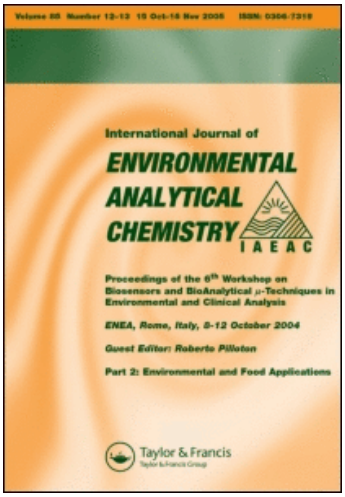

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Development of an Optical Fiber Fluorescence Setup for *in situ* PAHs Detection in Porous Media. Application to Pyranine Transport in Sand Columns

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DEVELOPMENT OF AN OPTICAL FIBER FLUORESCENCE SETUP FOR *IN-SITU* PAHs DETECTION IN POROUS MEDIA. APPLICATION TO PYRANINE TRANSPORT IN SAND COLUMNS

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An optical method based on fluorescence spectroscopy was developed for *in-situ* non-destructive, real time, organic pollutant detection and quantification in soil. Optical fiber-based light-induced fluorescence probes allowing *in-situ* specific chemical detection were constructed. Pyranine was chosen as a model fluorescent Polycyclic Aromatic Hydrocarbon (PAH). The effect of sand particles on fluorescence measurements was established: the fluorescence intensity in water-saturated sand was eight times lower than in aqueous solutions, due to light scattering by the sand particles. To adapt the method to dynamic pollutant concentration measurements in soil, two different designs of light diffusers were constructed and compared. A light distributor with a quartz window was chosen for its higher sensitivity and reproducibility. The probes were introduced into two different columns: short ones used to study the effect of the measurement location in the column and longer ones to study pyranine transport. It was shown that, in columns, the measurement location plays an important role; measurements near the walls, in particular, were different from those performed more towards the center of the column in a given section. As a consequence, one should avoid measurements near the circumference. Preliminary results were successfully compared to a chemical transport model and revealed that the methodology is a powerful tool to measure *in-situ* concentration changes; on the other hand, fluorescent measurements can be used efficiently to determine transport parameters and give results comparable with those obtained with classical breakthrough curve fittings.

Keywords: Optical fibers; quartz light diffusers; pyranine; transport; *in-situ* fluorescence detection; sand columns

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INTRODUCTION

Organic pollutants are a major source of groundwater contamination due to accidental spills, use of agrochemicals or atmospheric deposition. Groundwater is a major resource for drinking water supply; its quality is closely connected to soil and infiltrating water quality. Classical methods for determining state variables such as concentration involve sampling of soil materials or soil solution. Such an approach is destructive and the information gained from samples is limited to only a specific point in time and space. Furthermore, the treatment of the sample may alter its properties dramatically. To avoid removal of the solid matrix or of soil solution, the most promising alternative approach is to use minimally invasive non-destructive *in-situ* real-time analysis. As for all analytical methods, important requirements for *in-situ* non-destructive measurements that do not disturb the transport being measured are selectivity, sensitivity and small size. As a consequence, background signals and solid matrix interference must be as low as possible.[1] Kumke et al.[2] reviewed the principal aspects of environmental analysis with particular references to recent developments in *in-situ* and on-site investigations. After a comparison of different instrumental spectroscopic methods for investigation of PAH contaminants in water and soils, they concluded that fluorescence spectroscopy and ion detection, often coupled with mass spectrometry, appeared at present to be the most promising methods.[2]

Light-induced fluorescence is a sensitive method, with a large scope of applications, for non-destructive measurements of fluorescing compounds, but also for non-fluorescing compounds where they can be tagged with fluorescent reagents. The basic principles of fluorescence spectroscopy are well described in the literature.[3,4] Contrary to most other methods, fluorescence spectroscopy is really a trace analysis method since it works better at low than at high concentrations.[1] Light-induced fluorescence spectroscopy using lasers[5,6] or other powerful sources[7] is largely used in biological and environmental science. In recent years, fiber-based fluorescence instrumentation has been developed and used for the detection of organic contaminants in groundwater and soils.[8–11] Lieberman et al.[12] developed a fiber-based laser-induced fluorescence set-up for the identification of mineral oil pollution in soils. A similar mobile system for fluorescence spectroscopy of oil pollutants in soil was successfully developed by Schade and Bublitz.[13] Fluorescence spectroscopy has successfully been used for the detection of PAHs in air and in natural waters[14,15] but not in dynamic conditions and the results were not compared to mathematical models.

The goal of the present work is to develop fiber-based probes and to use them to quantitatively study the transport of a model PAH in soil using *in-situ* detection in laboratory conditions. A pure quartz sand and pyranine, a polycyclic

aromatic dye, were used in batch experiments to determine the best detection conditions as well as the best probe location inside the columns, and also to improve the characteristics of the instrument and of the probes themselves. The system was then used to study the dynamic behavior of pyranine in a water-saturated sand column by non-destructive *in-situ* quantification. The measured concentration profiles were compared to simulated curves, calculated on the basis of parameter values determined from the pollutant breakthrough curves. We show that *in-situ* measurements can be used to accurately characterize pollutant transport parameters given adequate positioning of the probe inside the column.

