose zone acts as a filter that helps remove chemical and biological contaminants. Widespread groundwater contamination, however, reveals that this filter is leaky. For example, agrochemicals, contaminants from waste repositories, and other toxic compounds can leach through the vadose zone to pollute the groundwater. Dye tracers are invaluable tools to understand flow pathways and transport mechanisms, thereby helping to better manage and protect water resources.

[5] Many dyes have been used as hydrological tracers; the most prominent are probably Fluorescein/Uranine and Rhodamine WT. The selection of a specific dye as a tracer depends on a variety of factors including the purpose of the experiment, the physical and chemical characteristics of the medium, and the method of tracer detection. Apparently, no single, ideal dye tracer exists. With the exception of a few selected dyes a systematic and comprehensive comparison of dye tracer characteristics is lacking.

[6] The purpose of this manuscript is to review the use of dyes as tracers in hydrology, with particular emphasis on use in the vadose zone. We provide (1) a brief summary of different human-applied tracers, (2) a historical sketch of the use of dyes as tracers, (3) a description of relevant chemical characteristics of dyes used as tracers, (4) a compilation of dyes used as subsurface tracers, (5) a description of dye tracer visualization and quantification, and (6) a toxicological assessment of dye tracers.

2. HUMAN-APPLIED TRACERS IN HYDROLOGY

2.1. Definitions and Characteristics

[7] Human-applied tracers are applied purposely to investigate certain aspects of the hydrological system. Commonly, these tracers are used to analyze flow pathways, velocities and travel times, hydrodynamic dispersion, recharge, and discharge. In most cases the tracer is used to track the movement of water. Consequently, an ideal water tracer has the following characteristics [*Kaufman and Orlob*, 1956; *Church*, 1974; *Davis et al.*, 1980; *McLaughlin*, 1982]:

1. The tracer is conservative in behavior. The tracer moves in a manner similar to water, that is, (1) without sorption to soils, sediments, or rocks and (2) without degradation during the time frame of interest.
2. The tracer has low background concentration. The tracer is clearly discernible from the background of the system.
3. The tracer is insensitive to changes in solution chemistry. The tracer's fate and transport behavior are unaffected by changes in pH, alkalinity, or ionic strength of the aqueous solution.
4. The tracer is detectable either by chemical analysis or by visualization.
5. The tracer generates a low toxicological impact on the study environment.

[8] As concluded by others [*Kaufman and Orlob*, 1956; *Church*, 1974; *Davis et al.*, 1980], an ideal water tracer is nonexistent. The tracer closest to ideal is the water molecule itself, containing the stable isotopes of ^{2}H or ^{18}O.

[9] Less frequently, tracers are used to track the movement of compounds other than water, particularly when the compounds themselves are restricted for experimentation because of health risks. A prime example is the use of nonpathogenic microorganisms as indicators of the fate and transport of pathogenic microorganisms, such as human enteric viruses [*Keswick et al.*, 1982; *Snowdon and Cliver*, 1989; *International Assocation on Water Pollution Research Control Study Group on Health-Related Water Microbiology*, 1991; *Jin and Flury*, 2002]. In these cases the main criterion for a good tracer is how well the tracer mimics the fate and transport of the target compound.

[10] Human-applied tracers are different than environmental tracers. Environmental tracers are substances that occur naturally in the environment or are released inadvertently to the environment through human activities and later, owing to their persistence, become useful hydrological tracers. In subsurface hydrology the most commonly used environmental tracers are isotopes of H (^{2}H and ^{3}H), O (^{18}O), and Cl (^{36}Cl and ^{37}Cl), but many other isotopes and synthetic chemicals have been used as well. Several reviews and monographs on environmental tracers and their uses have been published [*Knutsson*, 1968; *Payne*, 1972; *White*, 1976; *Phillips*, 1994, 1995; *Clark and Fritz*, 1997; *Scanlon et al.*, 1997; *Käss*, 1998].

2.2. Types of Human-Applied Tracers

[11] Many different types of human-applied tracers are used in subsurface hydrology and are reviewed and compiled in several publications [*Drew*, 1968; *Knutsson*, 1968; *Church*, 1974; *White*, 1976; *Davis et al.*, 1980; *Keswick et al.*, 1982; *McLaughlin*, 1982; *Käss*, 1998]. For completeness, we provide a brief summary of these tracers.

2.2.1. Temperature

[12] Well injection of water with a temperature different from the ambient water temperature allows detection of the thermal pulse with spatially and temporally resolved temperature measurements [*Keys and Brown*, 1978]. Temperature tracing is useful for locating high-permeability zones in an aquifer [*Keys and Brown*, 1978], providing the temperature differences between injected and background waters are small to avoid significant changes in density and viscosity of the fluid [*Davis et al.*, 1980].

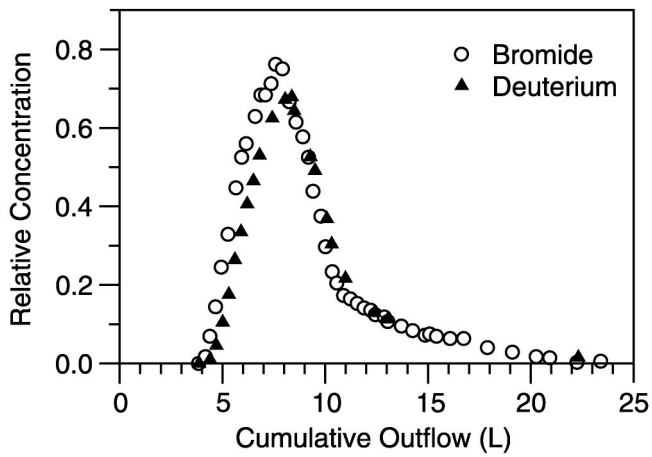

Figure 1. Breakthrough curves of bromide and deuterium through a 2.5-m-long column of loamy sand, showing accelerated movement of bromide due to anion exclusion [from *Bowman* 1984b]. Reproduced by permision of Soil Science Society of America.

2.2.2. Isotopes

[13] Common isotopes used as tracers in subsurface hydrology are the stable isotopes ^{2}H, ^{13}C, ^{15}N, ^{18}O, and ^{34}S and the radioactive isotopes ^{3}H, ^{51}Cr, ^{60}Co, ^{82}Br, and ^{131}I [*Drew*, 1968; *Knutsson*, 1968; *Gaspar and Oncescu*, 1972; *White*, 1976; *Davis et al.*, 1980]. Owing to increased awareness of radiation risks, radioactive tracers are used infrequently [*Davis et al.*, 1980]. Currently, isotopes used as human-applied tracers are usually short-lived, such as ^{75}S with a half-life of 119.7 days. In the form of selenate this isotope can be used as a water tracer [*Dunnivant et al.*, 1998]. Accidental spills of radioisotopes from waste sites [*Knutsson*, 1968] and industrial facilities [*Hoehn and Santschi*, 1987] create unintentional tracer experiments. Deuterium ($^{2}H_2O$) at low concentrations is considered the most ideal water tracer; however, like most other stable isotopes, sophisticated instrumentation is required for chemical analysis and quantification.

2.2.3. Inorganic Anions

[14] In addition to deuterium, Cl^- and Br^- are considered almost ideal conservative tracers for water movement. These anions rarely sorb to soil particles, and often chloride and bromide move faster than the average water molecule. In column experiments these characteristics are manifested by a breakthrough earlier than one pore volume or a faster breakthrough compared to deuterium or tritium (Figure 1). This phenomenon is attributed to the repulsion of the anions from the negatively charged solid particles and is often called anion exclusion. Chloride, Br^-, and NO_3^- adsorb mainly as diffusive ion swarms and outer-sphere complexes and, as such, can be excluded from the diffusive ion swarm by electrostatic repulsion [*Sposito*, 1989]. Anion adsorption and exclusion are dependent on pH, since pH often affects the net proton charge of soil particles. The pH of the soil environment is particularly relevant in two cases: (1) when ions are present that do not protonate significantly, such as, Cl^-, Br^-, and NO_3^-, and (2) when the soil contains a high percentage of variably charged minerals.

[15] Anions like PO_4^{3-} or F^- sorb to the solid phase by ligand exchange and are less affected by anion exclusion; but, because of strong sorption, these anions are unsuitable as hydrological tracers. Iodide sorbs to some degree to soil minerals [*Davis et al.*, 1980; *Bowman*, 1984b], has a low oxidation potential, and oxidizes under aerobic conditions [*Bowman*, 1984b], limiting its use as a water tracer.

[16] Compared with F^-, Cl^-, I^-, and NO_3^-, the bromide ion is the most suitable as a human-applied tracer in field studies. Nitrate is subject to chemical transformations, and Cl^- occurs in large quantities in soils and aquifers. The concentrations of bromide in natural waters are ~300 times smaller than those of chloride [*Davis et al.*, 1980]. The toxicity of bromide is low [*Flury and Papritz*, 1993], and, unless an excessive amount is applied, no toxicological problems should arise. On the basis of bromide toxicity data, *Flury and Papritz* [1993] proposed a quality criterion of 1 mg L^{-1} of groundwater. Below this concentration, chronic toxicological effects on aquatic organisms should be nonexistent.

[17] A special class of tracers are metal-ethylene diamino tetraacetic acid (EDTA) complexes, which can have a neutral or negative charge. Metals used for complexation are Cu, Zn, Co, Pb, and Cr [*Knutsson*, 1968; *White*, 1976; *Davis et al.*, 1980]. The health risk that these heavy metals pose limits the use of these EDTA complexes in field applications.

[18] Anions will not behave conservatively if the soil or sediment material possesses a dominant positive charge. Electrostatic adsorption of anions will occur, leading to considerable retardation of anions like Cl^- or Br^- [*Sposito*, 1989; *Seaman et al.*, 1996].

2.2.4. Fluorocarbons

[19] Chlorofluorocarbons (CFCs), which have been released to the environment by human activities since the 1940s, are classified as environmental tracers. CFCs were also proposed as human-applied tracers [*Malcolm et al.*, 1980] and were considered useful because they were nonreactive, were resistant to breakdown, and had low toxicity [*Davis et al.*, 1980]. In 1974, however, CFCs were linked to the destruction of the stratospheric ozone layer, and therefore they should not be used as human-applied hydrological tracers anymore.

2.2.5. Sulfur Hexafluoride

[20] Sulfur hexafluoride (SF_6) can be used as a gas phase and a liquid phase tracer. SF_6 is a nontoxic, colorless, odorless gas with density of 6.602 g L^{-1}, melting point of −50.75°C, vapor pressure of >1000 kPa for temperatures >0°C, and water solubility ranging from of 33.2 mg L^{-1} at 29.6°C to 74.0 mg L^{-1} at 2°C [*Wilson and McKay*, 1993; *Lide*, 1994].

[21] Anthropogenic emission of SF_6 to the environment began in 1953 [*Wilson and McKay*, 1993; *Busenberg and Plummer*, 2000]. Because of its persistence and stability in the environment, SF_6 has been a useful environmental tracer in atmospheric investigations [*Maiss et al.*, 1996] and groundwater dating [*Busenberg and Plummer*, 2000].

[22] SF_6 is used as a human-applied tracer for studying mixing and gas exchange in oceans, lakes [*von Rohden and Ilmberger*, 2001; *Bullister et al.*, 2002], and groundwater [*Wilson and McKay*, 1993, 1996; *Dillon et al.*, 1999]. In addition, *Kung* [1998] reported that SF_6 may be a useful tracer for detection of plutonium leakage from storage containers. SF_6 is also a potential geothermal tracer [*Upstill-Goddard and Wilkins*, 1995]. SF_6 is nontoxic, detectable at low concentrations (10^{-16} mol L^{-1}) [*Käss*, 1998], chemically and biologically stable, inert, and relatively inexpensive. The gas occurs in low background concentrations in the environment [*Wilson and McKay*, 1993; *Käss*, 1998] and requires no complicated technology for measurement and analysis [*Busenberg and Plummer*, 2000]. In saturated sand column tests, dissolved SF_6 has been found to move like bromide [*Wilson and McKay*, 1993]. However, because of the chemical's slight hydrophobicity, retardation could be expected in materials high in organic matter content [*Wilson and McKay*, 1996].

[23] The chemical properties and experimental evidence indicate that SF_6 may be useful as a human-applied tracer. However, SF_6 gas potentially produces a greenhouse warming effect 23,900 times higher than CO_2 [*Busenberg and Plummer*, 2000]; therefore the injection of SF_6 for tracing purposes should be considered with caution.

2.2.6. Ethanol, Benzoate, and Fluorobenzoates

[24] Ethanol and benzoate (benzoic acid) were found to be useful conservative tracers for groundwater movement [*Malcolm et al.*, 1980]. In a series of recharge and injection experiments both organic compounds moved like bromide. Benzoate, particularly because of its excellent sensitivity to spectrophotometry, was recommended as an excellent groundwater tracer [*Malcolm et al.*, 1980]. Benzoate and benzenesulfonic acids have also been used as geothermal groundwater tracers [*Adams et al.*, 1989].

[25] A variety of fluorinated benzoate compounds have been proposed as tracers [*Stetzenbach et al.*, 1982; *Bowman*, 1984b; *Bowman and Gibbens*, 1992] (Figure 2). The performance of the benzoate tracers was compared using bromide as a reference tracer [*Bowman*, 1984b; *Bowman and Gibbens*, 1992]. In laboratory column tests all benzoate tracers exhibited negligible sorption to the soil and aquifer materials. The mobility of the benzoates mimicked that of bromide; however, under field conditions some of the benzoate tracers appeared to degrade. On the basis of their resistance to degradation, *Bowman and Gibbens* [1992] ranked the fluorobenzoates in the following order, with PFBA being the best tracer,

$$\text{PFBA} > \text{2,6-DFBA} > \text{2,3-DFBA} = \text{2,5-DFBA} = \text{3,4-DFBA} = \text{3,5-DFBA} > o\text{-TFMBA} > m\text{-TFMBA}.$$

Sorption and transport of the benzoate tracers depends on the pH conditions, since all these tracers contain a carboxylic acid group. The pK_a values are relatively low (Table 1), so that under most environmental conditions the tracers should be predominantly negatively charged. Results from sorption and transport experiments indicate that benzoate tracers behave conservatively as long as the pH of the pore solution remains about two pH units above the tracer's pK_a [*McCarthy et al.*, 2000].

[26] Questions remain regarding the suitability of fluorobenzoate tracers in material containing large amounts of clay and organic matter. Various fluorobenzoates behave differently under conditions of considerable organic matter and clay contents. According to a study by *Jaynes* [1994] the following fluorobenzoate tracers exhibited a minimal amount of retardation and degradation: PFBA, 2,5-DFBA, 2,6-DFBA, and *o*-TFMBA. The other fluorobenzoates tested, *m*-TFMBA, 3,4-DFBA, and 3,5-DFBA, retarded considerably and were deemed unsuitable tracers. (Note that *Jaynes* [1994] did not test 2,3-DFBA.) *Seaman* [1998] found that fluorobenzoates sorb to organic matter and hydrous Fe-oxides. Using highly weathered soil and aquifer material, the retardation of fluorobenzoates at pH 5 increased with increasing pK_a of the tracer. Retardation was attributed to partitioning to organic carbon and to sorption to Fe-oxides.

[27] The acute toxicity of fluorobenzoates to aquatic organisms appears low. Toxicological data indicate that the toxicity increases with the degree of fluorination, but for several fluorobenzoates, including PFBA, the lethal dose when 50% of the population is killed in a 96-hour

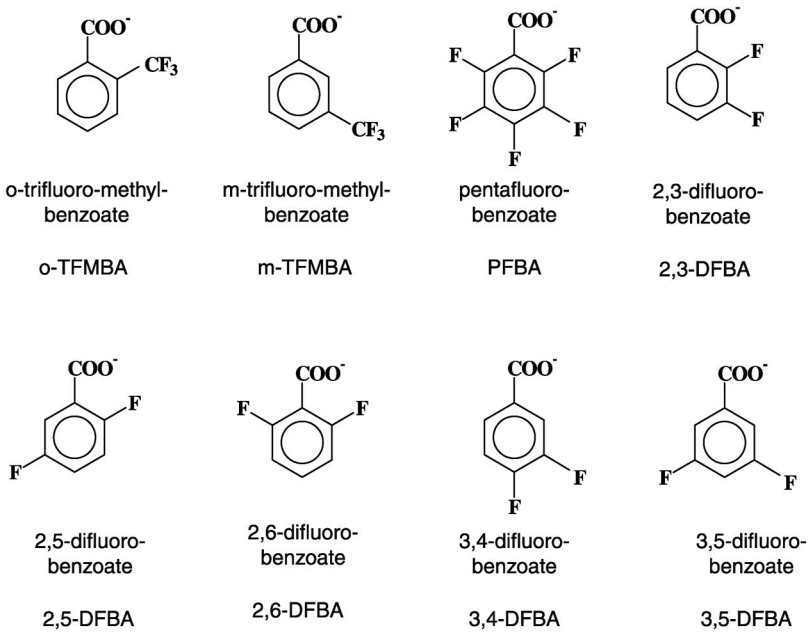

Figure 2. Fluorobenzoate tracers proposed by *Stetzenbach et al.* [1982] (m-TFMBA and PFBA), *Bowman* [1984b] (o-TFMBA, m-TFMBA, PFBA, and 2,6-DFBA), and *Bowman and Gibbens* [1992] (2,3-DFBA, 2,5-DFBA, 3,4-DFBA, and 3,5-DFBA).

