ground water

Technical Note/

Use of Fluorescein as a Ground Water Tracer in Brackish Water Aquifers

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Abstract

A drift and pumpback experiment was conducted in a brackish water sandfill. The sandfill was reclaimed from the sea in the eastern part of Singapore and contains sands with low organic and clay/silt contents. The high salinity in the ground water precludes the use of chloride and bromide as tracers in such an environment, and a field experiment was conducted to assess the viability of using fluorescein as a tracer in brackish water aquifers. Nitrate was used as a second tracer to serve as a check. Initial laboratory studies showed that fluorescence was unaffected over the range of electrical conductivity and pH of the ground water. Results from the field experiment show that fluorescein appears to behave conservatively.

Introduction

Chloride is often the tracer of choice in ground water tracing studies because it is widely considered to behave conservatively. For brackish water aquifers, however, the use of chloride can be hampered by the high background chloride concentration. Besides chloride, bromide has also been used in field tracer studies. However, the use of bromide in a high background chloride environment is complicated by interference from chloride ions when ion-selective electrodes are used for field detection of bromide. This complicates the analytic procedure as adjustments for background ionic strength using ionic strength adjusters have to be made. The use of sulfur hexafluoride (SF_6) has also been reported in the literature (Wilson and Mackay 1993; Clark et al. 1996; Gamlin et al. 2001). SF_6, however, is highly volatile, and great care has to be taken to limit the loss of the tracer during injection, sampling, and analysis.

Fluorescent dyes (Smart and Laidlaw 1977) have also been used in ground water tracing studies (Ptak and Schmid 1996; Corbett et al. 2000; Harden et al. 2003). Several factors make fluorescent dyes an attractive option as a ground water tracer in brackish water aquifers: (1) concentrations down to the μg/L level can be accurately measured by a fluorometer and hence only a small amount of dye needs to be used (Jensen et al. [1993] have reported that the high concentrations of chloride used in their experiment caused the tracer to sink) and (2) fluorescence can be detected directly in the field using a portable fluorometer. This means that concentration data can be acquired online, without the need for sample collection and separate laboratory analysis.

The fluorescent dyes that are commonly used as ground water tracers are rhodamine and fluorescein. Fluorescein was chosen as it has a lesser tendency to sorb. Studies by Sabatini and Austin (1991), Kasnavia et al. (1999), and Sutton et al. (2001) have shown that rhodamine dyes will sorb more readily compared to fluorescein. This observation has been verified in field experiments conducted by Ptak and Schmid (1996) and Harden et al. (2003). Fluorescein is also widely regarded to be conservative and stable over time, and it will not break down, unless exposed to direct sunlight (Corbett et al. 2000). It is also regarded as safe to use (Field et al. 1995). However, although fluorescein has been demonstrated as

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a viable tracer in many geological settings, its use in brackish aquifer systems is not widely reported in the literature.

The objective of this study is to assess the suitability of using fluorescein in ground water tracing work in a brackish, sandy aquifer. A drift and pumpback test, a common method of determining ground water flow velocity, was conducted using fluorescein as tracer.

Site Characteristics

The field study was conducted in a sandfill (average depth = 10 m) reclaimed from the sea off the eastern coast of Singapore. The sandfill is made up of marine sand dredged from the seabed. The mineral phases present in the sediments, identified from X-ray diffraction technique and quantified using the software package FULLPAT (Chipera and Bish 2002), were found to consist mainly of quartz and calcite. The average carbonate content, cation exchange capacity (CEC), and organic content of sand samples obtained from 5 to 6.5 m below the ground surface are listed in Table 1.