EXPERIMENTAL

Materials

The model molecule is a widely-used dye: pyranine (8-Hydroxy-1,3,6, trisulfonic acid, trisodium salt), a derivative of pyrene which is a priority pollutant. Due to its sulfonyl and hydroxyl groups, pyranine is quite soluble in water, in which its molar extinction coefficient at 404 nm is 1.72 10^4 L mol^{-1} cm^{-1}. At neutral pH, the pyranine maximum visible light absorption is at 404 nm and the maximum of its fluorescence is at 511 nm. The porous solid matrix used in this study is a pure and non-interactive quartz sand (SiO_2 > 99.9%) from Fontainebleau (Prolabo, France) with a grain size ranging from 150 to 210 μm.

Experimental Setup for Fluorescence Measurements

Figure 1 shows the experimental setup used for the fluorescence measurements. It has been designed to be easily transportable. Fluorescent compounds are excited with a 75 W high-pressure Xenon lamp, whose light is spectrally resolved by a quarter meter monochromator with a bandwidth of 5 nm. Full reflective and dichroic reflective optics serve to couple the light into a 600 μm diameter quartz core, silicon-cladded fiber (1.5 m long). The length of the fiber is not a limiting factor for on-site monitoring since up to 1 km-long fibers have already been used for this purpose. Excitation intensity is measured in the excitation light path by coupling a few percent of Fresnel reflection of a quartz plate onto a calibrated photodiode.

Fluorescence emission from the sample is collected with the same fiber, spectrally separated from the excitation path by the dichroic mirror and filtered with a second colored glass filter (cutoff at 425 nm) which virtually eliminates all

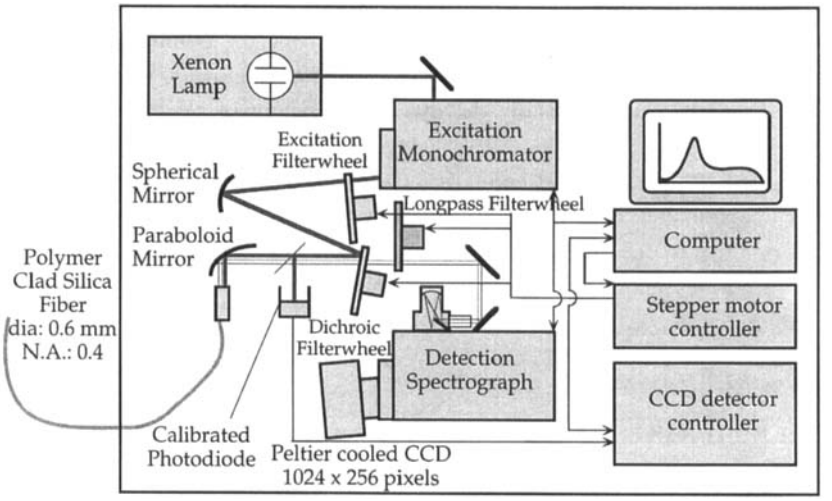

FIGURE 1 Experimental setup for fluorescence measurements.

reflected excitation light. Detection is based on a Peltier cooled spectroscopic charge coupled device (CCD 1024 × 256 pixels), with a UV-sensitive coating coupled to an imaging spectrograph. This combination allows low noise level fluorescence spectra to be achieved.

Quartz Light Distributors

The engineering of the fiber-based probes is a fundamental part of the whole measuring system. Due to the strongly heterogeneous optical properties of soils on a microscopic scale and due to the low penetration depth of light in natural soils (Figure 2), the fluorescence measurements must probe a reasonably-sized soil volume in order to obtain more representative results.

For this reason, two kinds of light distributors were developed: the first is presented in Figure 3a. It consists of a spherical light diffuser composed of a mixture of TiO_2 and a transparent epoxy glue. The distal end of the fiber is immersed several times into the mixture until a droplet-like diffuser is obtained.

Figure 3b shows the second type of probe composed of a quartz window of 4 mm diameter and 2 mm length which is glued to the end of a hollow stainless steel tube in which the fiber is inserted. The relationship between the numerical aperture of the fiber and the light opening angle is given by:

$$NA = n \sin \alpha_c \quad (1)$$

where NA is the numerical aperture of the fiber, n is the refraction index of the