Ceriodaphnia test was greater than 100 mg L^{-1} [*McCarthy et al.*, 2000]. Toxicity of fluorobenzoates to corn and soybean has been evaluated by *Jaynes* [1994].

[28] In summary, benzoate and fluorobenzoates are useful tracers that migrate, under most pH conditions found in soils and aquifers, similarly to bromide. Under low pH conditions, mobility usually decreases. Sorption and transport of fluorobenzoates can be affected by organic carbon, clay, and Fe-oxide content. In the presence of these three compounds the tracer behavior should first be evaluated with sorption or column tests. Benzoates can be separated by high-performance liquid chromatography and detected with high sensitivity by spectrophotometry [*Malcolm et al.*, 1980; *Bowman*, 1984a].

TABLE 1. Acid Dissociation Constants pK_a and Aqueous Diffusion Coefficients of Benzoic Acid (Benzoate) and Fluorobenzoate Tracers[a]

Fluorobenzoate	pK_a	*Aqueous Diffusion Coefficient,*[b] $m^2\ s^{-1}$ *at 25°C*
Benzoic Acid	4.19[c]	9.4×10^{-10}
2,3-DFBA	3.1–3.2[d]	8.6×10^{-10}
2,5-DFBA	3.1–3.2[d]	8.6×10^{-10}
3,4-DFBA	3.7–3.8[d]	8.6×10^{-10}
3,5-DFBA	3.4–3.5[d]	8.6×10^{-10}
2,6-DFBA	2.2–3.0[d]	8.6×10^{-10}
PFBA	1.5–2.7[d]	7.8×10^{-10}
m-TFMBA	3.8–3.9[d]	7.8×10^{-10}
o-TFMBA	3.0[d]	7.8×10^{-10}

[a]For comparison, the aqueous diffusion coefficient for bromide at 25°C is 2.08×10^{-9} $m^2\ s^{-1}$ [*Lide*, 1994].
[b]Values are estimated by the Hayduk and Laudie method [*Tucker and Nelken*, 1990] based on the protonated molecule.
[c]Value is from *McMurry* [1990].
[d]Values are from *Bowman and Gibbens* [1992] and *Jaynes* [1994].

2.2.7. Polyaromatic Sulfonates and Other Sulfonic Acids

[29] A series of polyaromatic sulfonates have been tested as tracers for geothermal groundwater studies [*Rose et al.*, 1998, 2000, 2001] (Figure 3). These polyaromatic sulfonates are fluorescent and possess good thermal stability. On the basis of thermal decay kinetics determined in the laboratory, 2-napthalene sulfonate and 2,7-napthalene disulfonate are the most stable among the polyaromatic sulfonates tested [*Rose et al.*, 2001]. In a field test in a geothermal groundwater system, 1,5-napthalene disulfonate moved similarly to Fluorescein/Uranine [*Rose et al.*, 1999]. Subsequently, 1,5-napthalene disulfonate was used in a large-scale infiltration test [*Nimmo et al.*, 2002] as a vadose zone tracer. No systematic comparisons, in terms of sorption properties to soil and aquifer material, exist for the different polyaromatic sulfonates, but variable sorption behavior is likely [*Reife and Freeman*, 1996] (see Figure 9).

[30] Piperazine-1,4-bis-(2-ethanesulfonic acid) (PIPES) has been used as a conservative tracer in column experiments [*Moline et al.*, 2001]. Little comparative information, however, is available to assess the chemical's suitability as a hydrological tracer. Experiments in pyrolusite-coated silica sand showed similar transport behavior of PIPES compared with bromide [*Jardine and Taylor*, 1995]. On the basis of molecular structure we expect

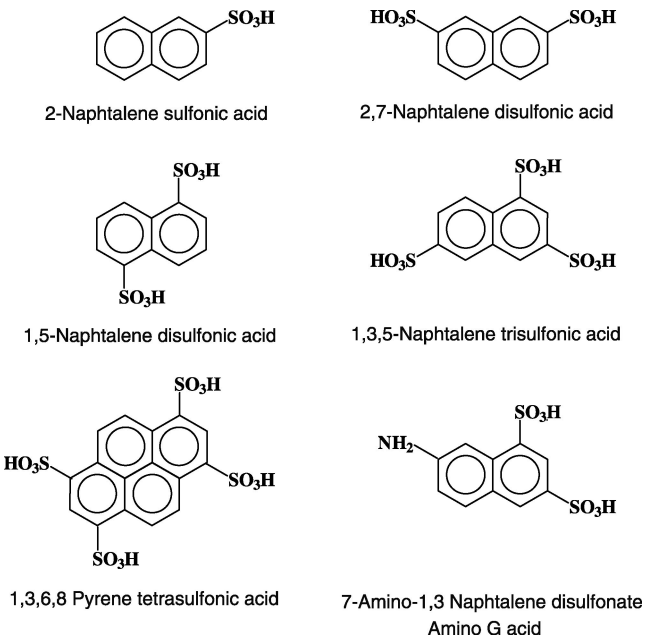

Figure 3. Polyaromatic sulfonates proposed as tracers [*Rose*, 2000, 2001].

benzenedisulfonic acid and 1,3-benzenedisulfonic acid to be better conservative tracers than PIPES (Figure 4).

2.2.8. Spores and Particles

[31] Solid and colloidal particles have been used frequently as tracers, particularly to investigate the hydrology of Karst regions [*Bauer and Zötl*, 1972; *Atkinson*, 1977]. Chaff has been reported as one of the earliest hydrological tracers. Philip the Tetrarch of Trachonitis threw chaff into a crater lake and then observed the chaff downstream in one of the springs [*Davis et al.*, 1980]. Clubmoss (*Lycopodium clavatum*) spores have also been used as tracers in karstic regions. The spores of *Lycopodium clavatum* are nearly spherical, have a diameter of ~30 μm, and have a density slightly higher than that of water [*Drew*, 1968]. Spores can be dyed with different colors and can therefore serve as multiple tracers. Sampling and detection of the spores is, however, rather cumbersome because water samples must be filtered and spores must be quantified by microscopy [*Davis et al.*, 1980].

[32] Synthetic colloidal particles are used to investigate colloid transport and colloidal processes in porous media. Synthetic microspheres are available in a variety of sizes and surface properties and can be stained with fluorescent dyes [*Haugland*, 2001].

2.2.9. Microorganisms

[33] Yeast, bacteria, and viruses have been proposed and used as hydrological tracers [*Davis et al.*, 1980; *Keswick et al.*, 1982; *Harvey*, 1997]. Some decades ago, bacteria and viruses were considered conservative tracers; however, researchers now know that microorganisms interact with the solid phase in aquifers [*Schijven and Hassanizadeh*, 2000; *Jin and Flury*, 2002]. Nevertheless, bacteria and viruses can serve as indicators of groundwater contamination. In karstic regions, microorganisms can serve as useful tracers for detecting flow pathways and flow connections [*Hötzl et al.*, 1991].

2.2.10. Dyes

[34] Dyes have proven to be powerful tracers [e.g., *Smart and Laidlaw*, 1977; *Davis et al.*, 1980]. Dyes can be directly observed or indirectly detected by a water sample analysis. The most commonly used dyes in groundwater hydrology are fluorescent, allowing detection at very low concentrations. Dyes consist of relatively large organic molecules and, as such, interact to some degree with the solid matrix in soils and aquifers. A variety of dyes are available as hydrological tracers. A particular dye is chosen based on the specific purpose of the tracing experiment. We will discuss dye tracers in more detail in the following sections.

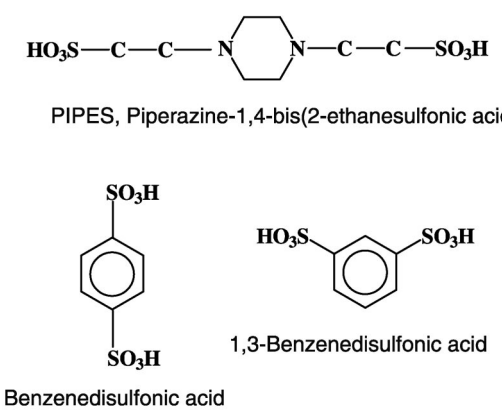

Figure 4. Piperazine-1,4-bis-(2-ethanesulfonic acid) (PIPES) proposed as a tracer [*Moline et al.* 2001] and other sulfonic acids potentially useful as tracers.

3. CLASSES OF DYES

[35] Dyes are usually classified either by their chemical structure or by their method of application. These two grouping systems are referred to as chemical and coloristic classification, respectively [*Zollinger*, 1991]. The most comprehensive catalogue of dyes is the *Colour Index* [*The Society of Dyers and Colourists*, 1971, 1999] which lists information on several thousands of different dyes, including chemical structures, selected physical and chemical properties, manufacturers, commercial and generic names, and methods of application. Supplemental volumes and amendments have been published since 1971. The third edition of the *Colour Index* consists of nine volumes and is also available on CD-ROM [*The Society of Dyers and Colourists*, 1999]. The first phase of the fourth edition, including pigments and solvent dyes, is available online only (Colour Index Fourth Online Edition, The Society of Dyers and Colourists, 2001,

http://www.colour-index.org). Additional phases will be published in coming years.

[36] The Colour Index [*The Society of Dyers and Colourists*, 1971, 1999] lists dyes by both chemical and coloristic classification, using the Colour Index (C.I.) constitution number and the C.I. generic name, respectively. The dye Brilliant Blue FCF, for instance, is identified by the constitution number C.I. 42090 or the generic name C.I. Food Blue 2. This classification system identifies each dye unequivocally. Although dyes with the same C.I. constitution number and generic name have the same chemical structure, they may differ in terms of the crystal structure (pigments), particle size (pigments, disperse dyes, and vat dyes), or additives and impurities [*Zollinger*, 1991]. Commercially manufactured dyes may vary considerably in degree of purity or consistency [*The Society of Dyers and Colourists*, 1999] and possibly also in the percentage and composition of isomers.

[37] Unfortunately, many commercial names exist for a single dye, and often several different dyes have the same commercial name. Without the Colour Index name or number specified, identification of a dye used in an experiment is difficult if not impossible. Therefore the unique Colour Index name and number must be reported in scientific communications. Furthermore, the five-digit Colour Index number allows easy identification of the chemical structure of the compound. For example, the C.I. number for Brilliant Blue FCF (C.I. Food Blue 2) is 42090. The first two digits, 42, denote the chemical class of triarylmethane dyes. The last three digits, 090, specify the individual dyes in this class. To provide room for new dyes, gaps of 5 or 10 numbers were placed between consecutive dye numbers. This numbering method has been inadequate for certain dye classes. As a result, six-digit numbers will be allocated in the future (Colour Index Fourth Online Edition). Within each class the colorants are arranged according to the following criteria [*The Society of Dyers and Colourists*, 1971]: (1) simpler molecular structures preceding more complex structures, (2) aliphatic compounds preceding aromatic compounds, and (3) the number of amino groups, hydroxy groups, or both. Consequently, colorants with Colour Index numbers consecutive to each other are generally similar in structure.

4. HISTORICAL SKETCH OF THE USE OF DYES AS TRACERS

[38] Systematic tracing of water with dyes began at the end of the nineteenth century in Austria, Belgium, France, Germany, Italy, and Switzerland. These experiments were mainly motivated by the increasing demand for clean drinking water for the growing urban population and by the use of rivers to generate power for industrial activities. The main purpose of dye tracing experiments at this time was to study the spatial extent of catchment areas and the connectivity of underground water flow pathways.

[39] Dying water for tracing purposes was proposed as early as 1864 by the historian Peter Kandler from Trieste, Italy [*Käss*, 1998]. In the absence of a suitable dye tracer, however, early tracing experiments were performed with substances such a starch, oil, and NaCl. NaCl was available in large quantities and could be readily detected via AgCl formation. In 1872 the source of a typhus epidemic in the city of Lausen, Switzerland, was identified with a NaCl tracer test carried out by F. Goppelsröder from the University of Basel [*Hägler*, 1873]. (Typhus is an acute, highly infectious disease caused by the bacillus *Samonella thyphi* and, as we know today, is transmitted mainly by contaminated food and water.)

[40] One of the first dye tracing experiments was performed in southern Germany in 1877 to prove the hydrologic connection between the Danube River and the Aach spring. The dye Fluorescein was used for the experiment in addition to slate oil and NaCl [*Knop*, 1875, 1878]. Fluorescein had recently been discovered in 1871 by the German chemist Adolf von Baeyer and was used as the tracer because of its strong fluorescence and limited soil adsorption properties [*Knop*, 1878]. Other dye tracing experiments followed in Switzerland, Belgium, Italy, and France (see brief description by *Käss* [1998]).

[41] The value of these early water tracing studies is exemplified by a remarkable experiment reported by *des Carrières* [1883]. In September 1882 a typhus epidemic broke out in the French city of Auxerre, located ~135 km southeast of Paris. The population of Auxerre at that time was ~16,900. The mortality rate ranged from 430 to 450 deaths per year or about eight deaths per week. Prior to 1882, typhus was a rare cause of mortality. In 1881 the disease caused only two deaths. Within 3 months from August 1882, however, 91 typhus victims were registered.

[42] Alerted by the typhus epidemic, a physician, Dionis des Carrières, noticed that certain neighborhoods of the city were severely affected by the epidemic, while others were completely unaffected. Since the neighborhoods obtained their drinking water from different sources, des Carrières suspected that the likelihood of contracting typhus was related to the water supply source. Yet he had no direct proof of his hypothesis. In a reunion of the regional medical society in November 1882, des Carrières learned that a typhus infection had been reported in August 1882 in the village of Vallan. Vallan is located ~7 km upstream of Auxerre on the same river from which Auxerre received part of its drinking water. After traveling to Vallan, des Carrières noted that the feces of the infected person had been thrown on a manure pile that was exposed to rain. He suspected that the bacilli leached from the manure pile, through the soil, into the groundwater, and out to the river. des Carrières proved the source of the infection

with an interesting tracer experiment. He dissolved 2 g of aniline (presumably C.I. Basic Red 9, C.I. 42500) and applied this solution to the soil near the manure pile. Soon thereafter, he observed the reddish color of the dye in the nearby spring, thus proving that the tracer moved through the soil to the spring and, subsequently, into the river. Interestingly, des Carrières was unable to repeat the experiment because the local population of Vallan, after recognizing the purpose of the experiment, became hostile and opposed further investigations.

[43] A second remarkable experiment was performed by *des Carrières* [1883] during his investigation of the typhus epidemic in Auxerre. In a village near Vallan, people complained about the bad odor of their drinking water. The physcian performed a tracer test to show that the bad odor originated from manure piles located ~30 m from the drinking water sources. He applied a yellow, unidentified colorant to the manure piles, followed by odored water, which he had prepared by distilling pits of cherries. After some time he, indeed, detected the yellow color, followed by the odored water, in the drinking water supply.

[44] Auxerre was plagued by typhus for many years, and a second epidemic broke out in 1902 [*Le Couppey de la Forest*, 1902]. Again, the source of the infection was investigated with a dye tracing experiment, this time using Fluorescein/Uranine as the tracer [*Le Couppey de la Forest*, 1902].

[45] In 1896 the dyes Fluorescein/Uranine and Methyleosine (presumably C.I. 45385), in combination with a bacterial tracer, were used to investigate the filtration capacity of the soil material that surrounded the drinking water supply canal for Torino, Italy [*Abba et al.*, 1899].

[46] Ever since these early experiments, dye tracers of different kinds have been used to investigate water pathways and flow rates through the vadose zone. Systematic investigations on the suitability of different dyes as tracers were reported as early as 1899 [*Trillat*, 1899]. *Trillat* [1899] compared nine dyes: Fuchsine (presumably C.I. 42685), Violet of Paris (C.I. 42535), Methylene Blue (C.I. 52015), Malachite Green (C.I. 42000), Auramine (C.I. 41000), Congo Red (C.I. 22120), Eosine (C.I. 45380), Safranine (C.I. 50240), and Fluorescein/Uranine (C.I. 45350). He filtrated the nine dye solutions through a 30-cm-thick layer of each of the following media: calcareous, sandy, clayey, and peaty soils and animal manure. The calcareous soil decolorized all dyes except Fluorescein/Uranine, and the peat decolorized all dyes. Fluorescein/Uranine was the only dye unaffected by the presence of animal manure [*Trillat*, 1899].

