Fluorescent Dye-Tracing as a Cost-Effective Tool in Applied Contaminant Hydrology: A Case Study of Synchronous Spectro-Fluorometry in a Heavily Oil-Contaminated Aquifer

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Abstract

Organic fluorescent dyes are rarely used to trace groundwater flow paths in organic-rich environments because most organic substances fluoresce and possibly camouflage the fluorescent dye's signal. In this study we report the results of two successful dye-tracing experiments in an aquifer beneath a 5 acre inaccessible factory where thousands of liters of cutting oil and chlorinated solvents have contaminated the subsurface for decades. The current remediation strategy includes a 3 m deep drainage trench surrounding the east side of the factory with 3 pumps that recover ~100 L of product daily.

Synchroscans of the background samples at different dilutions indicated that uranine, Na-naphtionate, and sulforhodamine B could be suitable for dye-tracing at the site. The diagnostic wavelength ranges of fluorescence peaks for these dyes are not in the ranges of background florescence wavelengths caused by the oil and its degradation by-products. We first introduced uranine in a monitoring well upgradient of the factory, and sulforhodamine B in a monitoring well closer to the recovery trench. The dyes were injected at very low concentrations to prevent the aquifer from being contaminated by remnant dyes after the test. Eight months later, we did a second dye-tracing test and injected uranine and Na-naphtionate to confirm and refined the results of the first.

In the first test, uranine reached the drainage system in ~12 days along what appears to be a preferential flow path. Breakthroughs of this dye in monitoring wells surrounding three sides of the factory indicated pronounced hydrodynamic dispersion within the next two months. In contrast, sulforhodamine B sorbed to the aquifer matrix or possibly its fluorescence was quenched by chlorinated hydrocarbons mixed with the cutting oil near the injection zone. This dye, which never reached the recovery trench, was not useful as a tracer at the site. The results of the second dye-tracing test further defined the major groundwater flow-paths east of the inaccessible factory building and delineated several immobile oil lenses, which hydraulically behave as pseudo-no flow boundaries. Most important, the dye testing showed that groundwater does not move directly towards the remediation pumping wells, but deviates by refraction in the horizontal plane from the maximum direction of the hydraulic gradient. This refraction implies pronounced preferential flow paths, immobile oil lenses and heterogeneities in the subsurface, probably caused by construction infilling and which could not be identified from standard hydrogeologic measurements. Furthermore, the intrinsic fluorescence of the groundwater clearly showed where the major zones of contamination were located at the water table.

Introduction

In 1990 a tool-producing factory was held responsible for contaminating unconfined groundwater with cutting oils and, to a lesser extent, chlorinated solvents. Since 1999 a drainage trench system outfitted with 3 pumps (DP1, DP2, DP3; Figure 1) recovers the oil. In addition, to prevent oil from discharging to an adjacent river, a 3 m deep barrier wall was constructed along the river shore and tied to the oil recovery system. The oil/water-emulsion passes through an oil-water separator for later collection and disposal.