A continuous multichannel tubing (CMT) (Einarson and Cherry 2002) multilevel system was installed at the experimental site. The CMT, manufactured by Solinst Canada Ltd. (Ontario; www.solinst.com), allows for depth-discrete ground water sampling. Temperature, electrical conductivity (EC), and pH were measured (~2 months before the current study) from samples obtained from the seven sampling ports of the CMT, and the results are shown in Figure 1. The ground surface is at elevation +3.77 m with reference to mean sea level (MSL), and the elevation of the water table was at about +1.3 m (MSL) at the time when the measurements were made. The lower EC values at shallower depths are attributed to the dilution of the ground water by the abundant rainfall (~2.4 m/year) experienced at the site. The increase in pH at approximately −3 m (MSL) is thought to be caused by the dissolution of calcite. The higher EC values at the deepest portion of the sandfill are attributed to the low basal flow conditions. Figure 2 shows the concentration profiles of major anions and cations analyzed in the laboratory on the ground water samples obtained from the CMT. The ion balance was within 7% for this particular analysis. The results show that the geochemistry of the ground water is dominated by the Na and Cl ions, which is reflective of its saline origin.

Table 1
Results of Chemical Analysis

Carbonate Content[1] (%)	CEC[2] (cmol/kg)	Organic Content[3] (mg/g)
12.91 ± 0.46	0.007268.3 × 10^{-4}	4.2 ± 0.039

[1] BS ISO 10693:1995(E) Soil quality—determination of carbonate content—volumetric method.
[2] BS ISO 11260:1994 (E) Soil quality—determination of effective CEC and base saturation level using barium chloride solution.
[3] BS ISO 10694:1995(E) Soil quality—determination of organic and total carbon after dry combustion.

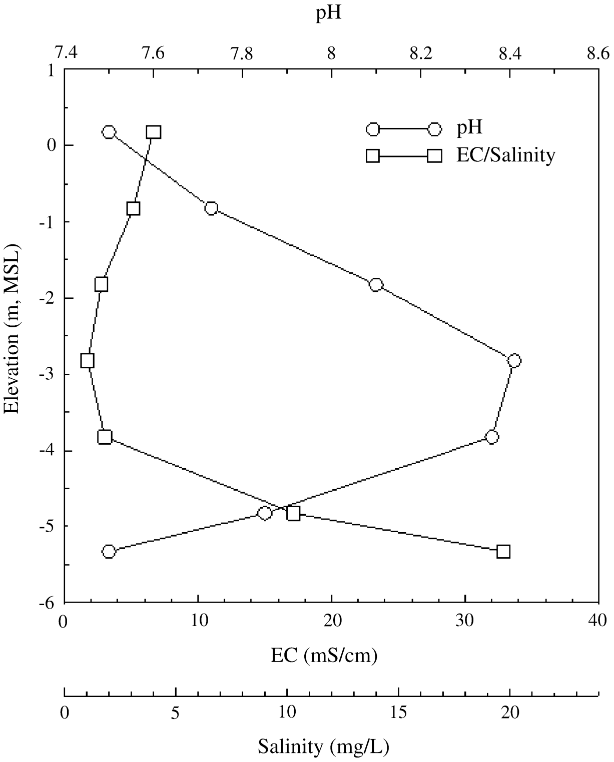

Figure 1. Variation of EC and pH, with depth at the experimental site. Ground elevation is at +3.77 m (MSL).

Materials and Methods

The fluorescein used was Acid Yellow 73, containing 70% active ingredient. Fluorescence was measured using a Turner Designs TD10-AU field fluorometer (Turner Designs 1999). The TD10-AU is capable of detecting fluorescein concentrations as low as 0.1 µg/L. The fluorometer was calibrated using 1, 10, and 100 µg/L standard solutions. The standard solutions were prepared by diluting 10 mg/L fluorescein stock solution (prepared with distilled water) with ground water. All samples, including the ground water used for preparing the standards, were filtered using 0.45-µm nylon membrane filters prior to analysis. To hold the samples and standard solutions during analysis, 25-mm borosilicate glass cuvettes were used.

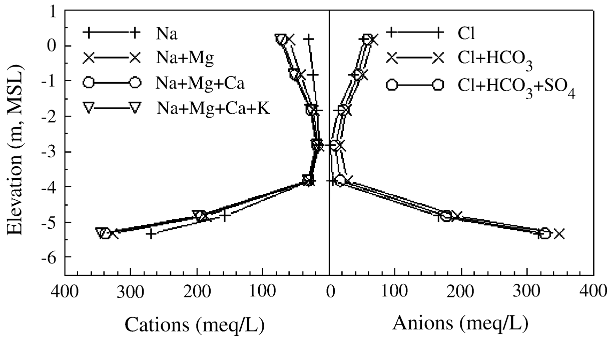

Figure 2. Major anion and cation analysis of ground water collected from CMT.