[47] At the turn of the century the city of Paris undertook extensive hydrogeological investigations of its watersheds and water supplies to ascertain the water purity and to prevent water pollution. Fluorescein/Uranine was used as the tracer [*Brard*, 1899; *Dole*, 1906]. *Dole* [1906] briefly reviewed several organic and inorganic agents that had been used for water tracing in these early studies. He mentioned the colorants Potassium Permanganate (C.I. 77755), Fuchsine (C.I. 42685), Congo Red (C.I. 22120), Methylene Blue (C.I. 52015), and Fluorescein/Uranine (C.I. 45350). For tracing the flow of water in rocks, particularly calcareous formations, he deemed Fluorescein/Uranine the most suitable substance. Fluorescein/Uranine's mobility is essentially unaffected by gravel, sand, or manure and can be detected at very low concentrations (especially after the invention of the fluorometer) [*Trillat*, 1899; *Dole*, 1906]. Fluorescein/Uranine has since been one of the most prominent dye tracers in karst studies.

[48] In earlier studies, Fluorescein/Uranine and other dyes were usually employed in large quantities to ensure visibility once several orders of magnitude of dilution occurred in natural water bodies [*Drew*, 1968]. Alternative methods included collecting the dye with activated charcoal or cotton strips and then extracting the dye for analysis [*Dunn*, 1957; *Murdock and Powell*, 1968; *Medville*, 1977]. These methods allow application and detection of smaller quantities of dye and integrate the tracer signal over a specific period of time.

[49] The use of dyes became a routine and popular research protocol for water tracing in calcareous rock formations. Some of the more common dye tracers used in calcareous formations were Fluorescein/Uranine (C.I. 45350), Pyranine (C.I. 59040), Rhodamine B (C.I. 45170), and Malachite Green (C.I. 42000). Dyes also became popular for investigating flow and transport characteristics in all kinds of aquifers to study hydraulic connectivity as well as flow velocities and dispersivities. Several reviews have been published on water tracers in general and dye tracers in particular [*Dole*, 1906; *Drew*, 1968; *Knutsson*, 1968; *White*, 1976; *Smart and Laidlaw*, 1977; *Davis et al.*, 1980]. Systematic and detailed investigations on tracer properties of selected, usually fluorescent, dyes have lead to an improved scientific understanding of dyes used as tracers [*Feuerstein and Selleck*, 1963; *Smart and Laidlaw*, 1977; *Viriot and André*, 1989].

[50] In addition to measuring hydraulic connections, flow velocities, and dispersivities, dyes are used to visualize flow pathways with a high degree of resolution. One of the first attempts to use staining techniques to visualize flow pathways in soils was reported by *Tamm and Troedsson* [1957]. The researchers applied a NH_4SCN solution onto the soil surface, opened a soil profile, and sprayed a $FeCl_3$ solution onto the profile. The Fe formed an intensive red-colored complex with the SCN ion, $FE(SCN)_x^{3-x}$, allowing visualization of the spatial distribution of SCN. The researchers also noted that the pine trees and the ground vegetation, located within a 5-m radius of the experimental site, were killed or seriously damaged.

[51] A similar principle of visualization was employed by *van Ommen et al.* [1988]. They applied iodide and then visualized the tracer by spraying the soil profile with a starch solution. The starch solution reacted with the iodide to form a dark violet-colored iodide-starch com-

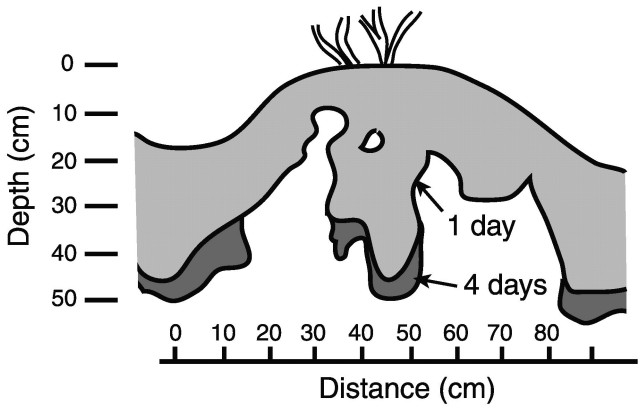

Figure 5. Distribution of Rhodamine WT under a potato plant after 1 day and 4 days following 3.3 cm of infiltration [from *Saffigna et al.*, 1976]. Reproduced by permission of American Society of Agronomy.

plex. This method has also been used successfully to visualize flow heterogeneities in column experiments [*Buchter et al.*, 1995].

[52] More recently, a method has been developed to visualize bromide in soil profiles [*Lu and Wu*, 2003]. Bromide is applied to the soil surface as the tracer and the soil profile is sprayed with a solution containing silver ferrocyanide ($Ag_4Fe(CN)_6$) and ferric iron Fe^{3+}. Prussian blue ($Fe_4[Fe(Cn)_6]_3$) then forms according to the following reaction:

$$3Ag_4Fe(CN)_6 + 12Br^- + 4Fe^{3+}$$

$$= Fe_4[Fe(CN)_6]_3 + 12AgBr.$$

The resulting blue color is readily visible in a soil profile.

[53] Direct application of dye solutions to visualize infiltration patterns and flow pathways in the vadose zone was reported frequently in the second half of the twentieth century, using dozens of different dyes. Figure 5 illustrates an infiltration pattern visualized with Rhodamine WT [*Saffigna et al.*, 1976]. Many types of dyes were tested for their suitability as soil water tracers. However, few researchers agreed on the best suitable tracer [*McLaughlin*, 1982]. Methylene Blue (C.I. 52015) was extensively used to visualize preferential flow pathways in clayey soils [*Bouma et al.*, 1977], but owing to its strong sorption to soil material it is used infrequently today. Dyes recommended for soil water tracing were the following: Erio Floxine 2G (C.I. 18050) [*Corey*, 1968], Pyranine (C.I. 59040) [*Reynolds*, 1966], Lissamine Yellow FF (C.I. 56205) [*Smettem and Trudgill*, 1983], and Brilliant Blue FCF (C.I. 42090) [*Flury and Flühler*, 1994]. Brilliant Blue FCF, which was presumably first used as a hydrological tracer by T. Steenhuis and his group at Cornell University [*Pickering et al.*, 1988; *Steenhuis et al.*, 1990], has become the most prominent dye tracer in vadose zone hydrology.

5. CHEMICAL CHARACTERISTICS OF DYES RELEVANT FOR TRACING

5.1. Dye Adsorption to Solid Surfaces

[54] Most dyes are organic molecules with various functional groups attached to the molecular kernel. In general, organic dyes have an amphiphilic characteristic, that is, the molecule has both hydrophobic and hydrophilic properties. In addition, the functional groups of organic dyes can protonate and deprotonate depending on pH, thereby changing the net charge of the molecule. Because of these characteristics, interaction of the dye molecule with solid surfaces is rather complex. Sorption of dyes to solid surfaces involves one or a combination of the following interactions: hydrophobic, van der Waals, ion exchange, covalent bonding, and hydrogen bonding [*Zollinger*, 1991; *Schwarzenbach et al.*, 1993]. Dyes are manufactured to color other materials. The process of coloring requires sorption of the dye molecules to the target materials. Sorption interactions of dyes are therefore of paramount industrial importance, and a large body of literature on this topic exists [*Ratee and Breuer*, 1974].

[55] The sorption of a chemical at equilibrium conditions is often described by a sorption isotherm. For dyes, various representations of sorption isotherms are used (Figure 6). Most of these isotherms are found for other organic chemicals as well. Interestingly, some dyes aggregate in both the solution and the sorbed phase. This aggregation is due to van der Waals' forces and is more likely to occur when large planar surfaces are present in the molecular structure [*Zollinger*, 1991]. Aggregation in solution is indicated by a concentration-dependent absorption spectrum. The formation of dimers in xanthene dyes at large concentrations leads to a bimodal absorption spectrum, that is, one absorption maximum at a smaller and another at a larger wavelength compared to the monomeric absorption maximum [*Förster and König*, 1957; *Valdes-Aguilera and Neckers*, 1989]. A representative example of dimer formation is shown for the xanthene dye Fluorescein (Figure 7). Dimer formation also occurs for dyes belonging to other classes, for instance, the thiazine dye Methylene Blue [*Förster and König*, 1957] or azo dyes [*Hamada et al.*, 1985]. Methylene Blue is an example of a dye that can aggregate in the sorbed phase. In the sorbed phase, Methylene Blue can exist as a tetramer [*Kobayashi et al.*, 1989]. Because of aggregation, more dyestuff than expected can be sorbed onto solid surfaces compared to sorption based on ion exchange. This phenomenon is often called overdying in the dyestuff literature [*Zollinger*, 1991] (Figure 6).

[56] Sorption of acid dyes to wool and polyamide fibers often display a Langmuir isotherm, where the maximum sorption capacity b corresponds to the amino acid content of the fibers [*Zollinger*, 1991]. Langmuir isotherms are also frequently observed for acid dye sorption to soil minerals (Figure 8) [*Fahrenhorst et al.*, 1999;

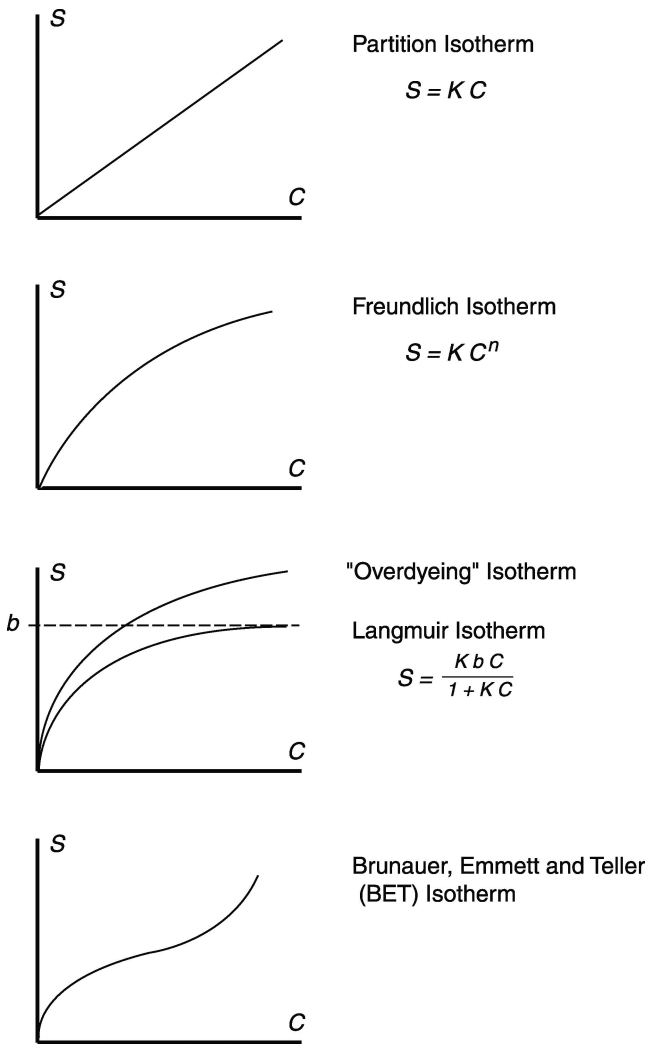

Figure 6. Example sorption isotherms that describe dye sorption. S and C are the equilibrium concentrations in the sorbed and solution phases, respectively, K is the sorption coefficient, n is an empirical constant, and b is the maximum sorption capacity. Reprinted from *Ratee and Breuer* [1974] with permission from Elsevier Science.

Ketelsen and Meyer-Windel, 1999; *German-Heins and Flury*, 2000].

[57] The number and type of functional groups attached to the molecular kernel of the dyes change the sorption characteristics of the molecule as a whole. This phenomenon is illustrated with aniline, naphthol, naphthalene, and their derivates when these dyes adsorb onto carbon material (Figure 9). In general, the more sulfonic acid groups that are attached to the molecular kernel, the less sorption there is to carbon. Note the dramatic effect of attachment of the first sulfonic acid group to aniline and naphthol. By inference, the more hydrophilic groups that are attached to the hydrophobic kernel, the less sorption there is to carbon material (Figure 9). These conclusions are fairly representative and applicable for many dyes, since dyes often contain benzene and naphthalene units.

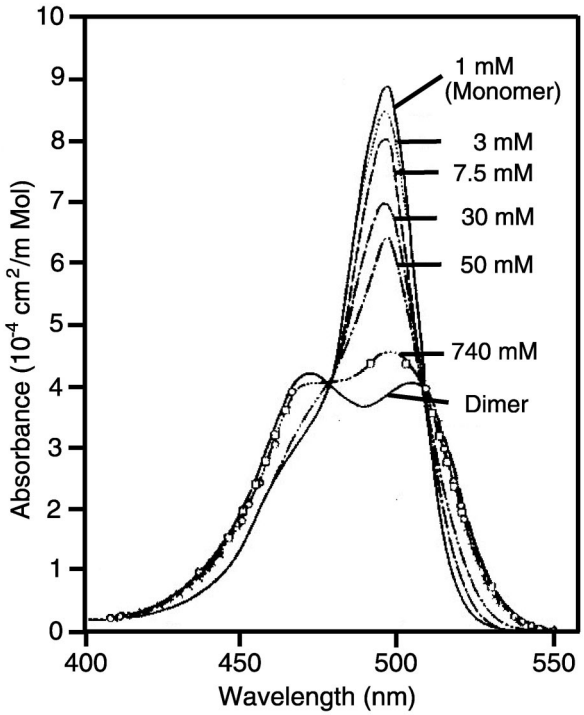

Figure 7. Absorption spectra of Fluorescein at various concentrations measured in 13.4 m NH_4OH. In this solution the molecule is present dominantly as di-anion (compare Figure 11). Reprinted from *Förster and König* [1957] with permission of the Deutsche Bunsengesellschaft für Physikalische Chemie.

[58] In addition to the number and type the relative position of functional groups affects the sorption properties of dye molecules. This phenomenon has been demonstrated for Rhodamine WT. Commercial Rhodamine WT consists of two isomers (Figure 10). The para isomer behaves more conservatively as a tracer than does the meta isomer [*Shiau et al.*, 1993; *Vasudevan et*

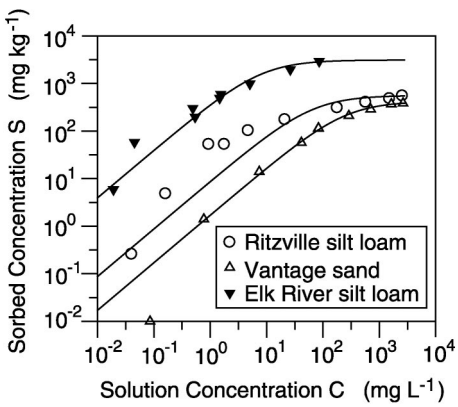

Figure 8. Measured (symbols) and fitted Langmuir (curves) sorption isotherms of Brilliant Blue FCF for three soils. The ionic strength was $I = 0.015$ M with $CaCl_2$. Standard deviations of measurements are smaller than symbols. Reprinted from *German-Heins and Flury* [2000] with permission from Elsevier Science.

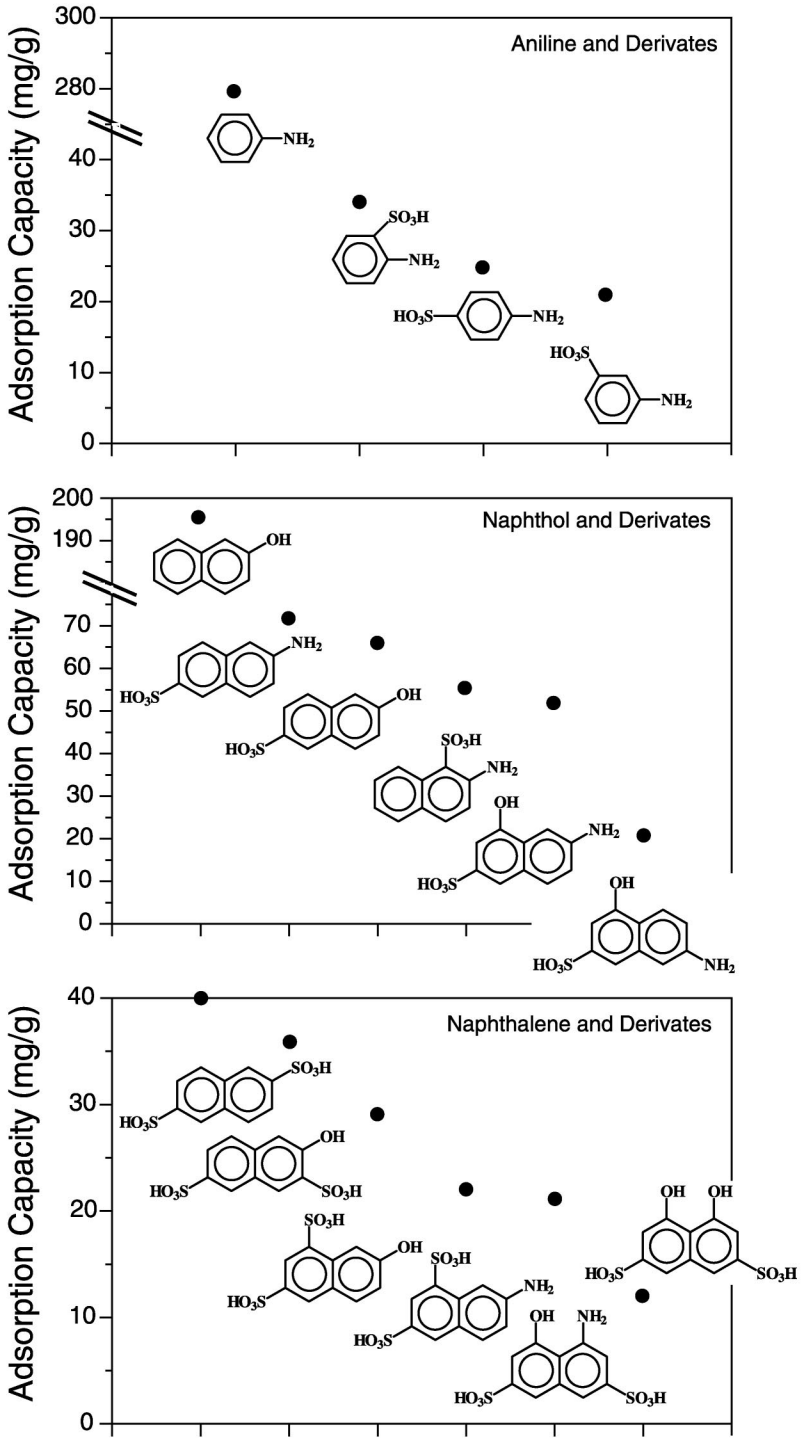

Figure 9. (top) Sorption of aniline and derivates, (middle) naphthol and derivates, and (bottom) naphthalene and derivates on carbon material. Figure 9 is drawn after data from *Reife and Freeman* [1996].

al., 2001]. During transport through porous media the two isomers will therefore experience chromatographic separation [*Shiau et al.*, 1993; *Sutton et al.*, 2001].