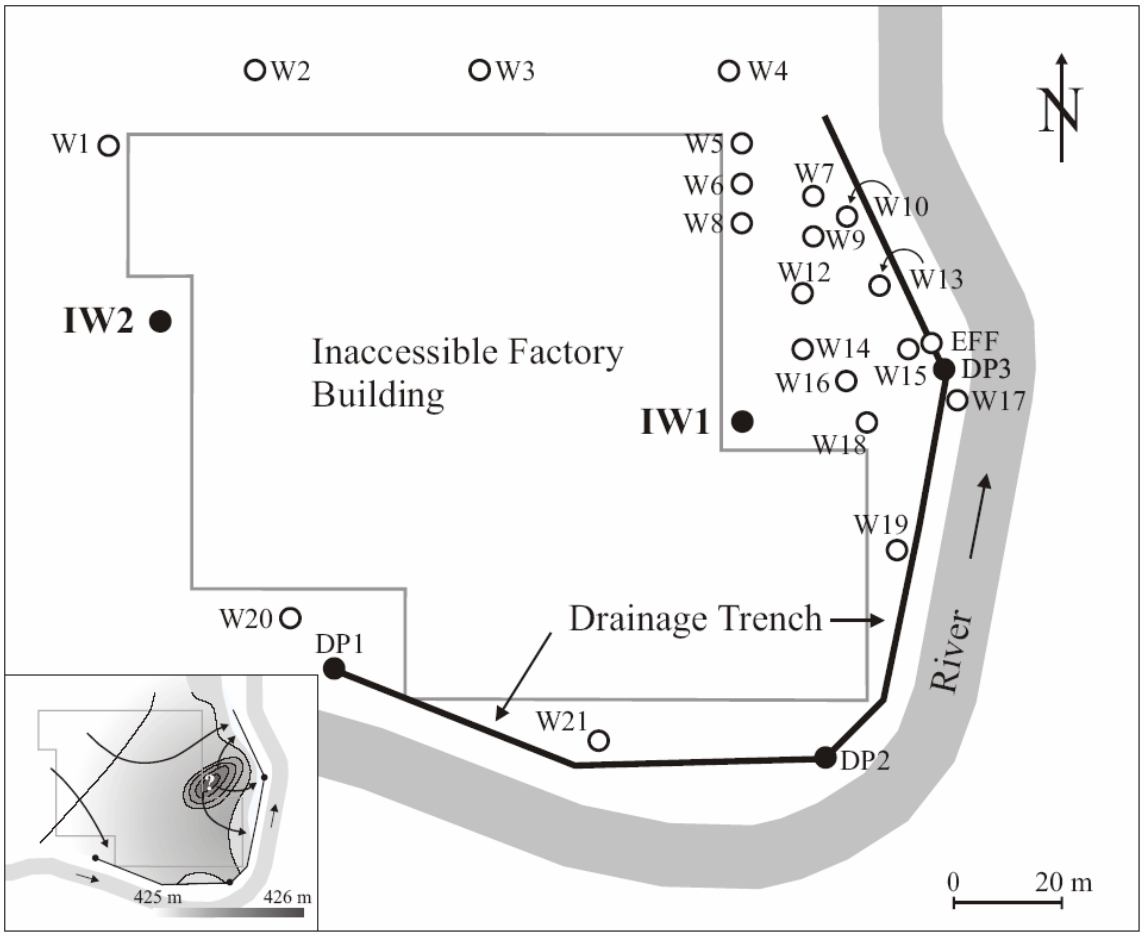

Figure 1: Location of drainage pumps (DP), monitoring wells (W) and injection wells (IW). The inset at the left bottom shows the 'water table surface measured on 2000 (by ERM Inc.).

However, the extent to which groundwater flow paths are induced to the drainage pumps is unknown and oil recovery is much less than anticipated. Water table measurements poorly defined details of the water table because much of the area is beneath the inaccessible factory (Inset in Figure 1) and oil on the water table makes measuring the actual head of the water table difficult (e.g. Fetter, 1998). Groundwater flow paths and velocities need to be clearly delineated to increase the efficiency of the remediation process.

We report in this paper the results of a project designed to test whether inexpensive, non-toxic fluorescent dyes can be used to trace groundwater that has been extraordinarily contaminated by hydrocarbons. Specifically, we tested the hypotheses that: (1) synchronous spectro-fluorometry can be used to locate organic contamination from the intrinsic fluorescence properties of the cutting oil, organic solvents and their degradation products, (2) the fluorescent dyes uranine (URA), Na-naphtionate (NAP), and sulforhodamine B (SRB) can be used to trace groundwater flow paths in heavily oil-contaminated aquifers, and (3) very high sensitivity of synchronous spectro-fluorometry enables very low dye concentrations to be traced and therefore allows for multiple tests in the same aquifer system.

Background

Organic fluorescent dyes have been qualitatively used for more than 150 years to trace water flow because of their ease of handling, cost-effectiveness (Käss, 1998; Pharr et al., 1992), low detection limits (Otz et al., 2002) and non-toxic properties (Käss, 1998; Smart, 1984; Smart et al., 1977). These water-soluble organic

substances include a large range of hydrologic tracers, all with different characteristic fluorescence "signatures". To do a dye-tracing test in an oil-contaminated aquifer, both the physical and chemical behavior of the intrinsic fluorescent dyes to be used and the fluorescence of the background need to be known (Kasnavia et al., 1999; Käss, 1998).

The background fluorescence signal of an oil-contaminated groundwater has distinctive wavelengths, some of them occurring in the general range of wavelengths produced by the fluorescent dyes. The success of a dye-tracing test in an oil-contaminated aquifer also depends on environmental conditions, such as pH, ionic strength, temperature, and substances that interact with the fluorescent substances (Käss, 1998). Sorption (Kasnavia et al., 1999; Käss, 1998; Mikulla et al., 1997, Smart et al., 1977) and oxidative degradation (Kobzey, 2001; Margesin et al., 2001; Margesin, 1999) may lead to significant losses of the injected tracer material in organic-rich environments. Because of these concerns and potential complications, most applied hydrogeologists abandoned the idea of using intrinsic fluorescence tracing or dye-tracing as methods to determine the location and extent of contaminant plumes.

It is not a new idea to use the intrinsic fluorescence properties of organic contaminants to study the spatial extension of contaminant plumes (Nahold et al., 1992; Qiang et al., 1992; Aldous et al., 1988; Käss, 1998; Baedecker et al., 1988; Pelikán, 1986; Käss, 1972; Nietsch, B., 1956), particularly with respect to oil spills in the marine and coastal environments (Page et al., 2002; Holdway et al., 2000; Eastwood, 1976). Pharr et al. (1992) recently even suggested that synchronous spectro-fluorometry might be useful to identify and classify organics such as gasoline, kerosene, diesel oil, and even PAH compounds. Oil based fuels have been successfully labeled with fluorescent dyes (Shamp, 1965).

The intrinsic background fluorescence caused by hydrocarbons and their degradation by-products need to be understood, in any case, before doing a dye-tracing test. As groundwater levels move up and down, organic substances may be significantly dispersed vertically (Pelikán, 1986). Because of their aliphatic and cyclic structures hydrocarbons and their degradation products have intrinsic fluorescence which may camouflage or mimic organic fluorescent dyes and lead to erroneous dye-tracing results (Aldous, 1988; Pharr et al., 1992).

Potential sorption to organic substances is primarily why fluorescent dyes are not typically used in organic-rich environments, even though different dyes have different sorption characteristics with respect to organic matter (Kasnavia et al., 1999; Käss, 1998). For example, uranine and sulforhodamine B adsorb to positively charged surfaces of carbonates, and to negatively charged silica surfaces (Sabatini, 2000; Kasnavia et al., (1999). However, sulforhodamine B sorbs less to organic material than do other dyes (Kasnavia et al., 1999). Those fluorescent molecules with carboxylic and sulfonic functional groups are water soluble, and theoretically less sorptive to organic matter than dyes without these functional groups. Charged functional groups on the dye molecule are also pH-dependent. Uranine fluorescence, for example, may be quenched reversibly below pH 5.5 (Käss, 1998).