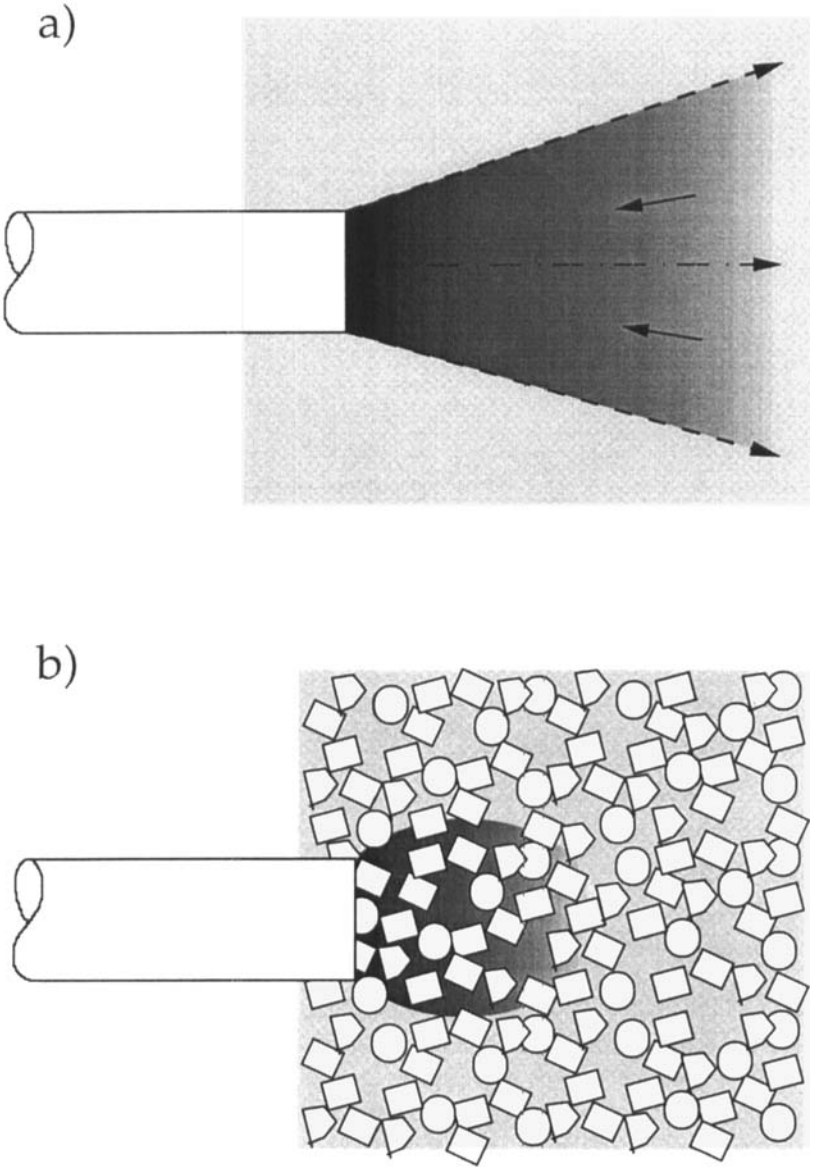

FIGURE 2 Schematic presentation of a naked fiber in solution (**a**) and in a sand/solution mixture (**b**). In **a**, excitation light propagates in the conic area and its attenuation is only due to the chromophore absorption. The fluorescence emission is gathered from about the same area. In **b**, excitation and emission light are scattered by the sand grains.

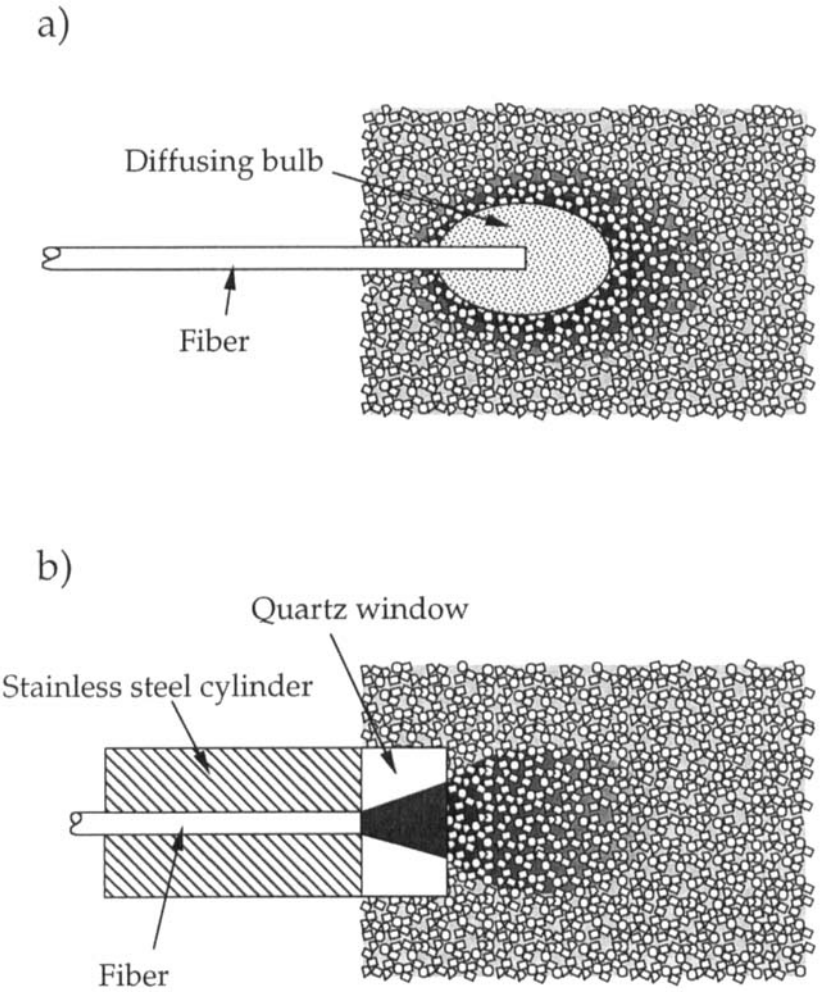

FIGURE 3 Schematic presentation of a droplet shape diffuser (a) and a quartz light diffuser (b) in a sand/solution mixture.

quartz window and α_c is the opening angle of the fiber. The opening angle here is 14.3° and the illuminated area is increased by a factor of 8 compared to that of the bare fiber because of the distance created between the fiber tip and the sand matrix. Furthermore, this second type of probe can be prepared in a more reproducible way than the first diffuser.

Performance of the In-Situ Fluorescence Measurements

Quantitative *in-situ* fluorescence measurements necessitate prior calibration. The two probes were calibrated in batch experiments by measuring fluorescence in pyranine solutions or sand/pyranine solution mixtures at different concentrations

both with the naked fiber and with the two optical probes. The batches consisted of 50 ml vials filled with 30 g of dry sand packed to a bulk density of 1.75 g cm^{-3}. The batches were then saturated with the appropriate pyranine solutions and the light diffusers inserted in the middle of the sand at a depth of approximately 0.5 cm. To be able to take into account the natural fluorescence of the sand, a background fluorescence measurement was systematically done, simultaneously in pure water and wet, packed sand. The background signal was subtracted from the sample fluorescence signal and the resulting peak was integrated between 432 and 678 nm.