[59] Extensive sorption tests have been conducted for various dye tracers including Brilliant Blue FCF [*Flury and Flühler*, 1995; *Perillo et al.*, 1998; *Allaire-Leung et al.*, 1999; *Ketelsen and Meyer-Windel*, 1999; *German-Heins and Flury*, 2000; *Kasteel et al.*, 2002], Fluorescein/Uranine [*Feuerstein and Selleck*, 1963; *Smart and Laidlaw*, 1977; *Sabatini and Austin*, 1991; *Kasnavia et al.*, 1999; *Sabatini*, 2000], Rhodamine B [*Feuerstein and Selleck*, 1963; *Smart and Laidlaw*, 1977; *Kasnavia et al.*, 1999], Sulforhodamine B [*Feuerstein and Selleck*, 1963; *Smart and Laidlaw*, 1977; *Wilson et al.*, 1986; *Kasnavia et al.*,

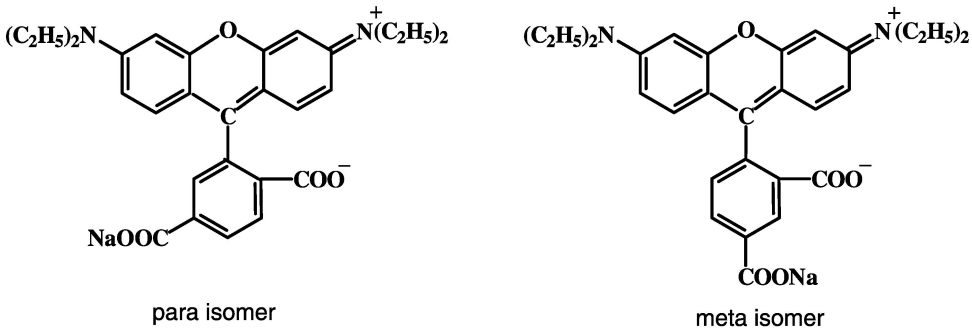

Figure 10. Isomers of Rhodamine WT [after *Shiau et al.*, 1993; *Vasudevan et al.*, 2001].

1999], and Rhodamine WT [*Smart and Laidlaw*, 1977; *Trudgill*, 1987; *Sabatini and Austin*, 1991; *Allaire-Leung et al.*, 1999; *Kasnavia et al.*, 1999]. These tests indicated that all dyes sorb to a certain degree, often in a nonlinear fashion, on subsurface materials. However, dyes remain valuable tracers if the sorption characteristics are known and the sorption is moderate. Although dye patterns may inadequately depict actual water movement patterns, the behavior of a sorbing molecule, carried by the aqueous phase, is illustrated.

5.2. Effects of Solution Chemistry on Absorption Spectra

[60] Since all dyes used as hydrological water tracers contain reactive groups attached to the molecular kernel, the net charge of the dye molecules will depend on the pH of the solution. Multiple reactive groups are common for dye tracers; therefore the pH-dependent net charge will often vary from +1 to −2, as illustrated for the xanthene dye Fluorescein (Figure 11). The absorption spectra of dyes displays varying sensitivities to pH. Some dyes are unaffected, some are affected under acidic conditions, others are affected under alkaline conditions (Figure 12). Dyes that show a pronounced shift in the absorption peak at different dissociation states are used in analytical chemistry as pH indicators. Examples are Phenolphthalein or Eriochrome Black T (Figure 13). For fluorescent dyes the fluorescence can also be affected by pH (Figure 14) [*Moser and Sagl*, 1967; *Smart and Laidlaw*, 1977; *Viriot and André*, 1989]. The change of the absorption and emission spectra of fluorescent dyes as a function of pH are directly related to the dissociation constants of the molecules or are due to structural changes [*Williams and Bridges*, 1964; *Smart and Laidlaw*, 1977]. Some xanthene dyes, such as Fluorescein, change from quinoid structure under alkaline conditions to leuco structure under acidic conditions (Figure 11), thereby drastically altering their physicochemical and spectral properties.

[61] Salinity affects dye absorption spectra to a much smaller degree than does pH. High concentrations of salts are required to influence absorption spectra. For the three examples shown in Figure 15, only the absolute value of absorbance changes. The shape of the spectra remains the same. Salinity effects on fluorescence have been reported by *André and Molinari* [1976] and *Smart and Laidlaw* [1977].

5.3. Fluorescence Quenching

[62] The fluorescence of chemicals can be quenched by a variety of mechanisms [*Williams and Bridges*, 1964]. For dye tracers, quenching can occur via a redox reaction involving the electron-donating anions, such as I^- and Br^-, or electron-accepting anions, such as NO_3^- [*Williams and Bridges*, 1964]. For a series of xanthene dyes, *Majumdar* [1961] reported the following sequence for the quenching efficiency of major anions found in subsurface waters: I > Br > Cl. This order of quenching efficiency corresponds to the electron-donating power of these anions [*Majumdar*, 1961]. Structural changes induced by solution pH can lead to a complete quenching. The change from the quinoid to leuco form in xanthene

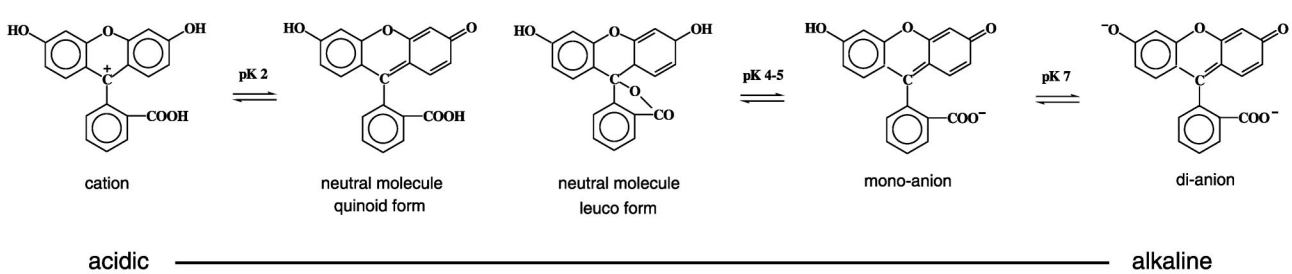

Figure 11. Structural form of the xanthene dye Fluorescein (adapted from *Lindqvist* [1960]). The leuco form occurs in organic, nonionic solvents.

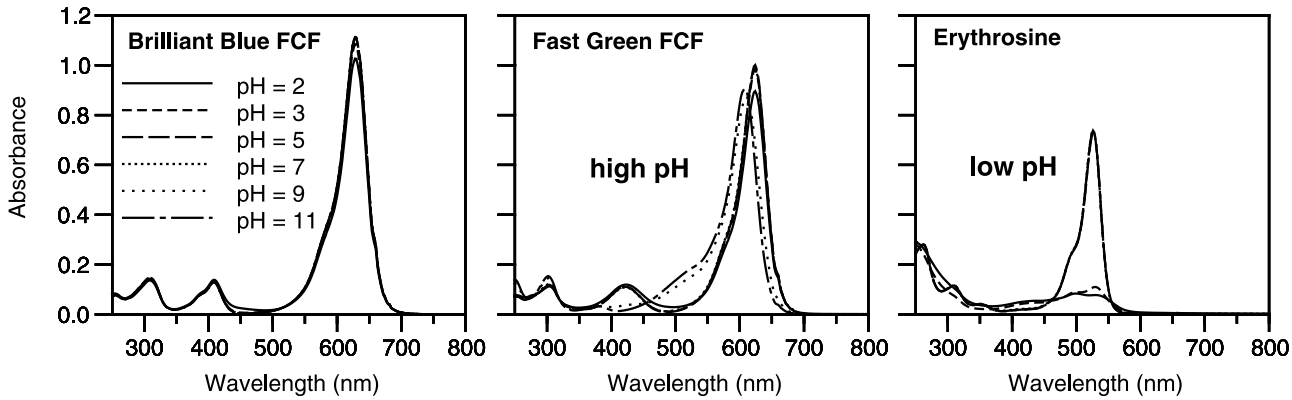

Figure 12. Absorption spectra of dyes as affected by pH. Brilliant Blue FCF (C.I. 42090) shows little pH sensitivity, Fast Green FCF (C.I. 42053) is affected at high pH, and Erythrosine (C.I. 45430) is affected at low pH.

dyes results in a complete loss of the fluorescence (Figure 11).

5.4. Metal Complexation

[63] Certain dyes form complexes with multivalent metals. If the complex formation results in a color change, the dyes can be used as metal indicators. A widely used metal indicator is the monoazo dye Eriochrome Black T (C.I. Mordant Black 11, C.I. 14645), which detects Ba, Ca, Cd, Pb, Mg, Mn, Sr, Zn, and rare earth elements [*Laitinen*, 1960]. The colorimetric analysis of metal complexation is related to the acid-base behavior of the dye (Figure 13). Since the colors are extremely sensitive, metal concentrations of 10^{-2} to 10^{-4} m*M* can be easily detected [*Laitinen*, 1960]. Such dyes are likely to form metal complexes in soil solutions or groundwater.

6. USE OF DYES AS HYDROLOGICAL TRACERS

6.1. Advantages and Disadvantages of Dyes

[64] Dyes as tracers have advantages and disadvantages compared with other human-applied hydrological tracers (Table 2). In any specific application these advantages and disadvantages must be considered in the choice of a suitable tracer. In addition to the criteria listed for a conservative tracer (section 2.1), a dye tracer should have the following characteristics:

1. It should have good visibility. If used for visualization purposes, the dye must possess good visibility in either sorbed or solution phase.

2. It should have a stable spectrum. Dye absorption spectra, as well as emission spectra of fluorescent dyes, can be affected by soil constituents. A good dye tracer is resistant to color changes when sorbed to solid surfaces.

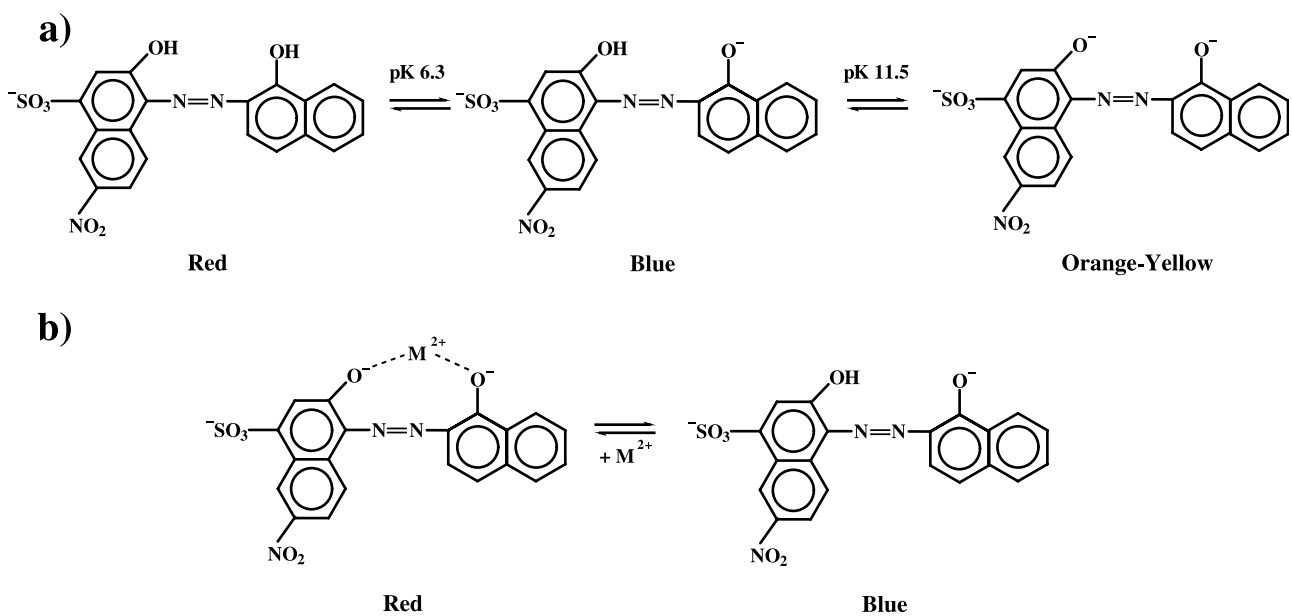

Figure 13. Indicator dye Eriochrome Black T (C.I. Mordant Black 11, C.I. 14645) illustrating (a) acid-base behavior and (b) metal complexation in the pH range 7 to 11. Figure 13 is drawn after information given by *Laitinen* [1960].

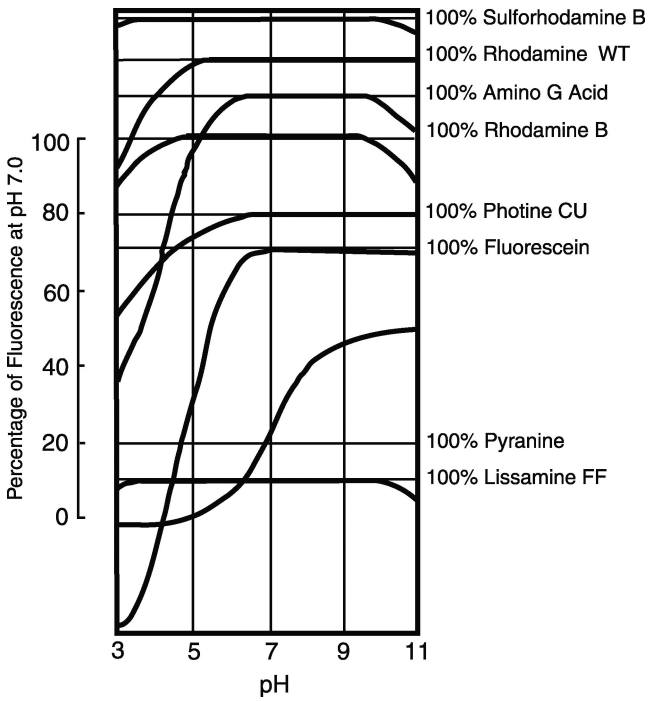

Figure 14. Effect of pH on the fluorescence of tracer dyes [from *Smart and Laidlaw*, 1977].

[65] Considering the physicochemical properties of dye tracers and the sorption characteristics, an ideal dye tracer does not exist [*Davis et al.*, 1980; *McLaughlin*, 1982] because some of the criteria for a conservative tracer are mutually exclusive [*Flury and Flühler*, 1995]. The task is then to find the best available tracer for the specific purpose of the investigation. Making compromises and weighing different criteria is unavoidable.

6.2. Groundwater Tracers

[66] The tracers used most frequently for groundwater tracing are Sulforhodamine B, Rhodamine B, Fluorescein/Uranine, and Rhodamine WT (Table 3), which are xanthene dyes. The Fluorescein ion can be associated with a proton or an alkali metal such as Na. The proton-associated form is often denoted as Fluorescein, whereas the Na salt-associated form is denoted as Uranine or Sodium Fluorescein. Fluorescein has a much lower solubility than Uranine, and, consequently, the latter is the common form used as a hydrological tracer. (This differentiation is not always made clear in the literature, and we therefore use the designation Fluorescein/Uranine in this review.)