Finally, weathering alters the intensity of fluorescent peaks and shifts them towards longer wavelengths. Curtis, (1977), and Killeen et al., (1981) developed comparative methods to classify the fluorescence spectra of oils and their weathered products. Most of these databases include short-term weathering (one week or shorter times), whereas in our case, we look at weathered oil products several decades old.

Study area

The field site was chosen because it offered a “worst-case” scenario to do a dye-tracing test. The study area is along a second-order small river in western New York, where glaciation has deposited basal till on top of Upper Devonian-age shale, siltstone and conglomerate. A factory leaked hundreds of thousands of liters of cutting oil over decades to the shallow, unconfined groundwater system beneath the factory. Now, perhaps up to half a meter of liquid oil lies on top of the water table in places. Sediments in the study are generally about 20 m thick, and consist of a heterogeneous mixture of silt, sand, gravel and fill material that was deposited on the river's floodplain. The depth to the water table ranges from 0.5 m to 1.5 m below the land surface, depending on proximity to the river.

A series of water table monitoring wells with screens about 4 meters long were installed at the site (Figure 1). Most monitoring wells were located within 40 meters of a drainage trench and were installed to monitor the remediation process. We had no access to factory building per say; all monitoring wells are located outside of the building. Slug tests from the monitoring wells give a range of horizontal hydraulic conductivity from 10^{-3} to 10^{-5} cm/s with no clear spatial zonation.

Groundwater flow at the western side of the site seasonally rotates about 40 degrees from the northeast to southwestern direction. However, groundwater flow generally flows always towards the river adjacent to the factory under a gradient of about 0.013. The small gradient, hydraulic complexities caused by lenses of oil, and aquifer heterogeneity make defining the water table difficult over this small area, and hence, we did the tracer test to better define the flow system. Measurements of what was considered the water table also define a local anomalous and apparent water table mound east of the factory (Inset in Figure 1) imposed on the overall hydraulic gradient towards the river. There is no obvious enhanced recharge at this location, under a paved parking lot.

Methods

Laboratory:

We used synchronous spectro-fluorometry for our study. Most of the synchroscans were run with a $\Delta\lambda$ of 21 nm for URA and SRB and $\Delta\lambda$ = 100 nm for NAP (Käss, 1998).We found that a $\Delta\lambda$ of 21 nm yielded the highest spectral resolution for cutting oils and derivatives, therefore $\Delta\lambda$ = 21 nm is sensitive to dyes and oil at the same time.

We first sampled contaminated water from the drainage pump DP3. These samples were filtered through Gelman Supor®-450 0.45μm membrane filters. Four dilutions of potential dyes such as eosine, lissamine, Na-naphtionate, pyranine, rhodamine WT, sulforhodamine B, sulforhodamine G, and uranine, were analyzed at concentrations of 0.1, 0.5, 1.0 and 2.0 ppb in the background contaminated water. From these tests, we determined that only uranine (URA), sulforhodamine, (SRB) and Na-naphtionate (NAP) might be suitable for the dye-tracing test at this site. The fluorescence of the other dyes was either significantly quenched or their specific emission peaks were camouflaged by the intrinsic fluorescent hydrocarbon background.

Field studies:

We injected dyes with a peristaltic pump (Cole-Parmer Masterflex E/S Portable Sampler) equipped with medical grade silicon tubing. Dye injection was done using methods described in Otz et al., (2003). For the first dye-tracing test, done after snowmelt in April 2003 when groundwater levels were high, 100 g sulforhodamine B (SRB) was injected as liquid into injection well IW1 (Figure 1) located about 35 meters east of the most northern drainage pump, DP3. Free phase oil about 20 cm thick lies on the water table at IW1 and the injection was made below the oil mass. Drainage pump DP2 is located about 70 meters south of DP3 and drainage pump DP1 is located about 100 meters to the west along the southern boundary of the factory property.

The dye was pumped into the groundwater below the oil to a depth of 4 m, followed by 50 L of water to flush the system. Two hours later, 100 g uranine was injected as liquid into IW2 located on the eastern side of the factory (Figure 1), farthest away from the drainage trench. The closest drainage pump to this site was DP1, about 75 meters to the southeast. As before, the line was then flushed with water. The hose of the peristaltic pump was discarded and a new hose was used at each injection site to avoid cross-contamination. The entire process, including dye injection and rinsing took 15 minutes per site. We did a second dye-tracing test eight months later when water levels were low. We used the same methods, but injected 250 g uranine and 2.5 kg Na-naphtionate instead of sulforhodamine B on the eastern edge of the factory at the same injection well (IW1) used in the first dye test. The results of the first test (Table 1) indicated that SRB was relatively immobile, so we chose to use NAP as a substitute dye (Table 2).

We sampled water from the monitoring wells with a peristaltic pump at a variable frequency for about half a year after each test. Dedicated polyethylene sampling tubes were installed in each well to prevent cross-contamination. The pump removed water sample at about 1 L/min for one minute before two samples were drawn into 30 mL amber glass bottles. Samples were filtered within 24 hours of receipt through a Gelman Supor®-450 membrane filters to remove any particulate material (Thurman, 1985).