Pollutant Transport Setup

Small Column

To assess the effect of the probe location inside the column on fluorescence measurements, short columns of 8 cm height and 5 cm diameter were equipped with 4 probe supports at the same height (4.5 cm from the bottom). Four light diffusers were inserted at different distances from the column wall: 0, 0.8, 1.6 or 2.5 cm (Figure 4). The bulk density of the sand in the column was 1.75 g cm^{-3} (the same as that in the sand batches), the porosity 34% and the natural saturation water content 30%.

Long Columns

To study pollutant transport in saturated conditions, the experimental setup presented in Figure 5 was used. It consists of specially-designed long columns (50 cm-long), equipped for the measurement of the water content. The latter was performed by Time Domain Reflectometry (TDR), a technique based on the measurement of the dielectrical properties of soils.[16] This technique, formerly developed for field measurements, was successfully adapted to soil column studies using small three rod probes.[17]

The columns, made of Plexiglas, were composed of various elements of 7 cm length and 5 cm diameter, some of which were designed to support the optical probes described in Figure 5. These probes were introduced into the column at depths of 4.5, 18.5 and 32.5 cm respectively from the inlet of the column. The light diffusers were placed in the middle of the column, i.e. 2.5 cm from the wall.

Other elements were designed to support triple-wire TDR probes of 5 cm length that were placed at 11.5 and 25.5 cm respectively from the bottom of the

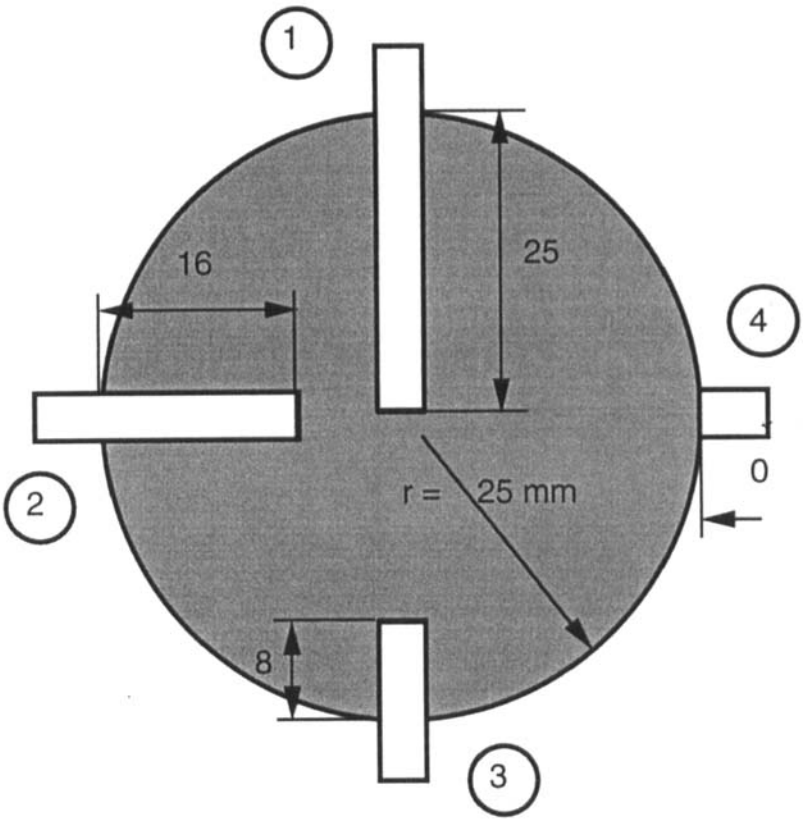

FIGURE 4 Position of the optical fiber diffusers in the horizontal section of a short column at 4.5 cm depth. Fibers 1, 2, 3 and 4 are placed at 2.5, 1.6, 0.8 and 0 cm distance respectively from the column wall.

column. In the present work, the TDR system was only used to control the stability of the saturation water content profile in the long sand columns during the experiments.

The physical characteristics of the sand placed in the columns were similar to those of the short columns. The columns were subjected to steady-state flows of distilled water at 66 or 185 $cm^3\ h^{-1}$ (average pore water velocities of 11 and 31 $cm\ h^{-1}$ respectively) using a peristaltic pump. The experimental system permitted the imposition of controlled variations of chloride (1 $g\ l^{-1}$) and pyranine (2.10^{-5} M) concentration at the input (step injections) and the recovery of samples at the bottom of the column. Pyranine and chloride samples were analyzed using a Shimadzu spectrofluorometer (RF-5000) and an Jon Chromatography DIONEX respectively. Chloride tracer and pyranine breakthrough curves (BTC)