TABLE 2. Advantages and Disadvantages of Using Dyes as Hydrological Tracers

Advantages	*Disadvantages*
Detectability at low concentrations	large molecules
Easy quantification in water	sorption and decay
Visualization	amphiphilic characteristics
Nontoxicity	toxicity
	complicated chemical interactions (e.g., pH-dependent charge, pH-dependent color, complex formation, decay, aggregation)

[67] The structures of common groundwater tracers are depicted in Figure 16. Excellent reviews and summaries are available on the use and characteristics of groundwater dye tracers [*Drew*, 1968; *Smart and Laidlaw*, 1977; *Davis et al.*, 1980; *Mull et al.*, 1988; *Viriot and André*, 1989]. On the basis of specific criteria such as solubility, sorption, mobility, and stability under different chemical environments some dyes have been recommended as the most suitable tracers. Examples are Fluorescein/Uranine [*Trillat*, 1899], Sulforhodamine G [*Moser and Sagl*, 1967], Rhodamine WT, Lissamine Yellow FF, and Amino G Acid [*Smart and Laidlaw*, 1977], and Rhodamine WT and Rhodamine B [*Wilson et al.*, 1986].

[68] Fluorescein/Uranine and Sulforhodamine B are also used as molecular markers in biochemistry [*Haugland*, 2001]. Fluorescein derivates, such as Calcein

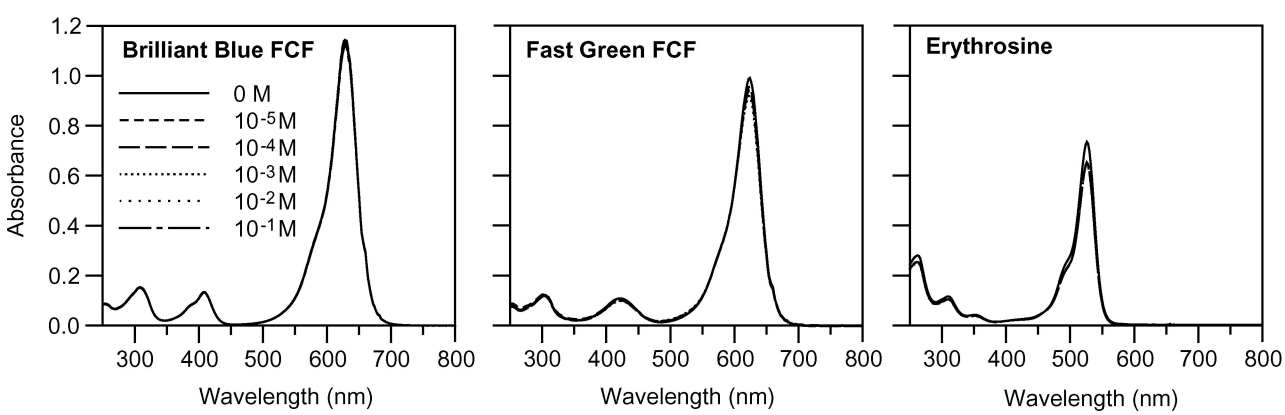

Figure 15. Absorption spectra of dyes as affected by electrolyte concentration. Concentrations are NaCl.

($C_{30}H_{26}N_2O_{13}$), Carboxyfluorescein ($C_{21}H_{12}O_7$), and Fluorescein sulfonic acid ($C_{20}H_9Na_3O_8S$), are common molecular markers [*Haugland*, 2001]. Because these dyes contain carboxylic and sulfonic acid groups attached to the Fluorescein kernel, they are potentially good hydrological tracers as well.

6.3. Vadose Zone Tracers

[69] Many different dyes have been tested or used as vadose zone tracers (Table 4). The most prominent vadose zone tracers are shown in Figure 17. Some of these tracers are also frequently used in groundwater or surface water investigations. In contrast to groundwater tracers, vadose zone tracers are often employed to visualize the spatial flow patterns of water or solutes. Therefore a tracer's visibility in soils and other subsurface materials is of paramount importance. Methylene Blue (C.I. 52015) has excellent visibility in soils and has been extensively used to visualize macropore flow in soils (Table 4). Methylene Blue is a cation and sorbs strongly to most soil minerals. This characteristic renders the dye a strong coloring agent but limits its mobility compared to anionic dyes. Screening tests have been performed to find the most suitable vadose zone tracers, resulting in different dye recommendations including Pyranine [*Reynolds*, 1966], Erio Floxine [*Corey*, 1968], Lissamine Yellow FF [*Smettem and Trudgill*, 1983], Rhodamine WT [*Kung*, 1990], and Brilliant Blue FCF [*Flury and Flühler*, 1995]. Rhodamine WT and Brilliant Blue FCF are used most frequently. Because of its blue color, Brilliant Blue FCF is often more visible in soil media than the red-colored Rodamine WT.

[70] Many of the hydrological tracers are acid dyes (Tables 3 and 4). Acid dyes are usually anionic and highly water soluble and contain one or more sulphonic acid or other acidic groups [*The Society of Dyers and Colourists*, 1999]. These characteristics make this group of dyes particularly suitable as tracers. Acid dyes are found in many of the chemical classes of dyes. Some tracer dyes are basic dyes. Basic dyes form cations in aqueous solutions [*The Society of Dyers and Colourists*, 1999] and strongly sorb to most subsurface media.

6.4. Methods of Application of Vadose Zone Dye Tracers

[71] Dye tracers for vadose zone hydrological studies can be applied in two forms: (1) as a liquid dissolved in an aqueous solution or (2) as a powder that is subsequently dissolved by the infiltrating water. The solution form is recommended, since the actual dye concentration of the infiltrating water is unknown when using the powder application method. Dye solutions can be applied to the soil surface with sprinklers or infiltrometers [*Ghodrati and Jury*, 1990; *Flury et al.*, 1994] or directly injected into soil or sediment layers, depending on the specific purpose of the tracer experiment.

[72] Similar to other tracers, dyes can be applied as step or pulse inputs. Pulse inputs of dyes require larger dye concentrations than step inputs because more dilution of the dye occurs during transport when a pulse is applied. Dye concentrations must be high enough to allow dye visibility after orders of magnitude of dilution. The required concentrations depend on the visibility of the dye relative to the background color. Because background conditions are often site-specific, concentrations are best determined with a preliminary test. For the dye tracer Brilliant Blue FCF, for instance, concentrations for step input experiments on a variety of soil types ranged from 1 to 4 g L^{-1} [*Flury et al.*, 1994].

[73] Transport behavior of dyes will be affected to some degree by the application rate. Higher rates of solution application will increase water flow velocities and the number of flow pathways, thereby altering the amount of contact area and the time for dye sorption to occur [*Perillo et al.*, 1998]. Laboratory tests can be used to determine these effects prior to the field study.

7. ANALYSIS OF DYE TRACING EXPERIMENTS

7.1. Image Analysis and Interpretation of Dye Patterns

[74] Dye tracer experiments in the vadose zone have commonly been analyzed as binary images. Binary imagery of dye patterns detects the dye's presence or absence. This type of analysis has revealed the nonuniformity of water infiltration and water flow in the vadose zone. Preferential flow research relies heavily on the use of dye tracers. An example of binary dye patterns observed in soils is shown in Figure 18.

[75] Binary dye images allow analysis of spatial patterns by fractal geometry [*Hatano and Booltink*, 1992; *Hatano et al.*, 1992; *Baveye et al.*, 1998], depth profile calculations of dye coverage [*Ghodrati and Jury*, 1992; *Flury et al.*, 1994], or identification of soil structures associated with dye patterns [*Petersen et al.*, 1997]. Much information, however, is hidden in the actual concentration distributions of the dye tracer. With advances in image analysis, dye concentrations in a soil profile can be determined. Figure 19 illustrates the advantage of measuring dye concentrations with image analysis compared to the use of binary images or soil cores.

[76] Image analysis techniques have been developed to quantify dye tracer concentrations in laboratory sand columns [*Schincariol et al.*, 1993; *Aeby et al.*, 1997] and field soils [*Ewing and Horton*, 1999; *Forrer et al.*, 1999, 2000]. These image analysis procedures are based on representing the colors in the red-green-blue or hue-saturation-value color space and manipulating the numerical values in the color space appropriately. Such experimental techniques open new avenues for higher-resolution analyses of water flow and solute transport processes in the subsurface. Two-dimensional tracer dis-

TABLE 3. Dyes Used as Groundwater Tracers, Sorted by Chemical Class

Dye Class	*Commercial Name*	*C.I. Generic Name*[a]	*C.I. Number*[a]	*Hue*[a]	*Source*[b]
Disazo	Congo Red	C.I. Direct Red 28	22120	yellowish red	*Trillat* [1899]
Stilbene	Uvitex CF	C.I. Fluorescent Brightener 134	40619	blue	*Glover* [1972]
	Leucophor BS	C.I. Fluorescent Brightener 49	40620	NA	*Glover* [1972], *Viriot and André* [1989]
	Photine CU,[c] Tinopal 5BM-GX	C.I. Fluorescent Brightener 28	40622	blue	*Smart and Smith* [1976], *Smart and Laidlaw* [1977], *Viriot and André* [1989]
	Photine CSP	C.I. Fluorescent Brightener 145	40636	blue	*Smart and Smith* [1976], *Viriot and André* [1989]
Diphenyl methane	Auramine	C.I. Basic Yellow 2	41000	bright yellow	*Trillat* [1899]
Triphenyl methane	Malachite Green	C.I. Basic Green 4	42000	bright bluish green	*Trillat* [1899]
	Paris Violet, Methyl Violet	C.I. Basic Violet 1	42535	bluish violet	*Trillat* [1899]
	Fuchsine Acid	C.I. Acid Violet 19	42685	bright reddish violet	*Trillat* [1899]
Xanthene	Sulforhodamine B, Lissamine Red, Pontacyl Brilliant Pink B, Erio Acid Red XB, Lissamine Red 4B, Kiton Rhodamine B, Acid Rhodamine B, Pontacyl Brilliant Pink, Pontacyl Pink	C.I. Acid Red 52	45100	bright bluish pink	1
	Rhodamine 6G	C.I. Basic Red 1	45160	bluish pink	*Behrens and Teichmann* [1982], *Behrens et al.* [2001]
	Rhodamine B	C.I. Basic Violet 10	45170	(bright) reddish violet	2
	Amido-Rhodamine G, Sulforhodamine G	C.I. Acid Red 50	45220	bright yellowish pink	3
	Uranine,[d] Fluorescein, D&C Yellow 7	C.I. Acid Yellow 73	45350	bright yellow	4
	Eosine, Eosine Yellow, D&C Red 22	C.I. Acid Red 87	45380	yellowish pink	5
	Erythrosine, Erythrosine Bluish, FD&C Red 3	C.I. Acid Red 51, C.I. Food Red 14	45430	bluish pink/ yellowish pink/bright bluish red	*Viriot and André* [1989]
	Rhodamine WT	C.I. Acid Red 388	NA	NA	6
Thiazole	Primuline	C.I. Direct Yellow 59	49000	greenish yellow	*Viriot and André* [1989]
Azine	Safranine	C.I. Basic Red 2	50240	bright bluish pink	*Trillat* [1899], *Viriot and André* [1989]
Thiazine	Methylene Blue	C.I. Basic Blue 9	52015	(bright) greenish blue	*Trillat* [1899]
Aminoketone	Brilliant Sulfoflavin FF, Lissamine FF, Lissamine Yellow FF, Brilliant Acid Yellow 8G, Lissamine Flavine FF	C.I. Acid Yellow 7	56205	bright greenish yellow	7
Anthraquinone	Pyranine, D&C Green 8	C.I. Solvent Green 7	59040	yellowish green	8
Optical brighteners	Tinopal CBS-X	C.I. Fluorescent Brightener 351	NA	bluish/reddish blue	*Behrens and Teichmann* [1982], *Behrens et al.* [2001]
	Tinopal ABP	C.I. Fluorescent Brightener 336	NA	bluish/reddish blue	*Behrens et al.* [2001]

TABLE 3. (continued)

Dye Class	*Commercial Name*	*C.I. Generic Name*[a]	*C.I. Number*[a]	*Hue*[a]	*Source*[b]
	Uvitex WGS	C.I. Fluorescent Brightener 61	NA	bluish violet	*Glover* [1972]
	Leucophor CK	C.I. Fluorescent Brightener 231/232	NA	blue	*Glover* [1972], *Viriot and André* [1989]
	Leucophor C	NA	NA	NA	*Glover* [1972]
	Calcophor White ST	NA	NA	NA	*Smart* [1984]
C.I. number unknown	Amino G Acid, 7-amino-1,3-naphtalene-disulfonic acid	NA	NA	NA	*Smart and Laidlaw* [1977], *Viriot and André* [1989], *Smart* [1984], *Field et al.* [1995], *Rose and McPherson* [1997], *Rose et al.* [1998]
	Diphenyl Brilliant Flavine 7GFF	C.I. Direct Yellow 96	NA	bright greenish yellow	*Smart* [1984], *Field et al.* [1995]

[a]NA indicates data are not available.

[b]Sources are as follows: 1, *Feuerstein and Selleck* [1963], *Moser and Sagl* [1967], *Scott et al.* [1969], *Church* [1974], *Rochat et al.* [1975], *André and Molinari* [1976], *Smart and Laidlaw* [1977], *Behrens and Teichmann* [1982], *Smettem and Trudgill* [1983], *Laidlaw and Smart* [1982], *Smart* [1984], *Wilson et al.* [1986], *Viriot and André* [1989], *Field et al.* 1995], *Kasnavia et al.* [1999], *Sabatini* [2000], *Behrens et al.* [2001]; 2, *Feuerstein and Selleck* [1963], *Wright and Collings* [1964], *Moser and Sagl* [1967], *Marking* [1969], *Scott et al.* [1969], *Church* [1974], *Rochat et al.* [1975], *Smart and Laidlaw* [1977], *Aulenbach et al.* [1978], *Abidi* [1982], *Behrens and Teichmann* [1982], *Laidlaw and Smart* [1982], *Laane et al.* [1984], *Smart* [1984], *Abidi et al.* [1986], *Viriot and André* [1989], *Field et al.* [1995], *Behrens et al.* [2001]; 3, *Moser and Sagl* [1967], *Rochat et al.* [1975], *André and Molinari* [1976], *Behrens and Teichmann* [1982], *Laidlaw and Smart* [1982], *Smart* [1984], *Hötzl et al.* [1991], *Field et al.* [1995], *Behrens et al.* [2001]; 4, *Knop* [1878], *Brard* [1899], *Trillat* [1899], *Le Couppey de la Forest* [1902], *Dole* [1906], *Dunn* [1957], *Sowards* [1958], *Feuerstein and Selleck* [1963], *Moser and Sagl* [1967], *Murdock and Powell* [1968], *Drew* [1968], *Marking* [1969], *Mather et al.* [1969], *Church* [1974], *André and Molinari* [1976], *Smart and Smith* [1976], *Medville* [1977], *Smart and Laidlaw* [1977], *Behrens and Teichmann* [1982], *Smart* [1984], *Diehl and Markuszewski* [1985], *Diehl et al.* [1986], *Adams et al.* [1989], *Viriot and André* [1989], *Adams and Davis* [1991], *Hötzl et al.* [1991], *Sabatini and Austin* [1991], *Rose and Adams* [1994], *Field et al.* [1995], *Rose et al.* [1998], *Kasnavia et al.* [1999], *Sabatini* [2000], *Behrens et al.* [2001]; 5, *Trillat* [1899], *Bandt* [1957], *Behrens and Teichmann* [1982], *Smart* [1984], *Viriot and André* [1989], *Field et al.* [1995], *Behrens et al.* [2001]; 6, *Scott et al.* [1969], *Parker* [1973], *Church* [1974], *Rochat et al.* [1975], *André and Molinari* [1976], *Smart and Smith* [1976], *Smart and Laidlaw* [1977], *Aulenbach et al.* [1978], *Davis et al.* [1980], *Abidi* [1982], *Behrens and Teichmann* [1982], *Laidlaw and Smart* [1982], *Bencala et al.* [1983], *Johnson and Steinheimer* [1984], *Laane et al.* [1984], *Smart* [1984], *Abidi et al.* [1986], *Bencala et al.* [1986], *Steinheimer and Johnson* [1986], *Wilson et al.* [1986], *Ruark and Bockheim* [1988], *Tai and Rathbun* [1988], *Zellweger et al.* [1988], *Jensen and Krongaard-Kristensen* [1989], *Viriot and André* [1989], *Sabatini and Austin* [1991], *Turner et al.* [1991], *Shiau et al.* [1993], *Rose and Adams* [1994], *Soerens and Sabatini* [1994], *Field et al.* [1995], *Pang et al.* [1998], *Kasnavia et al.* [1999], *Rose et al.* [1999], *Behrens et al.* [2001], *Vasudevan et al.* [2001], *Sutton et al.* [2001]; 7, *Moser and Sagl* [1967], *Smart and Smith* [1976], *Smart and Laidlaw* [1977], *Behrens and Teichmann* [1982], *Wilson et al.* [1986], *Smart* [1984], *Viriot and André* [1989], *Field et al.* [1995]; 8, *Atkinson et al.* [1973], *Smart and Smith* [1976], *Smart and Laidlaw* [1977], *Behrens and Teichmann* [1982], *Smart* [1984], *Viriot and André* [1989], *Field et al.* [1995], *Rose and McPherson* [1997], *Behrens et al.* [2001].