A preliminary study was first carried out in the laboratory prior to field-testing to study the effect of EC on fluorescence. Ground water for the laboratory study was obtained from six different depths from a second CMT installed close to the experimental site. The EC of the ground water samples ranged from 0.6 to 44.0 mS/cm (salinity = 0.37 to 27.3 mg/L), and the pH ranged from 7.79 to 8.46. The samples were each spiked with fluorescein to concentrations of 0.1, 1, 10, 50, and 100 μg/L. Calibration standards were prepared with the ground water samples where the EC = 26.5 mS/cm and pH = 7.98.

During the drift and pumpback experiment, nine external calibration standards (concentrations ranging from 0 to 200 μg/L), six calibration check solutions, and six blanks were included with the field samples to be analyzed. All standards and check solutions were prepared using ground water pumped from a fully screened well after discarding the first three well volumes. In addition, nitrate was added as a second tracer in the field experiment. The background nitrate concentration is ~0.16 mg/L. Sea water has relatively low amounts of nitrate, and there are no known sources of nitrate at the site. Samples were filtered using 0.45-μm nylon filters and analyzed by flow injection analysis (Lachat Instrument, Quickchem 800, Loveland, Colorado). Sample analysis for nitrate also included five blanks, five external calibration standards with concentrations ranging from 1 to 100 mg/L nitrate as N, and a calibration check after every eight samples.

Temperature, pH, and EC in the field and the laboratory were measured using a Thermo Orion model 6150 pentrode. pH and EC were checked against pH4, pH7, and pH10, and 1413 mS/cm standard solutions, respectively.

Drift and Pumpback Experiment

The theory and methodology of the drift and pumpback test are described in Leap and Kaplan (1988) and Hall et al. (1991). The test consists of emplacing a known quantity of tracer in a screened well and allowing the tracer to drift out of the well (under natural gradient conditions) for an interval of time known as the drift period. At the end of the drift period, the tracer is pumped back at a constant rate until the center of mass of the applied tracer is obtained.

At the start of the test, 4.77 mg of fluorescein (F_o = 4.77 mg) and 33.7 g of sodium nitrate (N_o = 5.55 g nitrate as N) were diluted in 54.9 L of ground water (EC = 6.8 mS/cm) obtained after pumping three well volumes from the fully screened well. The tracers were emplaced in the well by the method suggested by Hall (1993). One sample each was taken from 1, 3, and 6 m below the water table from the well immediately after the introduction of the tracers. The concentration of fluorescein in the three samples were 93.4, 83.8, and 83.6 μg/L, indicating that the tracer was fairly well mixed inside the well. After a drift period of 24 h, the mass of fluorescein and nitrate inside the well decreased to 0.45 mg and 0.27 g (nitrate as N), respectively, indicating that ~91% of the fluorescein and 95% of the nitrate left the well during the 24-h drift period. Pumpback was carried out by pumping ground water from the well at a rate of ~15 L/min over a period of 4 h. The total pumpage is ~2.5 times the pore volume described by the radius of tracer extent into the aquifer, estimated to be 0.4 m. Twenty-three samples (each sample containing 80 mL) were collected during pumpback, stored in Agilent amber glass bottles, and put on ice prior to transportation to the laboratory. Sample analysis for nitrate and fluorescein was completed within 5 d from the end of the experiment. The flow rate measured with a flowmeter (calibration checked on site before the start of the experiment) was recorded each time a sample was taken. A calibration check on the flowmeter was also carried out at the end of pumpback by the volumetric method.

Results and Discussion

The results of the laboratory study are shown in Table 2, where it is evident that the measured fluorescein concentration remains relatively unchanged over the entire range of EC values in the ground water. Similar results were obtained when a limited number of tests were repeated by preparing the calibration standards using water of different EC values.