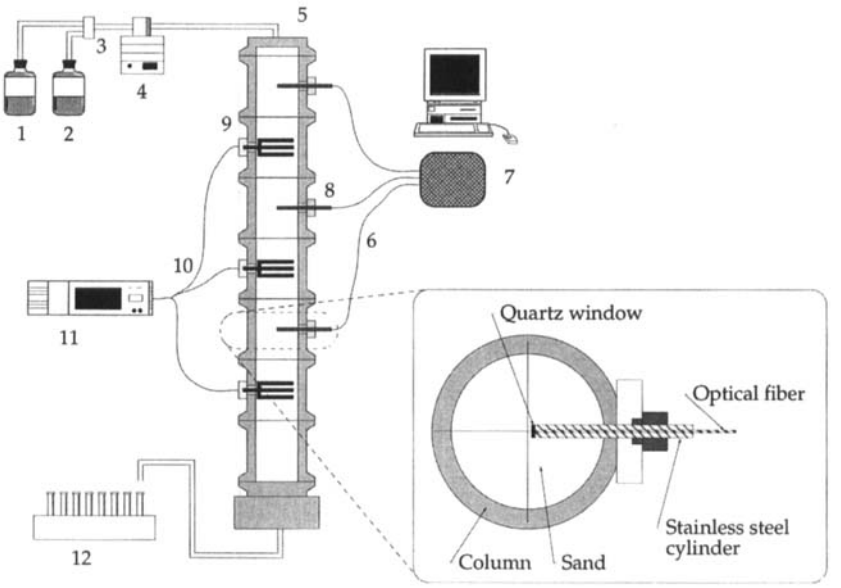

FIGURE 5 Experimental setup for pyranine transport study. 1- Pyranine or chloride solution, 2- water, 3- valve, 4- peristaltic pump, 5- sand column (50 cm long), 6- optical fiber, 7- fluorometer, 8- quartz light diffuser, 9- TDR electrode, 10- co-axial cable, 11- Tektronix cable tester, 12- fraction collector.

were thus obtained and presented in a dimensionless form to facilitate the interpretation of the results. The experiments consisted of the monitoring of the movement of step-injected pyranine solutions by *in-situ* concentration measurements with four (short column) or three (long column) optical probes simultaneously.

Each probe was calibrated independently by saturating the columns with solutions of different pyranine concentrations during 5 pore volumes to insure concentration equilibrium in all the porous media. Under water-saturated conditions, the calibration curves were linear.

Theoretical Section

For steady-state water-flow conditions, solute transport in porous media can be described by the following equations:[18]

$$(\theta m + f\rho_d K)\frac{\partial Cm}{\partial t} + (\theta im + (1 - f)\rho_d K)\frac{\partial Cim}{\partial t} = \theta mDm\frac{\partial^2 Cm}{\partial z^2} - \theta mVm\frac{\partial Cm}{\partial z} + \sum_j \phi_j^i \quad (2)$$

and

$$(\theta im + (1 - f)\rho_d K)\frac{\partial Cim}{\partial t} = \alpha(Cm - Cim) \quad (3)$$

where f is the solid fraction in contact with mobile water, K is the distribution coefficient for linear sorption of the solute (L^3 M), f is the solid fraction in contact with mobile water (−), ρ_d is the soil bulk density (ML^{-3}), θm and θim are the volumetric mobile and immobile water contents (L^3L^{-3}) respectively, Cm and Cim are the solute concentrations (ML^{-3}) in the mobile and immobile water fractions respectively, Vm is the mobile water velocity ($L\ T^{-1}$), Dm is the dispersion coefficient (L^2 T), α is the mass transfer coefficient between mobile and immobile fractions (T^{-1}), ϕ is a sink/source term ($M\ L^{-3}\ T^{-1}$), z is the distance (L) and t is time (T).

The model can be expressed in a dimensionless form by defining five parameters:

$$P = \frac{V_m L}{D_m} \quad To = \frac{V t_p}{L} \quad R = 1 + \frac{\rho_d K}{\theta} \quad \beta = \frac{\theta_m + f\rho_d K}{\theta + \rho_d K} \quad \omega = \frac{\alpha L}{q} \quad (4a,b,c,d,e)$$

where P is the Peclet number (related to the dispersion coefficient), To is the dimensionless pulse duration, t_p is the pulse duration (T), R is the retardation factor (related to solute adsorption), β represents the mobile water fraction and ω the solute dimensionless transfer coefficient between the mobile and immobile water fractions. The CXTFIT code[18] was used to identify independently the hydrodynamic parameters (P, ω and β) by fitting breakthrough curves (flux concentrations) obtained with the chloride tracer and then by proceeding to the identification of the other parameters.[19] The curves measured inside the columns (in situ) were then compared to the one calculated with CXTFIT (resident concentrations).

RESULTS AND DISCUSSION

Batch Experiments

Probe Calibration

A/ Naked fiber

Figure 6 shows the intensity of the fluorescence of pyranine, measured with a naked fiber, as a function of its concentration in aqueous solutions (a) and in sand/solution mixtures (b) in the batch systems described previously. A sensi-

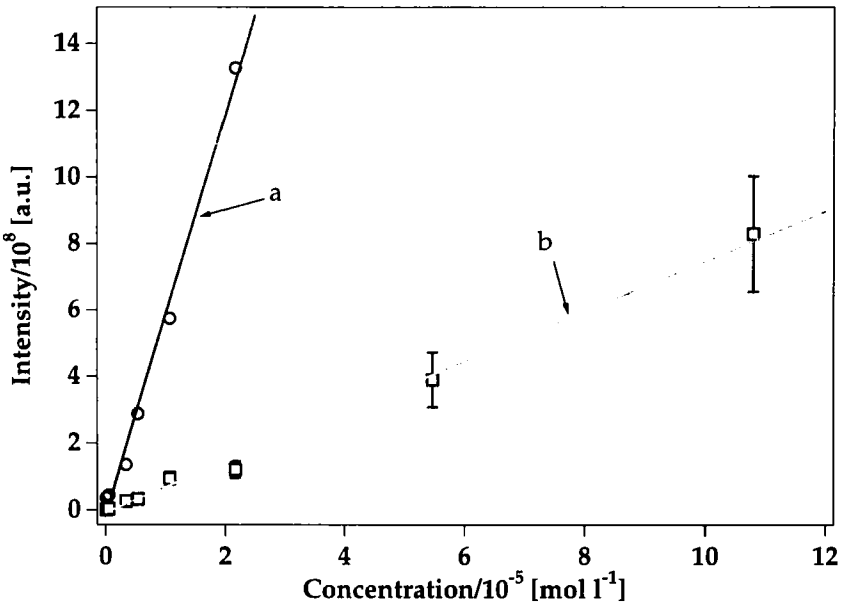

FIGURE 6 Fluorescence intensity as a function of the pyranine concentration measured with a naked fiber in solution (a) and in sand/solution mixture (b). Absence of error bars means that symbols are bigger than the error bars.