[c]Photine CU is denoted in the tracer literature [*Smart and Smith*, 1976; *Smart and Laidlaw*, 1977; *Viriot and André*, 1989] as C.I. Fluorescent Brightener 15 but is listed in the Colour Index as C.I. Fluorescent Brightener 28.

[d]Uranine is the Na salt of Fluorescein and is the form mostly used as a tracer because of its higher water solubility.

tributions can be obtained with a spatial resolution of 1 mm^2 (Figure 20).

[77] Advances have also occurred in two-dimensional imaging of fluorescent dyes in soil profiles [*Aeby et al.*, 2001; *Vanderborght et al.*, 2002b]. The two main advantages of using fluorescent imaging rather than visual imaging are (1) multiple tracers can be imaged separately, using optical excitations and filters that correspond to the fluorescence characteristics of the individual tracers, and (2) corrections for background inhomogeneities are easier to make. Optical inhomogeneities occur because the optical properties of soils vary spatially, and correcting for optical inhomogeneities is important [*Vanderborght et al.*, 2002b]. The fluorescent imaging technique was demonstrated using the following three fluorescent dye tracers that have different soil sorption characteristics: Brilliant Sulfoflavine (C.I. not available), Sulforhodamine B (C.I. 45100), and Oxazine 170 (C.I. 51004) [*Aeby et al.*, 2001]. Sophisticated equipment is needed for fluorescent imaging of dyes in soil profiles [*Aeby et al.*, 2001]. However, the capability of simultaneously detecting tracers with different sorption characteristics offers a unique experimental tool to gain insight about flow and transport in the vadose zone.

[78] Interpretation of dye patterns must take into account the mechanisms of sorption that occur during transport. Dye patterns will not exactly match the infiltration pattern of water; the dye front is retarded compared to the wetting front [*Flury and Flühler*, 1995; *Perillo et al.*, 1998; *Kasteel et al.*, 2002; *Hu et al.*, 2002]. Sorption behavior changes when the dye travels through different subsurface media, such as soil horizons or sediment layers. Given these constraints, dye patterns must be interpreted with caution.

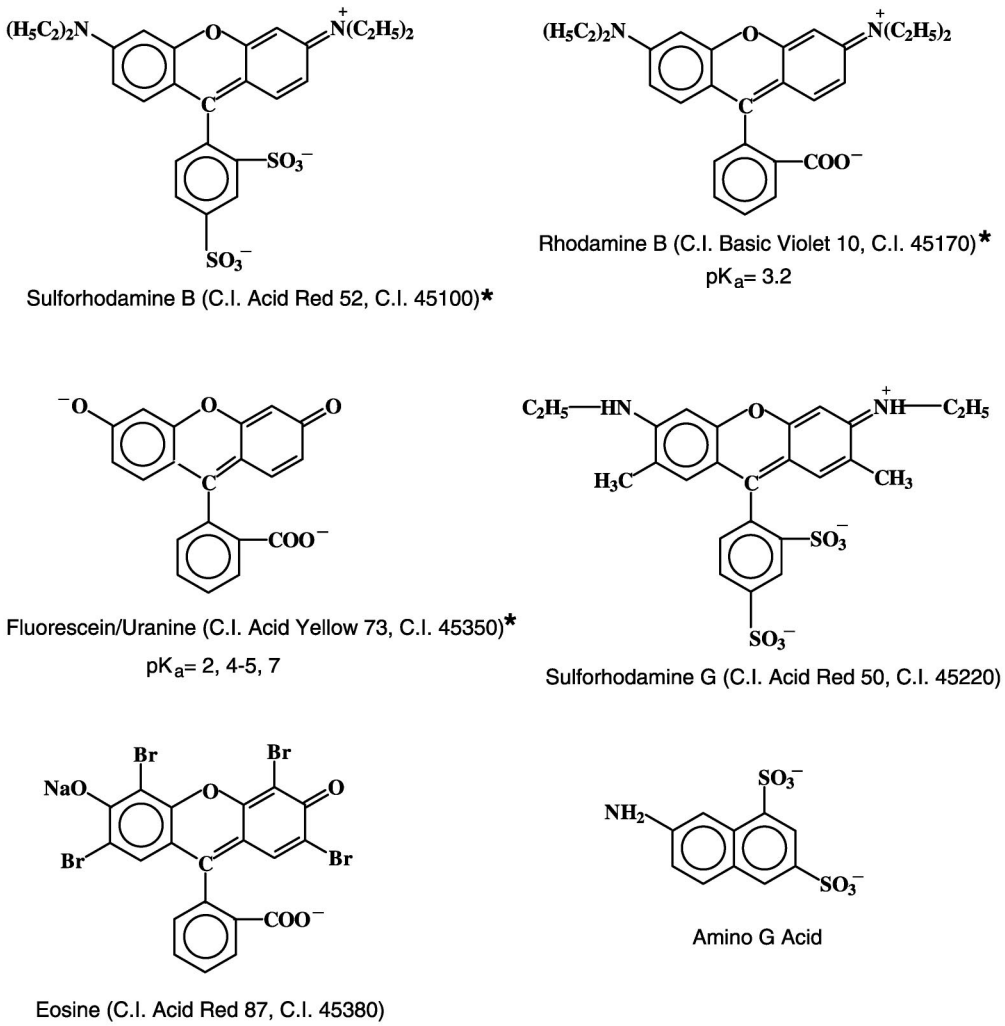

Figure 16. Structure of several common groundwater tracers (shown in completely dissociated form). All dyes, except Amino G Acid, belong to the xanthene dyes. The asterisk denotes dyes that are also used as vadose zone tracers. (Source of pK_a (acid dissociation constant) values for Rhodamine B is *Perrin* [1965] and for Fluorescein/Uranine is *Lindqvist* [1960].)

7.2. Fiber Optic Spectroscopy

[79] Fiber optic spectroscopy has received considerable attention in subsurface hydrology [*Kulp et al.*, 1988; *Nielsen et al.*, 1991; *Barczewki and Marschall*, 1992; *Benischke and Leitner*, 1992; *Ghodrati*, 1999]. Fiber optic sensors, in combination with fluorescence spectroscopy, offer the possibility of measuring tracer concentrations in situ. A fiber optic sensor can be installed underground and is able to detect multiple tracers. Since fluorescent dyes are readily detected with a fiber optic system, this method is attractive for hydrological tracing studies [*Kulp et al.*, 1988; *Schmid and Barczewski*, 1995]. In addition, fiber optic sensors can detect several types of contaminants such as benzene, toluene, phenol, xylene, and other organic compounds [*Chudyk et al.*, 1985; *Knezovich et al.*, 1990; *Apitz et al.*, 1992; *Bublitz et al.*, 1995; *Kumke et al.*, 1995].

[80] Tracers used for fiber optics spectroscopy include Fluorescein/Uranine, Rhodamine WT, and Pyranine [*Schmid and Barczewski*, 1995; *Ghodrati*, 1999]. In principle, any fluorescent dye can be detected. Fiber optic measurements can be used to construct tracer breakthrough curves in column experiments [*Kulp et al.*, 1988; *Ghodrati*, 1999; *Garrido et al.*, 1999, 2000] or to detect flow directions in field studies. In contrast to image analysis techniques, fiber optic sensors can measure in real time; however, spatial resolution is poor. Image analysis techniques allow detailed spatial resolution of tracer concentrations but poor temporal resolution.

8. TOXICOLOGICAL ASPECTS OF DYE TRACING

[81] Most dyes are synthetic chemicals designed to stain and color other materials for aesthetic purposes. Whenever synthetic chemicals are released into the environment, toxicological impacts must be considered. Specific to water tracers that are purposely, and often

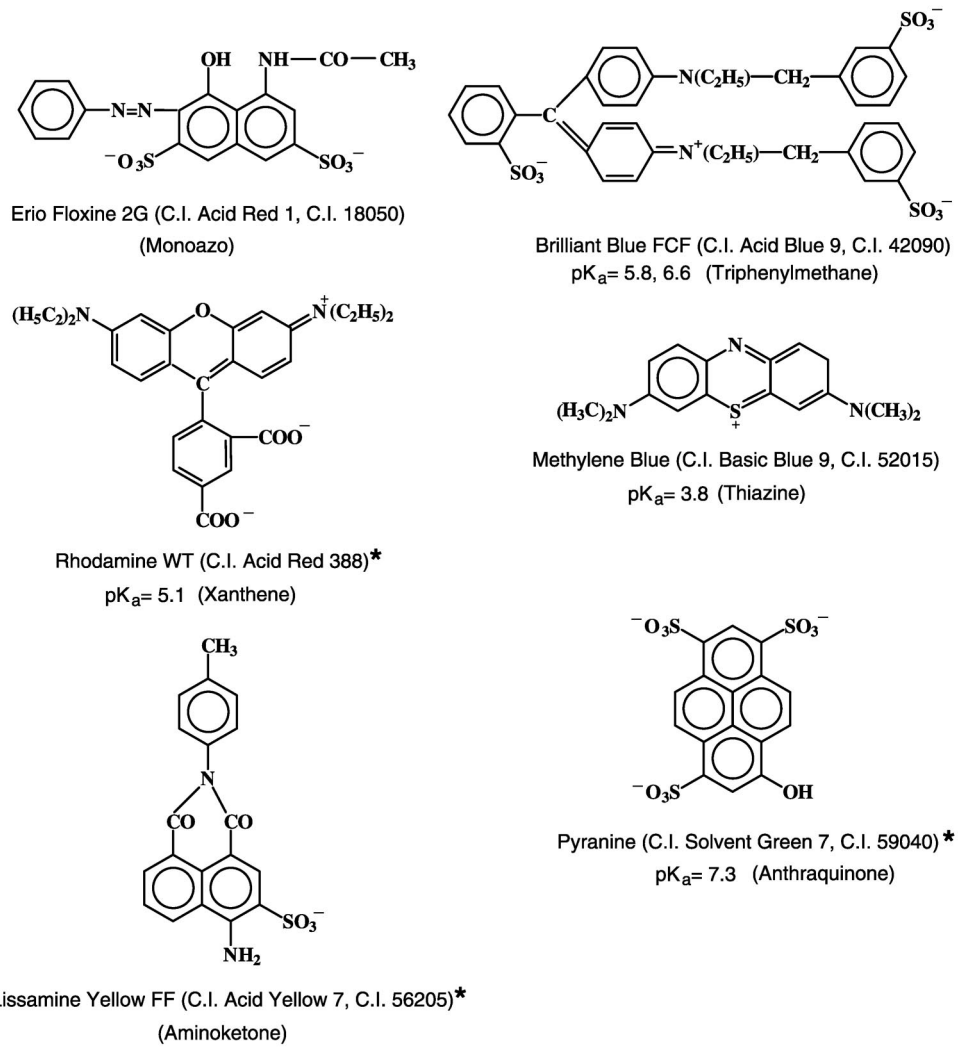

Figure 17. Structure of several common vadose zone tracers (shown in completely dissociated form). The asterisk denotes dyes that are also used as groundwater tracers. Only one of the two isomers, the meta isomer, is shown for Rhodamine WT. (Source of pK_a values for Brilliant Blue FCF is *Flury and Flühler* [1995], for Rhodamine WT (mixture) is *Shiau et al.* [1993], for Methylene Blue is *Perrin* [1965], and for Pyranine is *Haugland* [2001]).

directly, injected into surface and subsurface waters, the potential for water pollution exists. Removal of dye tracers from soils and aquifers is nearly impossible. Therefore the benefits gained from a dye tracer experiment must be weighed against the potentially, irreversible environmental impacts. Prior to use, the chemical's environmental toxicity and stability should be investigated. Unfortunately, toxicological reviews of dyes used as hydrological tracers are scarce and exist only for some fluorescent dyes [*Smart and Laidlaw*, 1977; *Smart*, 1984; *Field et al.*, 1995] and for Brilliant Blue FCF [*Flury and Flühler*, 1994]. Only a few toxicological investigations have been specifically carried out for hydrological tracing [*Bandt*, 1957; *Marking*, 1969; *Parker*, 1973; *Steinheimer and Johnson*, 1986], but general toxicological data for dyes are available in the toxicological literature.

[82] In general, sulfonate groups ($-SO_3^-$) tend to detoxify aromatic amines; dye molecules containing sulfonate groups are therefore usually less toxic than their parent compounds [*Zollinger*, 1991]. Not by coincidence, most food dyes contain one or more sulfonate groups [*Marmion*, 1991]. Sulfonate groups increase the solubility of dye molecules and render the molecule anionic, which might contribute to the detoxifying effect. Usually, the more soluble a chemical is, in combination with a net negative charge, the less toxic it is to mammals, since mammals tend to accumulate hydrophobic chemicals in their fat tissue. Cationic dyes have been found to affect bacteria, whereby the cations react with anionic groups in bacteria [*Little and Lamb*, 1973]. From a hydrological perspective the chemical characteristics for low toxicity are good news, because good tracers have high solubility

TABLE 4. Dyes Used or Evaluated as Vadose Zone Tracers, Sorted by Chemical Class

Dye Class	*Commercial Name*	*C.I. Name*[a]	*C. I. Number*[a]	*Hue*[a]	*Fluorescence*	*Purpose*	*Source*[b]
Monoazo	Cellitonecht Orange GR	C. I. Disperse Orange 3	11005	orange/yellowish red	no	visualization of flow patterns	*Ghodrati and Jury* [1990]
	Setacyl Scarlet RNA Supra	C.I. Disperse Red 1	11110	red/yellowish red/bluish red	no	adsorption and mobility in porous media	*Corey* [1968]
	Hisperse Orange B2-R	C.I. Disperse Orange 25	11227	bright reddish orange	no	visualization of flow patterns	*Clarke and Vincent* [1974]
	Metanil Yellow	C.I. Acid Yellow 36	13065	reddish yellow	no	mobility in porous media	*Corey* [1968]
	Pontacyl Fast Blue R	C.I. Acid Blue 92	13390	reddish blue	no	mobility in porous media	*Corey* [1968]
	Crimson GR	C.I. Acid Red 14	14720	bluish red	no	mobility in porous media	*Corey* [1968]
	Acid Orange A, D&C Orange 4, Orange II	C.I. Acid Orange 7	15510	bright reddish orange	no	mobility in porous media	*Corey* [1968]
	Allura Red, FD&C Red 40	C.I. Food Red 17	16035	yellowish red/ red	no	visualization of flow patterns	*Ghodrati et al.* [1999]
						screening test for adsorption and visibility	*Kung* [1990]
	Amaranth	C.I. Food Red 9 C.I. Acid Red 27	16185	bluish red	no	visualization of virus adsorption	*Singh et al.* [1986]
	Acid Orange GG	C.I. Acid Orange 10, C.I. Food Orange 4	16230	bright yellowish orange/bright orange	no	mobility in porous media	*Corey* [1968]
	Azo Fuchsine G	C.I. Acid Red 31	16540	bluish red	no	mobility in porous media	*Corey* [1968]
	Erio Floxine 2G Supra, Azophloxine	C.I. Acid Red 1, C.I. Food Red 10	18050	bright bluish red	no	adsorption and mobility in porous media	*Corey* [1968]
						visualization of flow patterns	*Ghodrati and Jury* [1990], *Stadler et al.* [2000], *Stamm et al.* [2002]
	FD&C Yellow 5, Tatrazine, Wool Yellow	C.I. Acid Yellow 23,C.I. Food Yellow 4	19140	yellow	no	demonstrations in solute transport	*Butters and Bandarayanake* [1993]
						mobility in porous media	*Corey* [1968]
						screening test for adsorption and visibility	*Kung* [1990]
Disazo	Acid Blue Black BXX	C.I. Acid Black 1	20470	bluish black	no	mobility in porous media	*Corey* [1968]
	Congo Red	C. I. Direct Red 28	22120	yellowish red	no	screening test for sorption and transport characteristics	*Trillat* [1899]
	Diphenyl Blue 2B	C.I. Direct Blue 6	22610	blue	no	adsorption and mobility in porous media	*Corey* [1968]
	Chicago Blue	C.I. Direct Dye	24395	NA	no	sorption characteristics	*Smettem and Trudgill* [1983]