Concentrations of fluorescein and nitrate in the samples collected during pumpback are shown in Figure 3 (shaded symbols). At the end of pumpback, fluorescein and nitrate concentrations in the samples decreased to ~4% and 7% of their initial values. The behavior of fluorescein can be compared with nitrate by considering the recovery curves for fluorescein and nitrate, indicated by the cumulative mass curve (open symbols) shown in the figure. The cumulative mass recovered was determined from the recovery data and pumping rate, $\sum C = \sum (\overline{Q}_i c_i)$, where $\sum C$ is the cumulative mass of fluorescein (mg) or nitrate (g nitrate as N) recovered, the subscript i refers to the ith sample, c_i is the concentration of fluorescein (μg/L) or nitrate (mg/L), and $\overline{Q}_i$ is the average flow rate (L/min) measured during the ith sampling interval. In Figure 3, $\sum C$ is normalized by the initial concentrations (F_o or N_o) for ease of comparison.

There is good agreement between the time variation of the cumulative mass curves for fluorescein and nitrate.

Table 2
Effect of EC on Fluorescence

	Spiked Fluorescein Concentration (μg/L)				
EC (mS/cm)	**0.1**	**1.0**	**10**	**50**	**100**
0.64	n.d.	0.78	9.42	49.07	101.33
1.21	n.d.	0.80	9.54	49.63	101.67
7.60	n.d.	0.73	9.34	48.93	100.03
10.62	0.06	0.90	9.56	49.80	101.33
26.56	0.08	0.99	9.49	49.23	100.67
42.40	0.13	0.98	9.55	48.97	102.00

Note: n.d. = not detected.

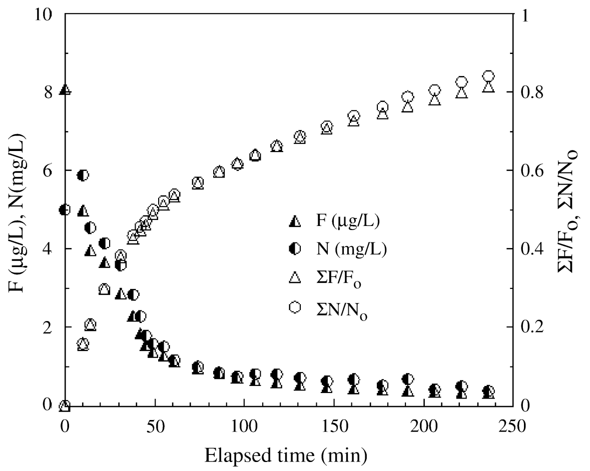

Figure 3. Recovery curves for fluorescein and nitrate during pumpback.

This indicates that fluorescein moved at the same rate as nitrate or that there is minimal retardation of fluorescein with respect to nitrate. Given that it is unlikely that both nitrate and fluorescein are equally retarded, this would imply that sorption is minimal. This is supported by supplementary laboratory tests on the sorption of fluorescein on the aquifer sediments where the distribution coefficient, K_d ($= q/C_e$ where q is the mass of fluorescein adsorbed onto a unit mass of sediment and C_e is the equilibrium concentration), was found to be low, ~0.01 to 0.1 (μg/kg)/(μg/L).

The total mass recovered was ~81% and 84% of the initial amounts of fluorescein and nitrate, respectively. Presumably, the remaining mass remained in the tail of the breakthrough curve or could have been lost through advection and sorption. Interestingly, given that fluorescein is not expected to break down, the similarity in results would also imply that denitrification was probably not significant.

Conclusions

Fluorescein is a suitable tracer to be used in brackish water aquifers, where tracers such as chloride and bromide could be impractical. The applicability of fluorescein was verified from laboratory and field (drift and pumpback) experiments. Laboratory experiments showed that fluorescence was unaffected for the range of EC and pH of the ground water. The behavior of fluorescein was compared with nitrate by considering the recovery curves for fluorescein and nitrate, during the pumpback phase of a drift and pumpback experiment. The comparison shows that fluorescein behaves similarly with nitrate, indicating that fluorescein moved at the same rate as nitrate or that there was no retardation of fluorescein with respect to nitrate. In addition, given that it is unlikely that both nitrate and fluorescein are equally retarded, this would imply that sorption is minimal.

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