

Optical Brighteners: Sorption Behavior, Detection, Septic System Tracer Applications

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Optical Brighteners: Sorption Behavior, Detection, Septic System Tracer Applications

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ABSTRACT

Laboratory soil column experiments were used to evaluate the optical brighteners (fluorescent whitening agents) Tinopal³ CBS-X (ASTM designation DSBP-1) and Tinopal³ 5BM-GX (ASTM designation DASC-4) and the fluorescent dye eosin Y (C.I. 45380) as adsorbing tracers in subsurface systems. In a low organic carbon content glacial outwash sand ($foc = 0.0034$, 97% sand by weight) the solid-water distribution coefficient (K_d) was determined to be $0.26 \text{ cm}^3/\text{g}$ for Tinopal CBS-X, $0.78 \text{ cm}^3/\text{g}$ for Tinopal 5BM-GX, and $0.024 \text{ cm}^3/\text{g}$ for eosin Y. All three compounds had simple sigmoidal breakthrough curves.

Optical brighteners can be detected in direct solution by fluorometry but suffer from interference associated with naturally occurring organic compounds. Unbrightened cotton can be used to qualitatively detect optical brighteners. Polyethersulfone filter media can be used to selectively remove optical brighteners from solution without changing the background fluorescence spectrum. The exposed filter medium can be analyzed as a solid sample in a scanning spectrofluorophotometer. The resulting spectrum can be used to measure the optical brightener concentration in the filtered sample. Polyethersulfone filters can be used to detect optical brighteners in samples collected in and around septic system drain fields at less than 1 ppb Tinopal 5BM-GX equivalent.

KEYWORDS

Optical brighteners, fluorescent whitening agents, detection systems, groundwater tracers, septic systems.

INTRODUCTION

Fluorescent dyes are used extensively for tracing surface water and groundwater because of their low detection limits, ease and economy of detection, availability and safety. Fluorescent dyes have successfully been used to delineating otherwise unpredictable groundwater basins in karst environments (Quinlan and Ray, 1981; Alexander and others, 1993). Fluorescent dyes have also been used as adsorbing tracers in an effort to predict the breakthrough of pesticides in agricultural settings (Sabatini and Austin, 1991; Everts and Kanwar, 1994.)

Optical brighteners (also known as fluorescent whitening agents) absorb ultraviolet light and fluoresce in the blue region of the visible spectrum. The main commercial use of optical brighteners is in laundry detergents and textile finishing. Consequently, optical brighteners are relatively inexpensive and have been subjected to rigorous toxicity testing. Optical brighteners are found in domestic waste waters having a component of laundry effluent, and therefore can enter the subsurface environment as a result of ineffective sewage treatment. The potential exists to use optical brighteners as tracers of sewage effluent in polluted aquifers and as artificial tracers in pristine aquifers. In either case an understanding of the interaction between the dye and solid aquifer material is required to properly interpret tracer test results.

A great deal of information is available on the characteristics and behavior of the most frequently used dyes: rhodamine WT (RWT) and uranine C (URC) also known as fluorescein (Smart and Laidlaw, 1977; Everts and others, 1989; Shiao and others, 1993.)

This paper describes three aspects of our investigation into the potential use of optical brighteners as subsurface tracers. A soil column was used to compare the transport behavior of optical brighteners and the fluorescent dye eosin Y (EOS) to URC and RWT. We discuss a methodology for detecting optical brighteners on cotton using a scanning spectrofluorophotometer, and report the discovery and preliminary field results of a novel detection method utilizing polyethersulfone filter media.

Laboratory experiments were conducted with two stock optical brighteners supplied by the manufacturer. Both compounds are designed for use in domestic laundry detergent formulation at concentrations up to 0.5% on weight of formulation. Tinopal³ CBS-X (TCBS) is a distyrylbiphenyl type whitener (see figure 1). TCBS is chlorine bleach stable in solution, has a high solubility (30% at 95C, 2.5% at 25C) and high fluorescence efficiency (Ciba, 1987). Tinopal 5BM-GX (T5BM) is a cyanuric chloride/diaminostilbene disulfonic acid derivative whitener (see figure 1). T5BM is beach stable only when sorbed to a substrate, is less soluble (1.5% at 50C) and has a lower fluorescence efficiency (Ciba, 1987). The optimal temperature range for sorption of both brighteners is in the 15C to 50C range.

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³ Tinopal is a registered trademark of Ciba-Geigy Corporation, Greensboro, North Carolina, USA.

SORPTION BEHAVIOR

Laboratory soil column experiments were conducted using a 30 cm (11.8 inch) long, 2.5 cm (1.0 inch) diameter borosilicate glass chromatography tube. Column end fittings and tubing were PTFE, with the exception of a silicone peristaltic pump drive section. The column was filled with repacked Rosemount Outwash aquifer material, obtained from a sand quarry near Coates, Minnesota. Column running parameters are listed in table 1. Organic carbon content was determined at the University of Minnesota Soil Science Research Analytical Laboratory. Column material grain size distribution was measured by standard sieve methods. Fines fraction was determined by inspection under an optical microscope. Hydraulic conductivity was calculated with the Hazen equation (see Freeze and Cherry, 1979, p. 350).