Trisazo	Pontamine Black ULR	C.I. Direct Black 38	30235	black	no	mobility in porous media	*Corey* [1968]
	Diphenyl Fast Light Red, Sirius Red	C.I. Direct Red 80	35780	bright bluish pink/red	no	adsorption and mobility in porous media	*Corey* [1968]
						sorption characteristics	*Smettem and Trudgill* [1983]
C.I. azoic diazo components	R salt	C.I. Azoic Diazo Component 13	37130	NA	yes	screening of dyes for stability of fluorescence and visualization	*Reynolds* [1966]
Stilbene	Uvitex CF	C.I. Fluorescent Brightener 134	40619	blue	yes	visualization of flow patterns	*Omoti and Wild* [1979]
	Tinopal 5BM-GX	C.I. Fluorescent Brightener 28	40622	NA	yes	toxicity evaluation	*Field et al.* [1995]
	Tinopal 2 BP	C.I. Fluorescent Brightener 24	40650	bluish violet	yes	visualization of flow patterns	*Omoti and Wild* [1979]
						screening of dyes for stability of fluorescence and visualization	*Reynolds* [1966]
Diphenyl-methane	Auramine	C.I. Basic Yellow 2	41000	bright yellow	no	screening test for sorption and transport characteristics	*Trillat* [1899]
Triphenyl-methane	Malachite Green	C.I. Basic Green 4	42000	bright bluish green	no	adsorption and mobility in porous media	*Corey* [1968]
						screening test for sorption and transport characteristics	*Trillat* [1899]
	Alphazurine B	C.I. Acid Blue 26	42045	bright greenish blue	no	mobility in porous media	*Corey* [1968]
	Acid Green 2 G Extra	C.I. Acid Green 3, C.I. Food Green 1	42085	bright green	no	mobility in porous media	*Corey* [1968]
	Brilliant Blue FCF, FD&C Blue 1	C.I. Acid Blue 9, C.I. Food Blue 2	42090	bright greenish blue	no	sorption characteristics	1
						toxicity	*Flury and Flhler* [1994]
						visualization of flow patterns	2
						demonstrations in solute transport	*Butters and Bandarayanake* [1993]
						screening test for adsorption and visibility	*Kung* [1990]
	Magenta Powder, Fuchsine	C.I. Basic Violet 14	42510	bright reddish violet	no	adsorption and mobility in porous media	*Corey* [1968]
						screening test for sorption and transport characteristics	*Trillat* [1899]
	Paris Violet, Methyl Violet	C.I. Basic Violet 1	42535	bluish violet	no	screening test for sorption and transport characteristics	*Trillat* [1899]
	Brilliant Blue R 250	C.I. Acid Blue 83	42660	bright blue	no	visualization of flow patterns	*Jacobsen et al.* [1997]

TABLE 4. (continued)

Dye Class	*Commercial Name*	*C.I. Name*[a]	*C. I. Number*[a]	*Hue*[a]	*Fluorescence*	*Purpose*	*Source*[b]
	Lissamine Green	C.I. Acid Green 50, C.I. Food Green 4	44090	bluish green	no	visualization of flow patterns	*Jarvis et al.* [1987]
Xanthene	Sulforhodamine B, Lissamine Red, Pontacyl Brilliant Pink B, Erio Acid Red XB, Lissamine Red 4B, Kiton Rhodamine B, Acid Rhodamine B, Pontacyl Brilliant Pink, Pontacyl Pink	C.I. Acid Red 52	45100	bright bluish pink	yes	sensitivity of fluorescence as function of pH, ionic strength, temperature, and background fluorescence; costs	3
						sorption characteristics	4
						photodegradation	*Church* [1974], *Smart and Laidlaw* [1977], *Laidlaw and Smart* [1982], *Behrens and Teichmann* [1982], *Viriot and André* [1989]
						toxicity	*Church* [1974], *Smart and Laidlaw* [1977], *Smart* [1984], *Field et al.* [1995], *Behrens et al.* [2001]
						visualization of flow patterns	*Omoti and Wild* [1979], *Aeby et al.* [2001], *Hu et al.* [2002], *Vanderborght et al.* [2002a, 2002b]
						transport tracer, breakthrough curves	*Reynolds* [1966], *Kaufman and Orlob* [1956], *Rahe et al.* [1979], *Stamm et al.* [2002]
						water movement in willow and wildrose	*Robinson and Donaldson* [1967]
						chromatographic separation of Rhodamine WT, Rhodamine B, Sulforhodamine B, Sulforhodamine G	*Rochat et al.* [1975]
	Rhodamine B	C. I. Basic Violet 10	45170	(bright) reddish violet	yes	sensitivity of fluorescence as function of pH, ionic strength, temperature, and background fluorescence; costs	5

					sorption characteristics	*Feuerstein and Selleck* [1963], *Church* [1974], *Smart and Laidlaw* [1977], *Aulenbach et al.* [1978], *Laidlaw and Smart* [1982]
					photodegradation	6
					toxicity	7
					visualization of flow patterns	*Bond* [1964], *Reynolds* [1966], *Omoti and Wild* [1979], *Scotter and Kanchanasut* [1981]
					chromatographic separation of Rhodamine WT, Rhodamine B, Sulforhodamine B, Sulforhodamine G	*Rochat et al.* [1975]
Uranine,[d] Fluorescein, D&C Yellow 7	C.I. Acid Yellow 73	45350	bright yellow	yes	sensitivity of fluorescence as function of pH, ionic strength, temperature, and background fluorescence; costs	8
					solubility and acid dissociation constants, titrations	*Diehl and Markuszewski* [1985], *Diehl et al.* [1986]
					sorption characteristics	9
					photodegradation	10
					toxicity	11
					visualization of flow patterns	*Bond* [1964], *Reynolds* [1966], *Ritchie et al.* [1990], *Omoti and Wild* [1979], *Scotter and Kanchanasut* [1981]
					transport tracer	*Abba et al.* [1899], *Reynolds* [1966], *Kaufman and Orlob* [1956], *Rahe et al.* [1979]
					screening test for adsorption and visibility	*Kung* [1990]
					fiber optics	*Nielsen et al.* [1991], *Ghodrati* [1999], *Garrido et al.* [2000]
Eosine, Eosine Yellow, D&C Red 22	C.I. Acid Red 87	45380	yellowish pink	yes	sensitivity of fluorescence as function of pH, ionic strength, temperature, and background fluorescence; costs	*Trillat* [1899], *Viriot and André* [1989]

TABLE 4. (continued)

Dye Class	*Commercial Name*	*C.I. Name*[a]	*C. I. Number*[a]	*Hue*[a]	*Fluorescence*	*Purpose*	*Source*[b]
						sorption characteristics	12
						photodegradation	*Behrens and Teichmann* [1982]
						toxicity	*Bandt* [1957], *Smart* [1984], *Field et al.* [1995], *Behrens et al.* [2001]
						visualization of flow patterns	*Reynolds* [1966]
						transport tracer	*Reynolds* [1966]
						screening test for adsorption and visibility	*Kung* [1990]
	Erythrosine, FD&C Red 3	C.I. Acid Red 51, C.I. Food Red 14	45430	bluish pink/ yellowish pink/bright bluish red	yes	sensitivity of fluorescence as function of pH, ionic strength, temperature, and background fluorescence; costs	*Viriot and André* [1989]
						visualization of flow patterns	*Glass et al.* [1987, 1988, 1989]
						screening test for adsorption and visibility	*Kung* [1990]
	Rhodamine WT	C.I. Acid Red 388	NA	NA	yes	sensitivity of fluorescence as function of pH, ionic strength, temperature, background fluorescence; costs	13
						sorption characteristics	14
						photodegradation	15
						toxicity	16
						visualization of flow patterns	17
						visualization of plant roots	*Ruark and Bockheim* [1988]
						water movement in willow and wildrose	*Robinson and Donaldson* [1967]
						transport tracer	*Aulenbach et al.* [1978], *Aulenbach and Clesceri* [1980], *Trudgill et al.* [1983], *Kung et al.* [2000]
						chromatographic separation of Rhodamine WT, Rhodamine B, Sulforhodamine B, Sulforhodamine G	*Rochat et al.* [1975]

						screening test for adsorption and visibility	*Kung* [1990]
Thiazole	Primuline	C.I. Direct Yellow 59	49000	greenish yellow	yes	screening of dyes for stability of fluorescence and visualization	*Reynolds* [1966]
						sensitivity of fluorescence as function of pH, absorption and emission spectra, solubility, detection limits, photostability	*Viriot and André* [1989]
Azine	Safranine	C.I. Basic Red 2	50240	bright bluish pink	yes	screening test for sorption and transport characteristics	*Trillat* [1899]
						sensitivity of fluorescence as function of pH, absorption and emission spectra, solubility, detection limits, photostability	*Viriot and André* [1989]
	Nigrosine WSB Concentrated Powder	C.I. Acid Black 2	50420	black	no	mobility in porous media	*Corey* [1968]
Oxazine	Oxazine 170	C.I. Basic Blue 3	51004	bright greenish blue	yes	visualization of flow patterns	*Aeby et al.* [2001]
Thiazine	Methylene Blue	C.I. Basic Blue 9	52015	(bright) greenish blue	no	visualization of flow patterns, macropores	18
						hydraulic function of three types of macropores	*Bouma et al.* [1977]
						visualization of virus adsorption	*Singh et al.* [1986]
						screening test for sorption and transport characteristics	*Trillat* [1899]
Aminoketone	Brilliant Sulfoflavin FF, Lissamine FF, Lissamine Yellow FF, Brilliant Acid Yellow 8G, Lissamine Flavine FF	C.I. Acid Yellow 7	56205	bright greenish yellow	yes	sensitivity of fluorescence as function of pH, ionic strength, temperature, background fluorescence; costs	*Moser and Sagl* [1967], *Smart and Laidlaw* [1977], *Wilson et al.* [1986], *Viriot and André* [1989]
						Sorption characteristics	*Smart and Laidlaw* [1977], *Smettem and Trudgill* [1983], *Trudgill* [1987]
						photodegradation	*Smart and Laidlaw* [1977], *Behrens and Teichmann* [1982], *Trudgill* [1987], *Viriot and André* [1989]

TABLE 4. (continued)

Dye Class	*Commercial Name*	*C.I. Name*[a]	*C. I. Number*[a]	*Hue*[a]	*Fluorescence*	*Purpose*	*Source*[b]
						toxicity	*Smart and Laidlaw* [1977], *Smart* [1984], *Field et al.* [1995]
						visualization of flow patterns	*Smettem and Collis-George* [1985]
						transport tracer	*Smettem and Trudgill* [1983], *Trudgill et al.* [1983]
						screening test for adsorption and visibility	*Kung* [1990]
	Brilliant Sulfoflavine[d]	NA	NA	NA	yes	visualization of flow patterns, quantification	*Stadler et al.* [2000], *Aeby et al.* [2001], *Vanderborght et al.* [2002a, 2002b]
Anthraquinone	Alizarin Red S	C.I. Mordant Red 3	58005	dull bluish red/ bright yellowish red	no	visualization of flow patterns, macropore flow	*Germann et al.* [1984]
	Pyranine, D&C Green 8	C.I. Solvent Green 7	59040	yellowish green	yes	sensitivity of fluorescence as function of pH, ionic strength, temperature, background fluorescence; costs	*Smart and Laidlaw* [1977], *Viriot and André* [1989]
						sorption characteristics	*Smart and Laidlaw* [1977]
						photodegradation	*Smart and Laidlaw* [1977], *Behrens and Teichmann* [1982], *Viriot and André* [1989]
						toxicity	*Smart and Laidlaw* [1977], *Smart* [1984], *Field et al.* [1995], *Behrens et al.* [2001]
						visualization of flow patterns	*Reynolds* [1966], *Smettem and Collis-George* [1985]
						transport tracer	*Reynolds* [1966], *Smettem and Trudgill* [1983], *Trudgill et al.* [1983]
						screening test for adsorption and visibility	*Kung* [1990]
						fiber optics	*Rahe et al.* [1999], *Ghodrati* [1999], *Garrido et al.* [1999, 2000]

	Setacyl Blue BN New	C.I. Disperse Blue 3	61505	bright blue	no	adsorption and mobility in porous media	*Corey* [1968]
						visualization of flow patterns	*Omoti and Wild* [1979]
Indigoid	Indigo Carmine, Indigotine, FD&C Blue 2	C.I. Food Blue 1, C.I. Acid Blue 74	73015	greenish blue	no	adsorption and mobility in porous media	*Corey* [1968]
						visualization in Hele-Shaw cells	*Harding and Wood* [1941]
						visualization of flow patterns	*Glass et al.* [1987, 1988]
Inorganic pigments	Ultramarine Blue	C.I. Pigment Blue 29	77007	bright violet/ bluish green	no	visualization of flow patterns, staining earthworm channels	*Ehlers* [1975]
Optical brighteners	Tinopal AN	C.I. Fluorescent Brightener 55	NA	reddish blue	yes	screening of dyes for stability of fluorescence and visualization	*Reynolds* [1966]
	Uvitex WG	NA	NA	NA	yes	visualization of flow patterns	*Omoti and Wild* [1979]
	Uvitex OB	C.I. Fluorescent Brightener 184	NA	blue	yes	visualization of flow patterns	*Murphy et al.* [1977]
C.I. number unknown	Amino G Acid, 7-amino-1,3-naphtalene-disulfonic acid	NA	NA	NA	yes	sensitivity of fluorescence as function of pH, ionic strength, temperature, background fluorescence; costs	*Smart and Laidlaw* [1977], *Viriot and André* [1989]
						soil water tracing, breakthrough curves	*Trudgill et al.* [1983], *Stamm et al.* [2002]
						sorption characteristics	*Trudgill* [1987]
						toxicity	*Smart* [1984], *Field et al.* [1995]
	Dehydro-thio-paratoluidine sulfonic acid[d]	NA	NA	NA	yes	visualization of flow patterns	*Omoti and Wild* [1979]
						screening of dyes for stability of fluorescence and visualization	*Reynolds* [1966]
	Diphenyl Brilliant Flavine 7GFF, Direct Yellow 7G	C.I. Direct Yellow 96	NA	bright greenish yellow		visualization of flow patterns	*Omoti and Wild* [1979]
						toxicity	*Smart* [1984], *Field et al.* [1995]
	Kiton Yellow EFF[d]	NA	NA	NA	yes	screening of dyes for stability of fluorescence and visualization	*Reynolds* [1966]
	Keyazine Rea XRS[d]	NA	NA	NA	NA	screening test for adsorption and visibility	*Kung* [1990]

TABLE 4. (continued)

Dye Class	*Commercial Name*	*C.I. Name*[a]	*C. I. Number*[a]	*Hue*[a]	*Fluorescence*	*Purpose*	*Source*[b]
	Chlorantine Fast Green[d]	NA	NA	NA	no	sorption characteristics	*Smettem and Trudgill* [1983]
	Oracet Yellow 8GF[d]	NA	NA	NA	yes	staining of resin for pore structure investigation	*Moran et al.* [1989]

[a]NA indicates data are not available.