tivity coefficient (slope of the curves: I/C) has been defined in order to facilitate the comparison between the different calibration curves. Its values are 5.810^{13} (a) and 7.510^{12} (b) (8 times lower) in aqueous solution and in the sand/solution mixture, respectively. This difference can be explained by the scheme presented in Figure 2. In a pyranine solution, the light propagates through the conic aperture of the fiber. In this space, it is absorbed by pyranine molecules and part of the fluorescence light is directed back into the fiber within the same area. In a sand/solution mixture, part of the exciting and emitted light is scattered by the sand. So the light does not penetrate as far as it does in solution and the fluorescence light is not entirely directed back to the detector[8]. Two problems may occur during measurements with naked fibers: the diameter of a fiber is 600 μm and the average diameter of a sand particle 200 μm; thus, a few grains in front of the fiber can limit light propagation. On the other hand, if the fiber is moved slightly, some solution can penetrate between the flat surface of the fiber and the sand grains. This quantity may change according to the position of the fiber in the porous medium and affect the reproducibility of the measurements. Furthermore, the fluorescence is influenced by the grain size (which determines the penetration depth of light and diffuse reflectance). This problem

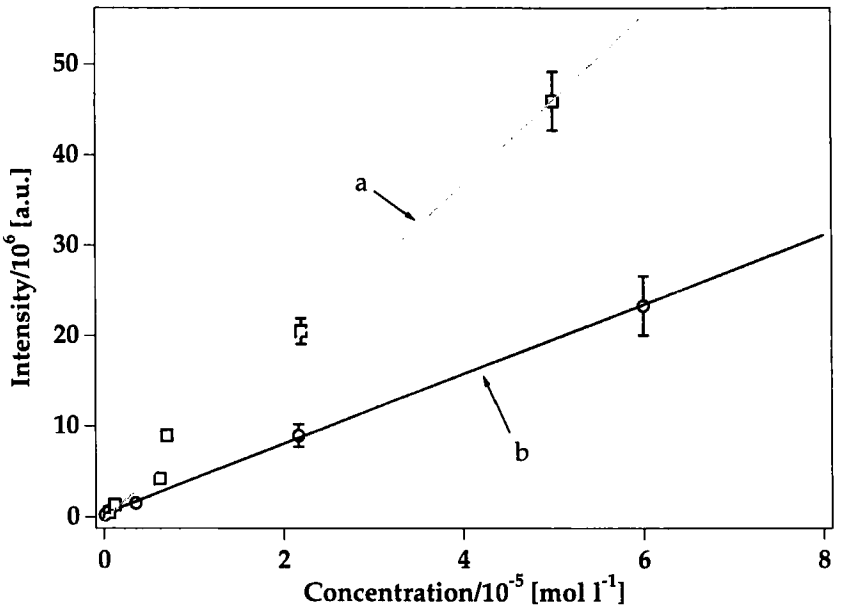

FIGURE 7 Fluorescence intensity as a function of the pyranine concentration measured with a quartz diffuser (a) and with a droplet shape diffuser (b)

should be enhanced in natural aggregated soils,[8] where diffusers calibration will be much more difficult.

B/ Light diffusers

In Figure 7, the fluorescence intensity is reported as a function of the concentration of pyranine for the measurements done with a quartz light diffuser (a) and with a droplet-shape diffuser (b). The sensitivity coefficient obtained with the droplet-shape diffuser is 410^{11}, about 10 times less than that of the naked fiber in sand. This difference is due to light losses in the diffuser. The results are more volume representative but the probe construction is not very reproducible and each diffuser has to be calibrated independently. Furthermore, as the diffuser is glued around the fiber, if any problem occurs, one has to change both the fiber and the diffuser. The sensitivity coefficient calculated with the quartz light diffuser (a) is 9.310^{11}, more than two times higher than that of the droplet shape diffuser. In this case, there are some light losses attributable to the distance between the distal end of the fiber and the sample, and to the reflections on the surfaces of the quartz window. The results obtained with four diffusers of the same type were identical (less than 2% standard deviation) and

a unique calibration curve was obtained, meaning that the diffuser construction was reproducible.

Compared to the naked fiber, the sensitivity with the two types of diffusers is lower in sand/solution mixtures, but the reproducibility is better and the problems caused by soil heterogeneity are strongly diminished as the measuring volume is increased. These calibrations revealed that the method is suitable for *in-situ* quantification of low levels of pyranine in porous media. The quartz light diffuser presented the most adapted configuration for fiber optic fluorescence measurements in heterogeneous media and were therefore chosen to perform the batch and column experiments. These diffusers permitted to limit the effect of small scale optical heterogeneities.[20]

Sorption isotherms

The sorption isotherm of Pyranine in sand was determined using the method described by Green and Karickhoff[21] and a classical Shimadzu spectrofluorometer for concentrations measurement. The results revealed that, as was expected from the sand physical properties (pure SiO_2, and no organic matter), pyranine was not sorbed onto the Fontainebleau sand, so the value of the distribution coefficient (K) is 0. As a consequence, it is not necessary to differentiate the fluorescence emitted by sorbed and dissolved pyranine molecules whose optical properties may be different due to modifications resulting from the interactions with particle surfaces.[1,22,23]

Column Experiments

Short Columns

The short columns experiments were designed to assess the effect of the probe location on the fluorescence measurements using the probe configurations shown in Figure 4. The results obtained at 4.5 cm depth with probes located at four different positions following a step injection of pyranine are presented in Figure 8. In order to simplify comparisons between the different experiments, results are presented in a dimensionless form: pyranine relative concentration (C/Co, where C is the measured concentration and Co is the concentration of injected solution) and relative volume (V/Vo, where V is the volume eluted from the column and Vo is the volume of water in the column).