Analysis:

All measurements were done at (22 °C ± 2 °C) and analyzed with a Shimadzu spectrofluorophotometer RF-5301PC. Synchroscans were obtained using an optically polished 10 mm/3.0 mL Suprasil quartz cell and measuring emissions from 320 to 720 nm wavelength with a $\Delta\lambda$ = 21 nm for URA and SRB, and 100 nm for NAP (Käss, 1998). We used an entrance slit 5/5 for URA and SRB, and slit 3/3 for NAP, and automated integration and a scanning speed of 10 nm/cm. The emission wavelengths chosen for the dyes were those recommended by Käss (1998) as 425 nm for NAP, 512 nm for URA, and 583 nm for SRB. After every 5th sample, the sample cell was rinsed twice with Nanopure water and the scan was checked for any deviation from the Nanopure water background fluorescence. After every 5th sample, the sample cell was rinsed with ethanol, polished inside with a Q-tip, and thoroughly rinsed with Nanopure water to remove any oily films or colloids that might have adsorbed to the cell walls. This procedure ensured high accuracy of the measurements and prevented any cross-contamination. Fluorescent intensities of the Nanopure scan were subtracted from the synchroscans from the sampled groundwaters.

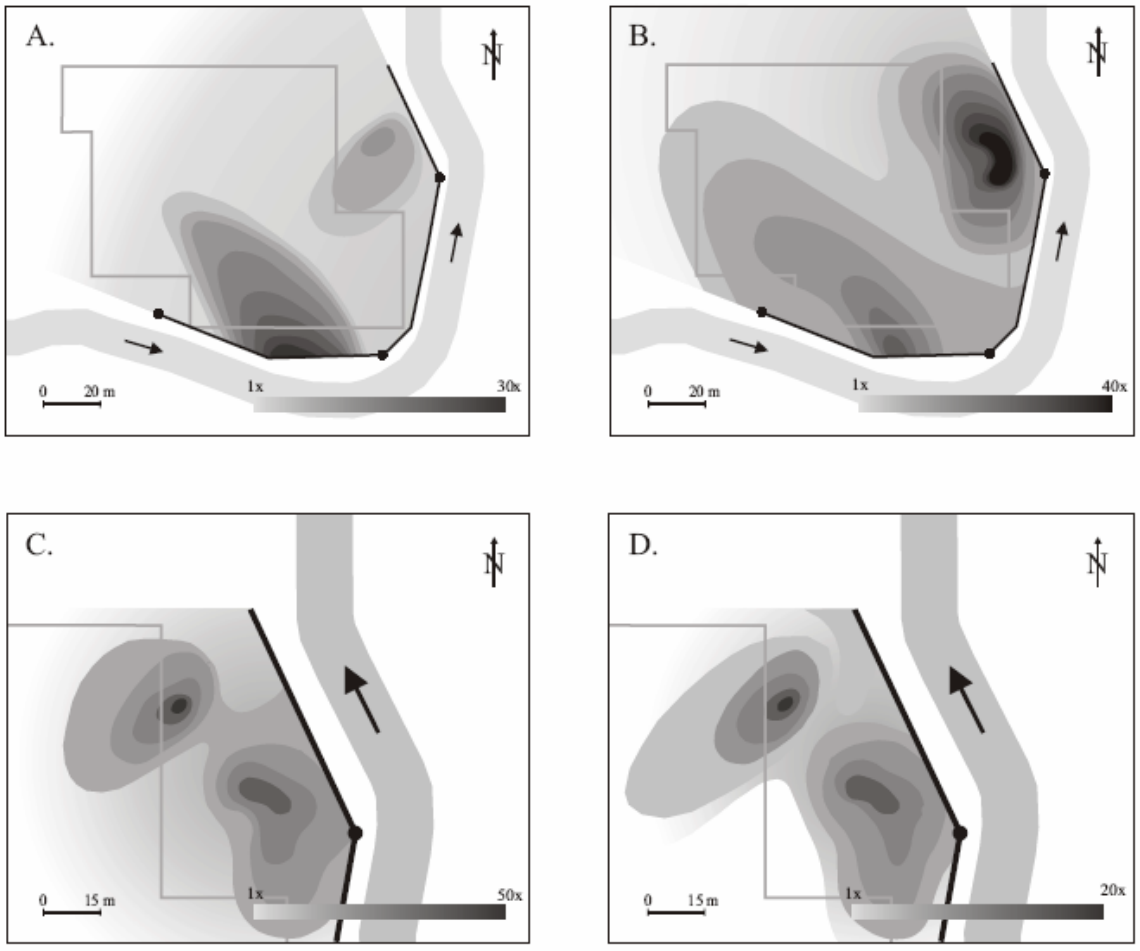

Figure 2: Intrinsic background fluorescence at different emission wavelengths. A. 512 nm, B. 583 nm for the emission background in 2002, before the first dyes were injected. C. 512 nm and D. 425 nm show the fluorescent emission background in 2003 before the second dye-tracing test started. Note that figures 2C and 2D show only the northeastern corner of the factory site, pertinent to this second dye-tracing test. The 512 nm emission wavelength is the major fluorescent peak for uranine, the 583 nm emission wavelength is the fluorescent peak for sulforhodamine B and the 425 nm peak is for Na-naphtionate.

Results

Intrinsic Background Fluorescence

Intrinsic background florescence for each of the diagnostic 'dye' emission wavelengths (420 nm, 512 nm, and 583 nm) is shown in Figure 2. These figures were prepared from analyses of samples collected from all monitoring wells (Figure 1) before the field injections of dyes were done. Before the first dye trace test, the intrinsic fluorescence defined an ovoid plume-like shape east of the factory approximately where the apparent groundwater mound on the water table was located.

We qualitatively extrapolated the probable zone of intrinsic fluorescence north from the drainage trench under the factory building. Free product is being produced at all drainage wells. Given the hydraulic gradient to the river, it is certain that oil and oil degradation products are also in groundwater under the factory, although the exact extent of this area of contamination remains unknown.