[b]Sources are as follows: 1, *Flury and Flühler* [1995], *Perillo et al.* [1998], *Allaire-Leung et al.* [1999], *Ketelsen and Meyer-Windel* [1999], *Schwartz et al.* [1999], *German-Heins and Flury* [2000], *Kasteel et al.* [2002], *Hu et al.* [2002]; 2, *Steenhuis et al.* [1990], *Flury et al.* [1994], *Natsch et al.* [1996], *Aeby et al.* [1997], *Gjettermann et al.* [1997], *Hatfield et al.* [1997], *Petersen et al.* [1997], *Baveye et al.* [1998], *Day et al.* [1998], *Gish et al.* [1998], *Jawitz et al.* [1998], *Ewing and Horton* [1999], *Forrer et al.* [1999], *Perillo et al.* [1999], *Schwartz et al.* [1999], *Allaire-Leung et al.* [2000a, 2000b], *Forrer et al.* [2000], *Bundt et al.* [2000], *Stadler et al.* [2000], *Peterson et al.* [2001], *Yasuda et al.* [2001], *Kasteel et al.* [2002], *Hu et al.* [2002], *Stamm et al.* [2002]; 3, *Feuerstein and Selleck* [1963], *Reynolds* [1966], *Moser and Sagl* [1967], *Scott et al.* [1969], *André and Molinari* [1976], *Smart and Laidlaw* [1977], *Laidlaw and Smart* [1982], *Wilson et al.* [1986], *Viriot and André* [1989]; 4, *Feuerstein and Selleck* [1963], *Church* [1974], *Smart and Laidlaw* [1977], *Laidlaw and Smart* [1982], *Smettem and Trudgill* [1983], *Kasnavia et al.* [1999], *Sabatini* [2000], *Hu et al.* [2002]; 5, *Feuerstein and Selleck* [1963], *Moser and Sagl* [1967], *Scott et al.* [1969], *Church* [1974], *Smart and Laidlaw* [1977], *Laidlaw and Smart* [1982], *Viriot and André* [1989]; 6; *Marking* [1969], *Church* [1974], *Smart and Laidlaw* [1977], *Behrens and Teichmann* [1982], *Laidlaw and Smart* [1982], *Viriot and André* [1989]; 7, *Marking* [1969], *Church* [1974], *Smart and Laidlaw* [1977], *Abidi* [1982], *Laidlaw and Smart* [1982], *Abidi et al.* [1986], *Smart* [1984], *Field et al.* [1995], *Behrens et al.* [2001]; 8, *Trillat* [1899], *Feuerstein and Selleck* [1963], *Moser and Sagl* [1967], *Church* [1974], *Andre and Molinari* [1976], *Smart and Laidlaw* [1977], *Laidlaw and Smart* [1982], *Viriot and André* [1989]; 9, *Feuerstein and Selleck* [1963], *Church* [1974], *Smart and Laidlaw* [1977], *Laidlaw and Smart* [1982], *Sabatini and Austin* [1991], *Kasnavia et al.* [1999], *Sabatini* [2000]; 10, *Marking* [1969], *Church* [1974], *Smart and Laidlaw* [1977], *Behrens and Teichmann* [1982], *Laidlaw and Smart* [1982], *Viriot and André* [1989]; 11, *Sowards* [1958], *Marking* [1969], *Church* [1974], *Smart and Laidlaw* [1977], *Laidlaw and Smart* [1982], *Smart* [1984], *Field et al.* [1995], *Behrens et al.* [2001]; 12, *Feuerstein and Selleck* [1963], *Church* [1974], *Smart and Laidlaw* [1977], *Laidlaw and Smart* [1982], *Sabatini and Austin* [1991], *Kasnavia et al.* [1999], *Sabatini* [2000]; 13, *Church* [1974], *Andre and Molinari* [1976], *Smart and Laidlaw* [1977], *Laidlaw and Smart* [1982], *Wilson et al.* [1986], *Trudgill* [1987], *Viriot and André* [1989]; 14, *Church* [1974], *Smart and Laidlaw* [1977], *Laidlaw and Smart* [1982], *Trudgill* [1987], *Sabatini and Austin* [1991], *Shiau et al.* [1993], *Di Fazio and Vurro* [1994], *Soerens and Sabatini* [1994], *Kanwar et al.* [1997], *Allaire-Leung et al.* [1999], *Kasnavia et al.* [1999], *Vasudevan et al.* [2001], *Sutton et al.* [2001]; 15, *Church* [1974], *Smart and Laidlaw* [1977], *Behrens and Teichmann* [1982], *Laidlaw and Smart* [1982], *Trudgill* [1987], *Tai and Rathbun* [1988], *Viriot and André* [1989]; 16, *Parker* [1973], *Church* [1974], *Smart and Laidlaw* [1977], *Abidi* [1982], *Laidlaw and Smart* [1982], *Johnson and Steinheimer* [1984], *Smart* [1984], *Abidi et al.* [1986], *Behrens et al.* [2001], *Steinheimer and Johnson* [1986], *Jensen and Krongaard-Kristensen* [1989], *Field et al.* [1995]; 17, *Saffigna et al.* [1976], *Kung* [1990], *Steenhuis et al.* [1990], *Trojan and Linden* [1992], *Allaire-Leung et al.* [2000a, 2000b]; 18, *Linden and Dixon* [1950], *Bouma and Dekker* [1978], *Bouma et al.* [1979], *Smettem and Collis-George* [1985], *Smettem* [1987], *van Stiphout et al.* [1987], *Steenhuis et al.* [1990], *Hornberger et al.* [1991], *Hatano and Booltink* [1992], *Hatano et al.* [1992], *Booltink et al.* [1993], *Vanderborght et al.* [2000]; 19, *Linden and Dixon* [1950], *Bouma and Dekker* [1978], *Bouma et al.* [1979], *Smettem and Collis-George* [1985], *Smettem* [1987], *van Stiphout et al.* [1987], *Steenhuis et al.* [1990], *Hornberger et al.* [1991], *Hatano and Booltink* [1992], *Hatano et al.* [1992], *Booltink et al.* [1993], *Vanderborght et al.* [2000]

[c]Uranine is the Na salt of Fluorescein and is the form mostly used as tracer because of its higher water solubility.

[d]Dye is not listed in the *Colour Index* [1971, 1999].

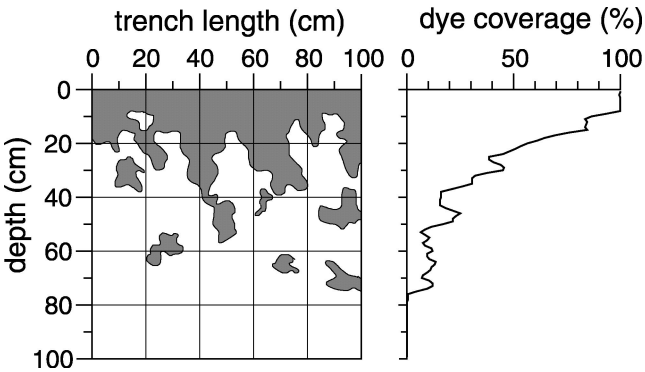

Figure 18. Flow pattern, and associated relative dye coverage, observed in a loamy soil after infiltration of 40 mm of Brilliant Blue FCF solution at the soil surface (adapted from *Flury et al.* [1994]).

and negative charge, that is, small sorption affinity to soil minerals.

[83] Dyes decompose by chemical degradation, photodegradation, and biochemical degradation. Biodegradation of colorants takes place slowly, since most synthetic dyes are xenobiotic [*Clarke and Anliker*, 1980; *Zollinger*, 1991]. Dyes are often designed to resist biodegradation, since we usually want the colors on fabrics, wood, or metal to resist fading. The natural system of microorganisms in rivers and lakes is missing the enzymes needed to degrade synthetic dyes under aerobic conditions [*Zollinger*, 1991]. Dyes degrade slightly faster under anaerobic compared to aerobic conditions [*Zollinger*, 1991].

[84] Human-applied tracers may react with naturally occurring compounds, contaminants, or water treatment agents to form toxic byproducts. An extreme example is the formation of highly toxic tribromomethans via chlorination of drinking water that contains Br^- and organic carbon [*Flury and Papritz*, 1993]. Similar reactions can take place with dyes. Chlorophenol compounds are suspected to form during chlorination of water containing dye tracers [*Smart*, 1984]. Rhodamine dyes, such as Rhodamine B and Rhodamine WT, can react with nitrite to form the carcinogenic compound diethylnitrosamine [*Abidi*, 1982; *Steinheimer and Johnson*, 1986]. Test results, however, indicate that under customary dye use practices, Rhodamine WT should not pose an environmental hazard [*Johnson and Steinheimer*, 1984].

[85] Halogenated xanthene dyes can be used as light-activated pesticides, particularly as insecticides [*Heitz*, 1995; *Wood*, 1996]. Upon absorption of light, halogen atoms cause oxygen to raise to the first singlet state. Singlet oxygen is a strong oxidizing agent and can attack cellular membranes and biomolecules [*Valenzo and Tarr*, 1995]. Insects that digest such dyes, usually die upon exposure to sunlight [*Heitz*, 1997]. The most effective dye insecticides are the xanthenes Rose Bengal (C.I. Acid Red 94, C.I. 45440), Erythrosine (C.I. Acid Red 51, C.I. 45430), and Phloxine B (C.I. Acid Red 92, C.I. 45410) [*Heitz*, 1995]. These dyes have much lower toxicities to humans and mammals compared to synthetic insecticides and therefore can be valuable pest control agents [*Heitz*, 1997].

[86] Regulations for the use of dyes as subsurface tracers are scarce. In the United States we are unaware of general, federal regulations issued by the U.S. Environmental Protection Agency (EPA) (M. S. Field, personal communication, Center for Environmental Assessment, EPA Office of Research and Development, Washington, D. C., 17 December 2001). State agencies may have regulations in place, but these will vary from state to state. The Washington State Department of Ecology, for example, will decide on a case by case basis whether a certain chemical is allowed in a tracer test. No specific regulations regarding dye tracers are in place (M. Shaleen-Hansen, personal communication, Surface and Groundwater Quality Management Unit, Water Quality Program, Washington State Department of

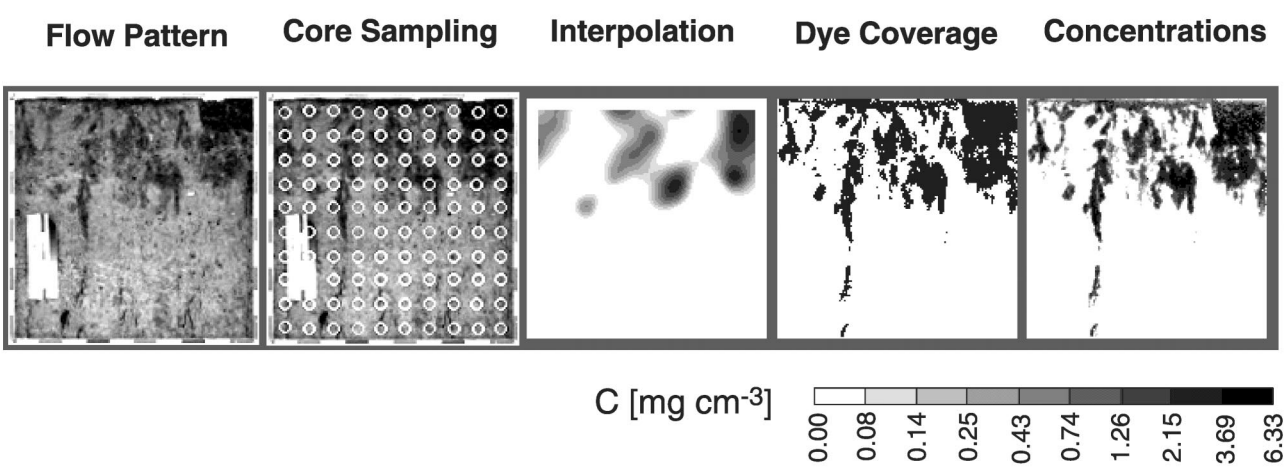

Figure 19. Spatial distribution of dye concentrations measured with different degrees of resolution. Adapted from *Forrer* [1997], modified by permission of I. Forrer.

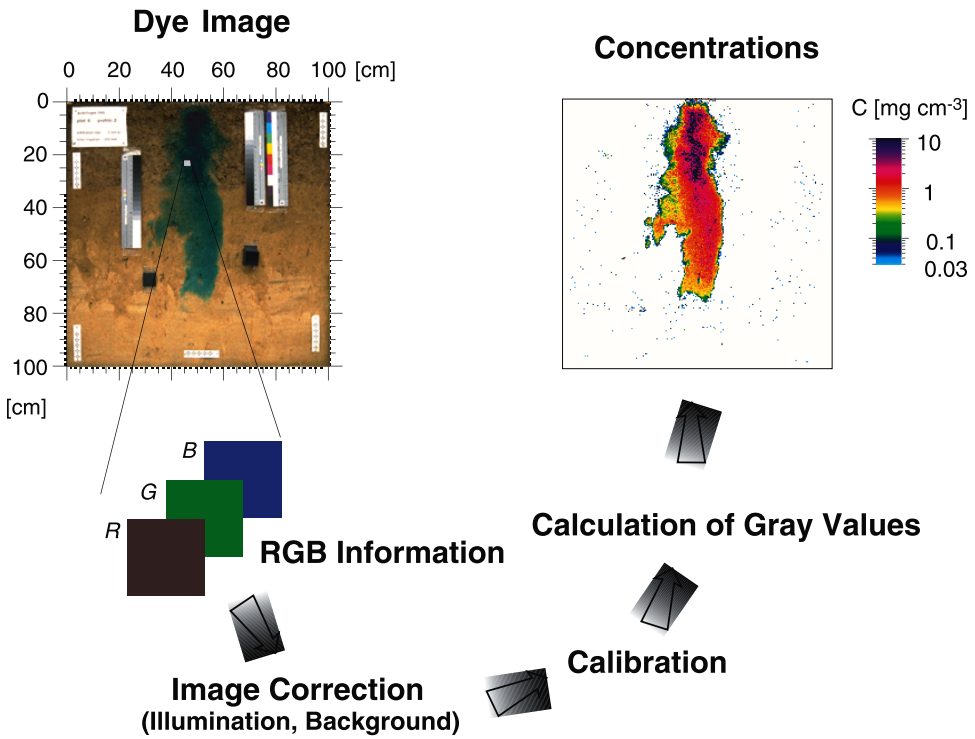

Figure 20. Image analysis procedure to determine tracer concentrations from color images. Adapted from *Forrer* [1997], modified by permission of I. Forrer.

Ecology, Olympia, Washington, 21 December 2001). General regulations at the federal and state level do classify wells for different types of material injections, including the application of dye tracers [*Mull et al.*, 1988; *Quinlan*, 1989]. Previously on the Drinking Water Contaminant Candidate List, Rhodamine WT has recently been removed because the EPA anticipates no adverse health effects when the dye is used as a tracer [*Federal Register*, 1998]. Water quality criteria established by the National Sanitation Foundation (Standards and Publications, available at http://www.nsf.org, 2001) for Rhodamine WT are 0.1 μg L^{-1} for drinking water, 10 μg L^{-1} for water entering a drinking water plant, and 100 μg L^{-1} for groundwater not associated with drinking water production (American National Standards Institute/National Sanitation Foundation Standard 60) [*Federal Register*, 1998].

[87] In comparison, the German Federal Environmental Agency (Umweltbundesamt) recently formed a committee to assess the toxicological and ecotoxicological impacts of water tracers [*Behren et al.*, 2001]. Eleven fluorescent dye tracers, primarily groundwater tracers, were tested for genotoxicology and ecotoxicology. Among the eleven, seven dyes were reported toxicologically safe (Fluorescein/Uranine, Eosine, Sulforhodamine G, Pyranine, Sodium Naphtionate, Tinopal CBS-X, and Tinopal ABP). The other four dyes (Sulforhodamine B, Rhodamine WT, Rhodamine B, and Rhodamine 6G) caused either genotoxicologically or ecotoxicologically adverse effects and were deemed unsafe as tracers [*Behrens et al.*, 2001].

[88] Overall, synthetic dyes should be considered toxic to the environment. A toxicologically sound alternative, particularly for field applications, may be certified food dyes. Food dyes are thoroughly tested to ensure nontoxicity to humans; however, colored foods contain only small amounts of dye, in most cases, 0.005–0.03% by weight [*Zollinger*, 1991]. These concentrations are far less than adequate for tracer studies; much larger concentrations would be required. Therefore, even with food dyes, toxic environmental effects are possible, and the use of food dyes should be carefully considered.

[89] On the basis of toxicological considerations a water concentration limit of ~1 mg L^{-1}, following the tracing experiment, has been proposed for Brilliant Blue FCF [*Flury and Flühler*, 1994] and 12 fluorescent tracers [*Field et al.*, 1995]. Given the results from these and other studies, dyes can be used safely and successfully to trace water movement in the subsurface if the dosage chosen results in water concentrations below a nontoxic value. The expected concentrations after a tracer experiment, however, particularly in the vadose zone, are often difficult to estimate. Therefore determining the appropriate amount of dye to ensure both unambiguous scientific results and environmental safety remains a difficult task [*Field et al.*, 1995].

9. CONCLUSIONS

[90] Dyes have been used for more than a hundred years to trace water flow and contaminant movement in the subsurface. The first dye used as a hydrological tracer was Fluorescein, shortly after its synthesis in 1871. Fluorescein has since become the most prominent dye for groundwater tracing. For tracing water in the vadose zone, various dyes have been proposed, the most prominent of which is Brilliant Blue FCF.

[91] Several thousands of different dyes are commercially available. These compounds have been designed for a specific purpose of dying. Hydrologists have screened some of the dyes for tracer properties. In general, the mobility of an organic molecule in a soil or aquifer medium is related to the molecule's solubility and charge. For instance, the greater the number of sulfonic acid groups in the dye molecule, the more soluble the dye is in water, and the more mobile the dye becomes in soil [*Corey*, 1968]. Many dyes, such as acid dyes, contain one or more sulfonic acid groups.

[92] An ideal dye tracer has yet to be found and might not exist. Several different compounds have been recommended as suitable water tracers, but all are more or less retarded in a soil medium. Sorption can be nonlinear and controlled by kinetic effects, so dye patterns must be interpreted with caution. Nevertheless, dyes are valuable tracers to visualize flow pathways and patterns in the vadose zone.

[93] Dyes are usually identified with their C.I. generic name or C.I. constitution number. This identification system ensures that colorants with the same C.I. name and number possess the same structure but does not guarantee the same purity for all preparations of a dyestuff. For use as a hydrological tracer the dye's degree of purity must be noted, since the ecotoxicological properties may depend on the purity of the dye.

[94] Toxicological as well as aesthetic aspects are important to consider in dye tracing studies. Most synthetic dyes are resistant to degradation in the environment. Food dyes pose the least environmental hazard and are recommended as hydrological tracers from the toxicological perspective.

[95] Recent developments in dye imaging and fiber optic spectroscopy have enabled the quantitative analysis of temporal and spatial dye concentrations patterns. Such techniques provide important new tools to improve our understanding of water flow and chemical movement in the vadose zone.

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