The CXTFIT code was used to determine the parameter values of the transport model (eq. 3 and 4); the latter were obtained from breakthrough curve fitting

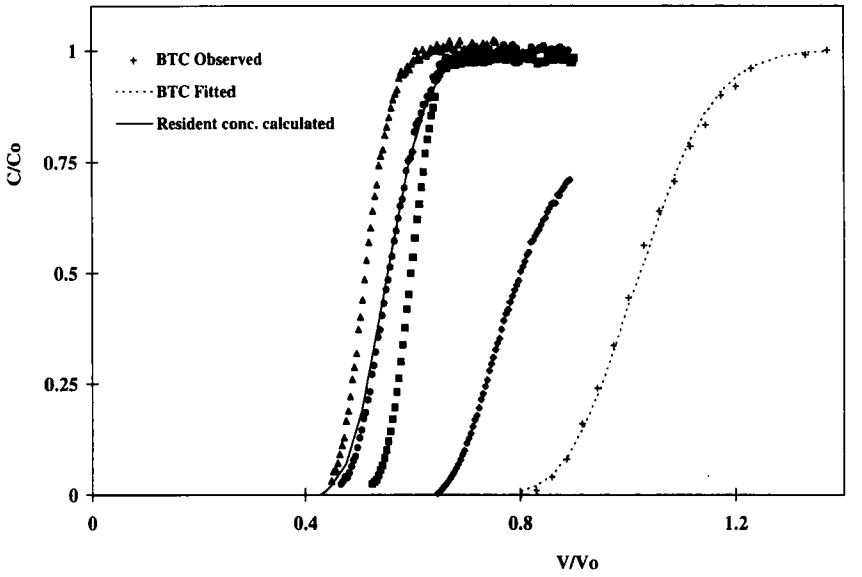

FIGURE 8 Influence of the probe position on the *in-situ* fluorescence measurement of pyranine in a saturated sand column. Fibers were placed at 0 (♦), 0.8 (▲), 1.6 (■) and 2.5 cm (●) from the column wall. The water flow was 66 $cm^3\ h^{-1}$.

and compared with those obtained with chloride breakthrough curves (Table I). The retardation factors calculated with chloride and pyranine breakthrough curves are the same and near unity, confirming that pyranine is not sorbed on the sand grains. The other parameters are also similar except for the dispersion coefficient which is slightly higher, probably because of the lower diffusion coefficient of pyranine.

On the basis of these parameters, temporal variations of resident concentrations were simulated at a depth of 4.5 cm (probe location) and compared to the measured values. The detection of the pyranine step at the three positions inside the column (0.8, 1.6 and 2.5 cm) gave curves similar in their shape but with a slight shift at both sides of the theoretical curve. These shifts are probably due to local heterogeneities in the water flow, meaning that at this scale of meas-

TABLE I Optimized parameters from chloride and pyranine breakthrough curves in a short, water-saturated sand column (r^2 = 0.982).

Optimized Parameters	*V* $cm\ h^{-1}$	*D* $cm^2\ h^{-1}$	*R* -	*β* -	*ω* -
Tracer (Cl^-)	11	0.2	1	0.99	0.001
Pyranine	11.04	0.23	1	0.99	0.001

urement and even with quartz diffusers, detection is still sensitive to microscopic heterogeneities. Even if a steady-state regime of water flow is reached at a macroscopic scale, at a microscopic scale, small variations in the water flow paths or in the water content (in front of the diffusers) induce varying solute pathways and thus a spreading of the curve around the theoretical curve depending on the microscopic detection site. Doing the measurements after a very long period of steady-state water flow conditions favors equilibrium and tends to eliminate this spreading.

The step of pyranine detected at the circumference of the sand column was systematically retarded and its shape was different from that of the curves measured inside the column. Thus, chemical detection performed close to the column wall is not neither efficient nor reproducible and leads to bad parameter estimation. This can be explained by lower water content and water flow close to the edge of the column that leads to an artificial retardation of pyranine as shown in Figure 8. This problem is only due to the column experiment (edge effects) but not of the measurement technique. As a consequence, the optical fiber must be placed far enough from the column wall and, if possible, close to the center, where observed and calculated curves are in best agreement.

Long Column

Pyranine transport was studied using the experimental setup described in Figure 5. A step injection of pyranine was monitored *in-situ* at three depths with the diffusers placed at the middle of the column. The resulting curves are presented in Figure 9. The experiments were performed with two different water flows and were duplicated. The curves measured *in-situ* and at the outflow (BTCs) were fitted with the CXTFIT model. The optimized parameters for both experiments are presented in Table II. The value of the retardation factor ($R = 1$) was obtained from the breakthrough curves; it is in agreement with the batch sorption results: pyranine is not sorbed on the sand ($Kd = 0$). Tracer experiments revealed that the immobile water fraction was of 1% ($\beta = 0.99$) and was thus negligible as well as the transfer coefficient ($\omega = 0.001$).