Before the second dye test was done at the eastern side of the factory during lower water table levels, the intrinsic fluorescence at 425 nm and 512 nm defined two plume-like areas east of the factory. One plume was located again near the apparent groundwater mound, and the other was separated from it by about 20 m and was closer to the factory wall. We chose to analyze emission wavelength 425 nm in this test, rather than 583 nm, because the former is more suitable for Na-naphtionate.

Results for the first dye-tracing test (4/8/2002):

2002 Dye injection 4/8/2002

100 g SRB in W-SRB 10:30
100 g URA in W-URA 12:00

Location	dye	1st appearance	days after inj.	Main peak	Main peak intensity	Detection limit intensity	dye found
DP1	URA	May 10, 2002	32	July 23, 2002	13.1	2.0	yes
	SRB					12.0	no
DP2	URA	April 22, 2002	14	July 9, 2002	10.9	3.0	yes
	SRB					5.0	no
DP3	URA	April 22, 2002	14	May 16, 2002	29.3	6.0	yes
	SRB					5.0	no
SE	URA	April 22, 2002	14	May 16, 2002	10.0	2.5	yes
	SRB					5.0	no
W4	URA	July 9, 2002	92	September 5, 2002	0.5	0.4	yes
	SRB	June 27, 2002	80	September 5, 2002	0.3	0.5	yes
W12	URA	July 3, 2002	86	July 23, 2002	5.1	8.0	yes
	SRB					12.0	no
W14	URA	June 27, 2002	80	July 9, 2002	5.1	15.0	yes
	SRB	August 6, 2002	120	August 21, 2002	13.5	20.0	yes
W16	URA					6.0	no
	SRB					8.0	no
W18	URA					12.0	no
	SRB					20.0	no
W20	URA	May 30, 2002	52	June 27, 2002	67.8	5.0	yes
	SRB					20.0	no
W21	URA	April 20, 2002	12	April 26, 2002	149.0	30.0	yes
	SRB					25.0	no

Table 1: Qualitative results of the first dye-tracing test

We anticipated in the first dye test that dye would move from the injection well IW1 down gradient to the pumping well DP3 and pass through monitoring wells W16, W14 and W18 halfway between them (Figure 1). Conversely, we did not anticipate dye moving north towards W4 on the northeastern side of the factory or towards W12 and drainage well DP2 to the south. We anticipated that dye breakthrough from the injection at IW2 on the western side of the factory would first appear at drainage well DP1, passing through monitoring well W20 (Figure 1).

The most surprising result of the first dye-tracing test was that URA dye was first detected in water sampled from monitoring well W21, located about 60 meters east of the anticipated breakthrough at W20 and

just 12 days after dye injection (Figure 3 and 4). This breakthrough curve shows the highest URA peak measured during the entire first dye-tracing test. After this initial breakthrough, a second increase in URA fluorescence at W21 occurred a full 80 days after dye injection (Figure 3).

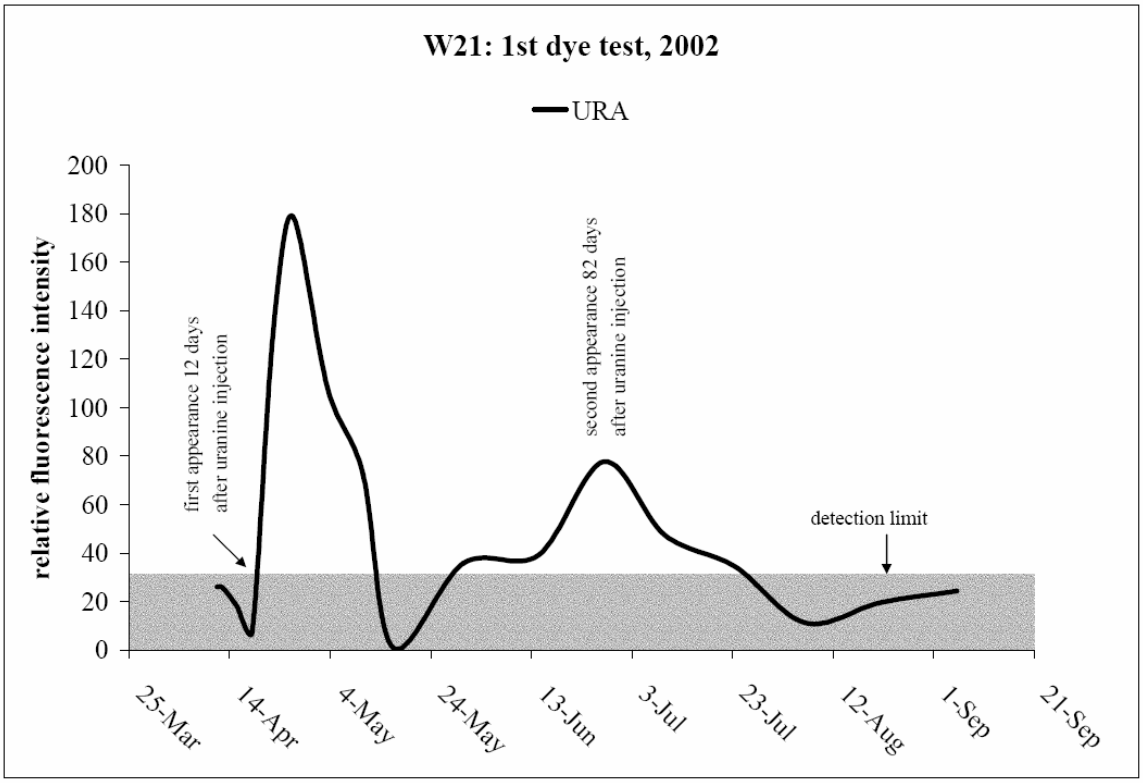

Figure 3: Uranine breakthrough curves in monitoring well W21 during the first dye-tracing test in 2002.

The main URA dye cloud first reached the drainage trench between DP3 and DP2, not at DP1, thirty six days after dye injection, at a relative fluorescence intensity fifteen times smaller than found at W21. The first URA peak appeared in water from DP3 thirty two days after dye injection. URA arrived in water sampled from W20, located 20 m upgradient of DP1 and 52 days after the dye was injected. The URA dye passed under the factory and reached W12, about 30 m east of the factory wall, fully 86 days after the URA injection. At about the same time, URA was first detected in W14, located south of W12 (Table 1). In contrast to the mobility of the URA, no SRB dye was detected in the pumping well DP3, or in monitoring wells W18 or W16, immediately down gradient from the injection point to the river. It took SRB months to travel only 30 meters from the injection point to adjacent W14, and these measurements were the highest found.

Remarkably, URA even was detected in monitoring well W4, 100 meter northeast of the injection point 92 days after dye injection. Similarly, SRB dye was detected 12 days earlier in water from this well. Both dyes continued to increase in concentration in this well even 150 days after the injection, when the first dye-tracing test ended on September 5, 2002. The transport of URA dye fundamentally defined a zone that encompassed the entire southern half of the factory and extended to the north off the factory site to a lesser extent (Figure 4). In contrast, SRB did not migrate far from the point of injection, near the apparent water table mound, but did migrate to the north towards W4.

Results for the second dye-tracing test (2/7/2003):

2003 Dye injection 2/7/2003

250 g URA and 2.5 kg NAP in W-SRB 11:40

Location	dye	1st appearance	days after inj.	Main peak	Main peak intensity	Detection limit intensity	dye found
DP2	NAP	March 21, 2003	42	September 30, 2003	7.3	4.0	yes
	URA	March 21, 2003	42	September 30, 2003	2.4	3.0	yes
DP3	NAP	May 1, 2003	83	June 26, 2003	16.6	15.0	yes
	URA	May 1, 2003	83	September 30, 2003	34.7	6.0	yes
W1	NAP					2.0	no
	URA					1.0	no
W2	NAP					1.6	no
	URA					0.8	no
W3	NAP					2.0	no
	URA					1.0	no
W4	NAP	March 21, 2003	42	March 21, 2003	0.9	0.6	yes
	URA	March 7, 2003	28	March 21, 2003	8.3	0.3	yes
W5	NAP	May 1, 2003	83	July 30, 2003	5.1	10.0	yes
	URA	May 1, 2003	83	May 1, 2003	6.1	3.0	yes
W6	NAP	July 30, 2003	173	September 30, 2003	6.1	6.0	yes
	URA	March 14, 2003	35	September 5, 2003	5.7	2.0	yes
W7	NAP	June 26, 2003	139	September 5, 2003	39.3	40.0	yes
	URA	May 29, 2003	111	September 5, 2003	34.4	15.0	yes
W8	NAP	May 1, 2003	83	July 30, 2003	21.4	20.0	yes
	URA	March 14, 2003	35	May 1, 2003	11.0	10.0	yes
W9	NAP	September 5, 2003	210	September 5, 2003	0.2	25.0	yes
	URA	May 1, 2003	83	September 5, 2003	12.4	8.0	yes
W10	NAP	September 5, 2003	210	September 5, 2003	14.1	40.0	yes
	URA	May 1, 2003	83	September 5, 2003	8.2	15.0	yes
W12	NAP	February 26, 2003	19	na	> 1000	30.0	yes
	URA	February 26, 2003	19	na	> 1000	8.0	yes
W13	NAP	May 15, 2003	97	September 30, 2003	46.1	35.0	yes
	URA	May 1, 2003	83	September 30, 2003	79.7	15.0	yes
W14	NAP	February 26, 2003	19	na	> 1000	35.0	yes
	URA	February 26, 2003	19	na	> 1000	15.0	yes
W15	NAP	May 15, 2003	97	September 30, 2003	53.9	12.0	yes
	URA	May 15, 2003	97	September 30, 2003	5.5	3.0	yes
W16	NAP	May 1, 2003	83	July 30, 2003	621.8	30.0	yes
	URA	May 1, 2003	83	July 30, 2003	> 1000	10.0	yes
W17	NAP					20.0	no
	URA					15.0	no
W18	NAP	May 1, 2003	83	July 30, 2003	24.3	30.0	yes
	URA					10.0	no
W19	NAP	April 3, 2003	55	May 15, 2003	2.9	4.0	yes
	URA	March 21, 2003	42	March 21, 2003	0.9	3.0	yes

Table 2: Qualitative results for the second dye-tracing test.

In the second dye test, both dyes URA and NAP moved northeast from the injection well IW1 several meters within 19 days to W12 and W14. URA once again reached W4, located about 60 meters directly north from the injection point (IW1), perpendicular to the hydraulic gradient towards the river. URA breakthrough occurred in this well 28 days after dye injection. NAP also moved north towards W4, but 1½ times slower. URA reached W6 and W8, located closer to the injection point, after a slightly longer time, 35 days, whereas NAP needed an additional 48 days before it could be detected in W8. Surprisingly both dyes reached DP2, due south of the injection point ~42 days after dye injection. Finally, URA and NAP were detected in water from monitoring wells W7 and W10, located about 40 meters to the northwest, but more than 100 days after the injection.