Compared to the parameters obtained from the breakthrough curves, the *in-situ* parameter characterization is good for the detection at 18.5 and 32.5 cm depths for the dispersion coefficient as well as for the pore water velocity (V) and for both water flows. On the contrary, the detection at 4.5 cm gave significant differences between *in-situ* and BTCs determined hydrodynamic parameters which can be due to either upper boundary condition effects and/or to local preferential flows induced by the sand surface or the injection method. Such preferential flows decrease because of mixing in the porous medium and dis-

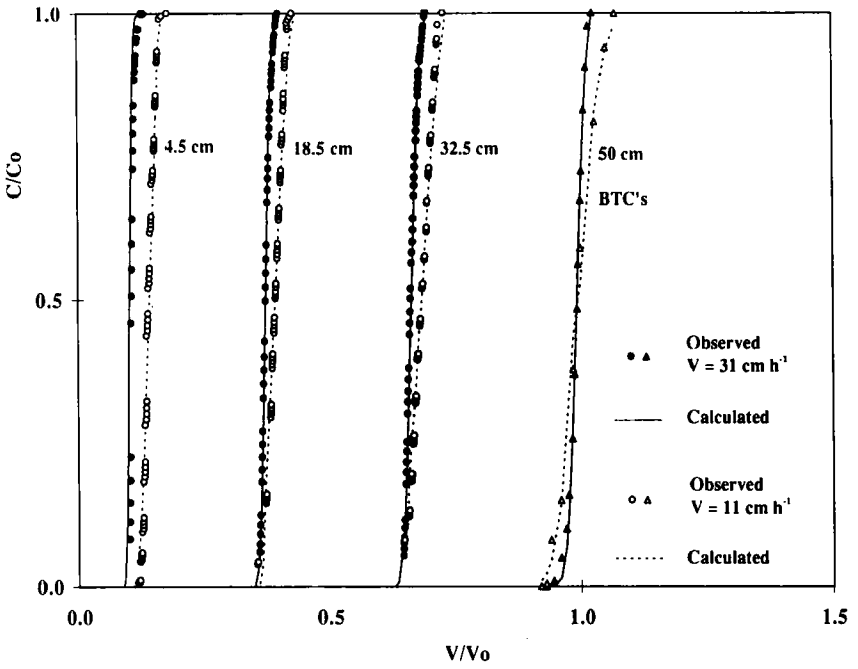

FIGURE 9 Detection of a step injection of pyranine with the optical fiber diffusers placed at 4.5, 18.5 and 32.5 cm depth in a 50 cm long column at two different water flows (66 and 185 $cm^3\ h^{-1}$).

appear after a few centimeters. The optical fiber method should be a very powerful tool to investigate such boundary effects.

These results prove that the method can be efficiently used to perform quantitative detection of pyranine (after characterizing the optimal optical, technical and physical detection conditions), and so to characterize the behavior of fluorescent pollutants in porous media.

TABLE II Optimized parameters from *in-situ* pyranine concentration measurements and pyranine breakthrough curves in a 50 cm-long water-saturated sand column at two different water flows (r^2 = 0.985).

	V = 11 cm h^{-1}		*V = 31 cm h^{-1}*	
Optimized Parameters	*V cm h^{-1}*	*D cm^2h^{-1}*	*V cm h^{-1}*	*D cm^2h^{-1}*
4.5 cm	7.2	0.182	26.2	0.453
18.5 cm	10.6	0.208	31.2	0.537
32.5 cm	10.7	0.208	31.1	0.591
BTCs	11.04	0.230	31	0.525

The best results were obtained with the higher water flow: in this case, the parameters optimized with the *in-situ* curves were not significantly different from those calculated with the breakthrough curves. For the lower water flow experiments, the fit of the *in-situ* curves led to a slight underestimation of water flow and of the dispersion coefficient of the sand. These results are consistent with the edge effects described previously and may explain the greater observed retardation factor.

The sand dispersivity coefficient λ (same order of magnitude than the size of sand particle) was estimated from the data of Table II by linear regression between water velocity and dispersion values. It was found to be 0.016 cm (r^2 = 0.98), which is within the range of the sand grain size (0.015–0.021 cm), demonstrating thus that the method is suitable for pore scale parameter estimation.

CONCLUSION

Optical fiber-based light fluorescence spectroscopy proved to be suitable and powerful for the detection and quantitative estimation of a pure PAH in porous media. Nevertheless, the measurement of PAH mixtures with static fluorescence emission spectroscopy should not be so easy because of the overlapping spectral features of these compounds. Quartz light diffusers allow accurate volume-representative measurements of pyranine concentration in a pure sand medium. The use of specially-designed sand columns helped to establish the effect of the location of the quartz light diffusers in a column section, a very important aspect for column transport studies. It appears that chemical detection performed near the wall of the columns leads to an incorrect characterization of pyranine macroscopic behavior. Similarly, chemical detection performed close to the column surface is disturbed by local heterogeneities of the flow due to boundary effects. These two types of probe positions should then be avoided.

On the contrary, when the detectors are placed at the middle of the column and far enough from the surface of the columns, the measured concentrations are in good agreement with the simulated values provided by the CXTFIT model with parameters obtained from classical breakthrough curve fittings, proving the method efficiency.

Fluorescence spectroscopy with optical fibers can have numerous environmental applications among which are hydrological tracing; monitoring of environmental organic tracers which are very often fluorescent compounds (rhodamine B, fluoresceine...); monitoring the remediation of polluted soils and the detection of PAHs or other fluorescing compounds.

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