Interpretation and Conclusions

Hydrocarbons degrade to a large suite of organic acids and other organic compounds that plausibly can interfere with or quench the fluorescent intensity of organic dyes. We found that uranine (URA), and Na-naphtionate (NAP), are appropriate to use in dye tracing tests in groundwater contaminated with cutting oils. URA and NAP particularly have fluorescence peaks that are not the same as the intrinsic background fluorescence spectra for the contaminated groundwater. Sulforhodamine B (SRB) is far less appropriate as a tracing dye, because it clearly is retarded near the injection well IW1for reasons unknown during transport. Near monitoring well W18, concentrations of chlorinated hydrocarbons are greatest in the oil (Hinchey, personal communication, 2003) and one possibility is that reactions of the SRB with these compounds quench its fluorescence.

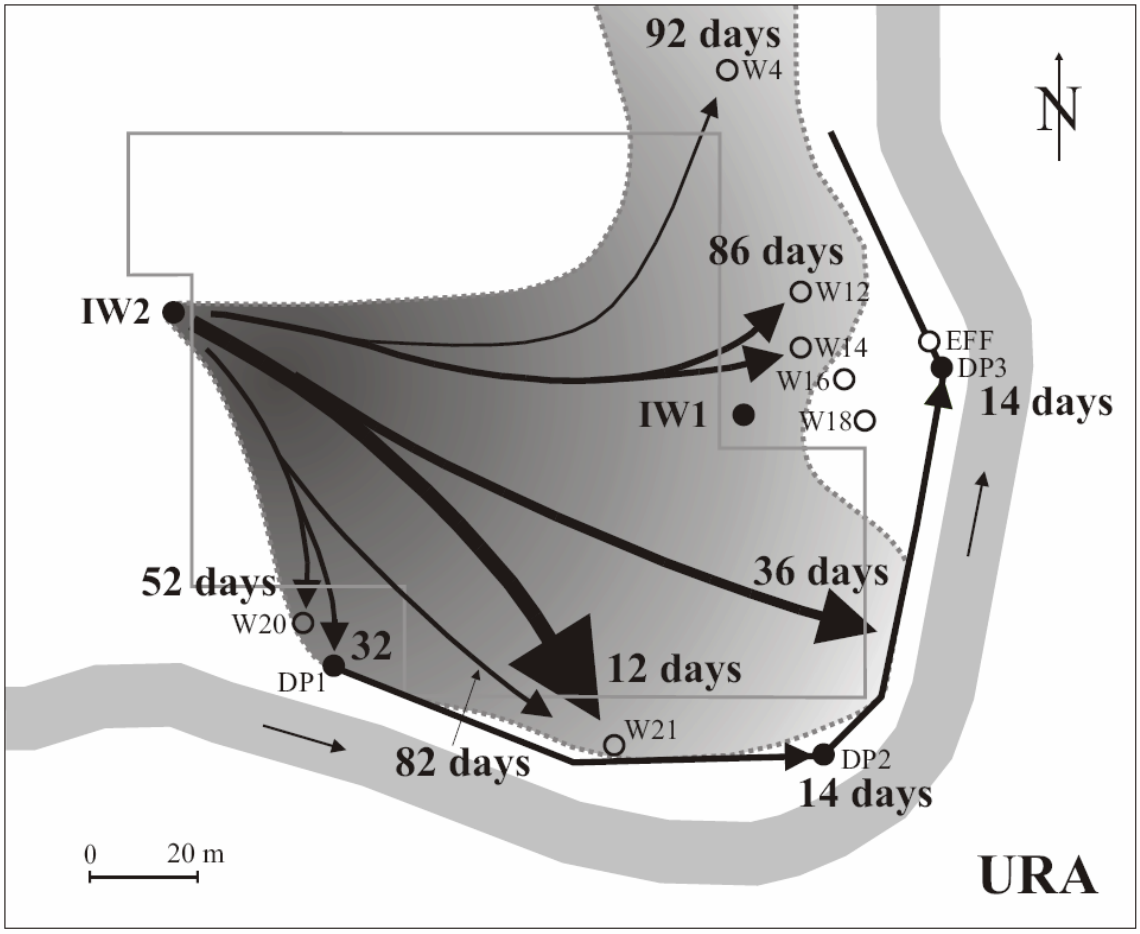

Figure 4: Travel times and estimated area covered for uranine during the first dye-tracing test in 2002.

The transport of URA from IW2 throughout the southern half of the factory site and to the northeast of the factory was completely unexpected. The multiple breakthroughs of URA at W21 between the drainage wells DP1 and DP2 suggest discrete secondary pathways for groundwater flow in the porous media under the factory, as well as a hydraulic obstruction between IW2 and the DP1. We do not know what these heterogeneities are, but clearly, the directions of groundwater flow under the factory are not constrained by the hydrodynamics of homogeneous and isotropic porous media. We suspect that infrastructure under the factory, as well as heterogeneities within the fill adjacent to it, causes groundwater flow from the injection well to trifurcate (at least), resulting in multiple breakthroughs at W21.

The marked dispersion of URA from the injection well located west of the factory to ultimately cover the entire southern part and northeastern part of the property speaks to the extreme heterogeneity that must be

present in the fill underlying the study site, as does SRB transport to the north from the IW1 injection east of the factory. The results of the first dye test show that standard hydraulic measurements of head, hydraulic conductivity, and potential flow nets and Darcy calculations derived from them, could not possibly have captured the true nature of contaminant transport in the groundwater flow system under the factory and proximate to it.

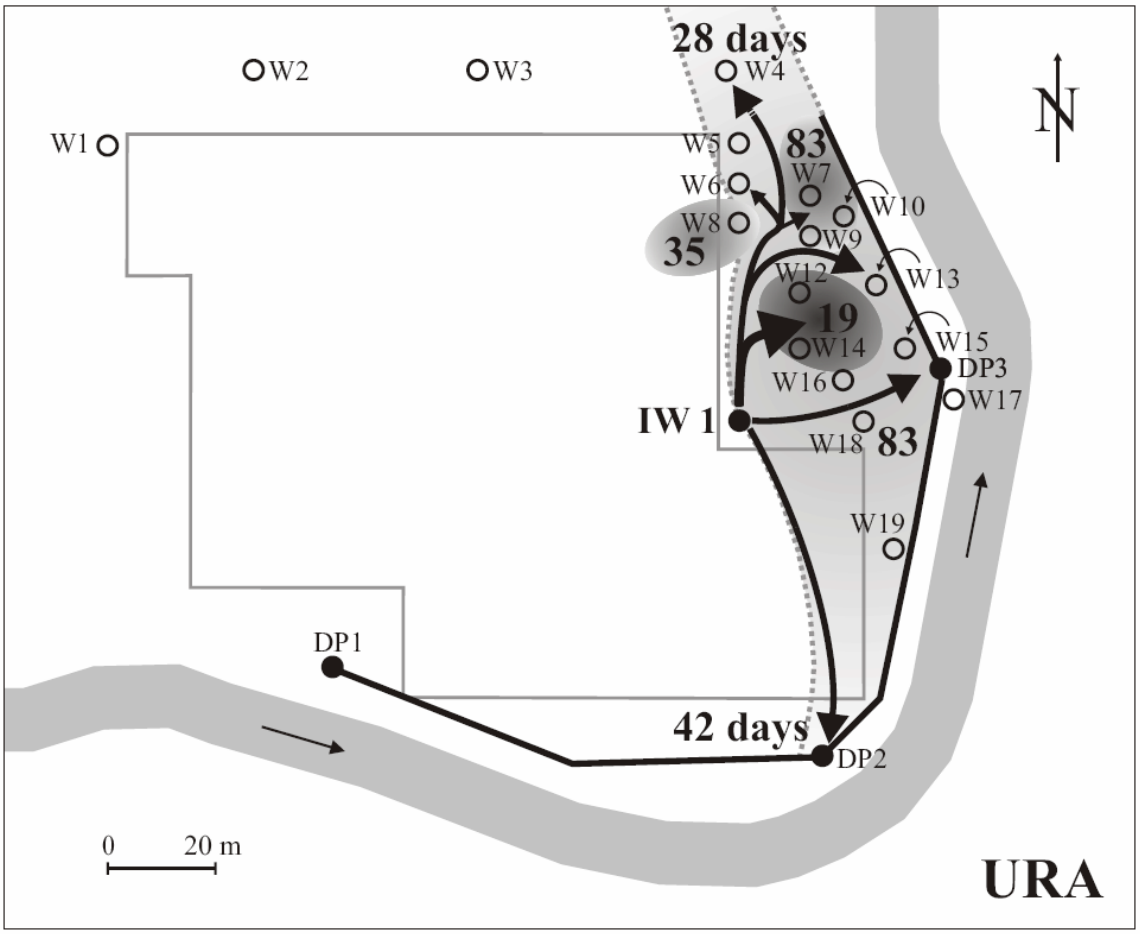

Figure 5: Travel times and estimated area covered for uranine and Na-naphtionate during the second dye-tracing test in 2003. Shown are 3 probable oil lenses east of the factory building defined by intrinsic fluorescence.

The second dye-tracing test upgradient of DP3 was designed to further evaluate flow paths near this major recovery well. The variable times for NAP and URA breakthrough, shown in Table 2, suggest that the apparent groundwater mound east of the western wall of the factory probably reflects measurements of oil elevations, or oil-emulsion elevations, on the water table. The breakthrough times for the dyes, faster to the north, and slower towards the pumping well DP3, contradict common wisdom that flow should be faster to pumping centers. One distinct possibility for this contradiction is that flow paths are forced around the oil and oil emulsion mass, which could behave as an hydraulic no-flow barrier, depressing the water table under it. Some water will flow under the oil, creating stagnant zones on the upgradient and down gradient sides where dye can adsorb to the oil and concentrate. Again, as in the first dye-tracing test, dye migrated north towards monitoring well W4 faster than to any other monitoring well or the recovery systems much closer.

Both dye-tracing tests indicate that heterogeneities in the flow system under the industrial site, be they lenses of tight porous media in the fill or anthropogenic structures such as buried pipes and construction debris, have created a far more complex flow field than was previously assumed from routine and standard hydrogeologic investigations. The locations of the pumping centers are not efficiently modifying the hydraulic

head to force contamination towards them, although contamination is moving towards the drain surrounding the southern end of the factory.

Our study shows there is no assurance that the travel velocities and flow paths calculated from standard hydraulic methods accurately define the rates and directions that groundwater moves at this industrial site which includes a large inaccessible factory. Commonly, field hydrogeologic studies done to characterize organic contamination in industrial areas last well over one year and include at least quarterly monitoring for contaminants or longer. Organic fluorescent dye-tracing tests, optimized to specific organic contamination class, can be done within a year at most places, even under low hydraulic gradients. The results of these tests can directly show where contamination moves under inaccessible parts of industrial facilities and are effective tools to assist in designing the best remediation strategies.

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