Table 1. Soil Column Parameters

Column internal volume (cm ³)	150	Hydraulic conductivity by Hazen method (cm/s)	1.4E-02
Fraction organic carbon content, foc	0.0034	Porosity, n	0.30
Median grain size diameter, d50 (mm)	0.34	Repacked bulk dry density, pb (g/cm ³)	1.85
Uniformity coefficient, d60/d10	2.8	Pore water velocity (cm/h)	30
Sand: coarse, medium, fine (%)	3, 37, 57	Hydrodynamic dispersion coefficient, Dx (cm ² /h)	3.4
Fines: silt, clay (%)	3, <1		

Breakthrough data were collected in three separate column runs. The column was not repacked between runs. The breakthrough of a 1.0 g/L solution of sodium chloride (run #1) was used to calculate column parameters. Hydrodynamic dispersion coefficient, Dx was extracted from an analytical solution to the advection dispersion equation for saturated porous media (see Freeze and Cherry, 1979, p. 391) fitted to the chloride breakthrough curve. Chloride concentrations were determined by mercuric nitrate titration of column discharge aliquots. Approximately five pore volumes of water with no NaCl added were used to flush the column following run #1. Run #2 involved a 20+ pore volume continuous input of a mixture of URC, RWT and TCBS. Run #2 was followed by approximately 50 pore volumes of flushing. Run #3 was conducted using a continuous input of EOS and T5BM. Column runs were conducted in darkness or under subdued red lighting to minimize potential dye photodegradation, at approximately 25°C.

Background ion concentrations have an effect on the transport characteristics of fluorescent dyes (Sabatini and Austin, 1991; Everts and Kanwar, 1994), so a pristine groundwater solvent was used in place of the traditional deionized water in an effort to more closely simulate field conditions. Groundwater was obtained from a flowing artesian well completed in the southern Minnesota Mount Simon aquifer. The water has previously been carbon-14 dated at over 10,000 years and contains no anthropogenic contaminants.

The fluorescent spectrum of the column discharge was monitored in the flow-through cell of a Shimadzu RF5000U scanning spectrofluorophotometer. Essential settings are listed in table 2. A synchronous scan mode was used at the detection wavelength separations ($\Delta\lambda$) listed. The relative dye concentration (C/C_0) was determined from the area of characteristic peaks in the discharge fluorescence spectrum, e.g. $C/C_0(\text{TCBS}) = \text{area of 440 nm peak in discharge} / \text{area of 440 nm peak in influent dye mixture}$ (see figure 2.)

Table 2. Dye Properties

Dye (ASTM designation / color index)	TCBS (DSBP-1)	T5BM (DASC-4)	URC (C.I. 45350)	RWT (Acid Red 388)	EOS (C.I. 45380)
Source	Ciba-Geigy	Ciba-Geigy	Fisher	Crompton Knowles	Fisher
Grade	commercial	commercial	purified	20% solution	88% powder
Batch #	34918038	1009	A-833	38	916991
Concentration, Co (ppb)	370	360	150	230	450
Detection $\Delta\lambda$ (nm)	95	95	15	15	15
Peak emission λ (nm)	440	440	508	573	525
Retardation factor, Rf	2.6	5.8	1.04	--	1.15
Kd (cm ³ /g)	0.26	0.78	0.006	--	0.024
Koc (cm ³ /g)	76.5	229	1.76	--	7.06

Note: Peak emission wavelength and detection wavelength separation refer to analysis of direct solution samples.

Peak areas were calculated by integration of a best fit non-linear function. Figure 2 illustrates the Co concentration fluorescent spectra of all the dyes except T5BM, which has a shape identical to TCBS. Each symbol in figure 2 is a discrete data value in the fluorometer scan output. The black lines in figure 2 are the fitted curves from which areas were calculated, they do not just link the symbols. The peaks of URC, EOS and RWT were adequately described by a single peak function, with a linear or no background function. TCBS and T5BM were each described by a complex function made up of three simple peaks functions (not shown) superimposed on a

small background peak (not shown). The subtraction of a background peak was required in the analysis for the optical brighteners to remove the effect of naturally occurring organic compounds which fluoresce in a similar region of the spectrum.

Retardation factors (R_f) were calculated as the number of pore volumes required to reach half influent concentration ($C = C_0/2$). The solid-water distribution coefficient (K_d) was backed out of the expression $R_f = 1 + (\rho_b / n) \cdot K_d$, where n = porosity and ρ_b = bulk density. The organic carbon-water distribution coefficient (K_{oc}) was calculated from the expression $K_{oc} = K_d / f_{oc}$, where f_{oc} = fraction organic carbon in the aquifer material.

Figure 1. Chemical Structures of Dyes

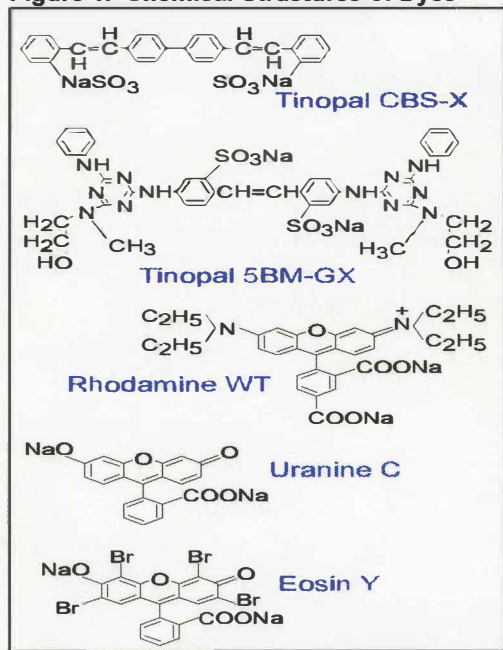
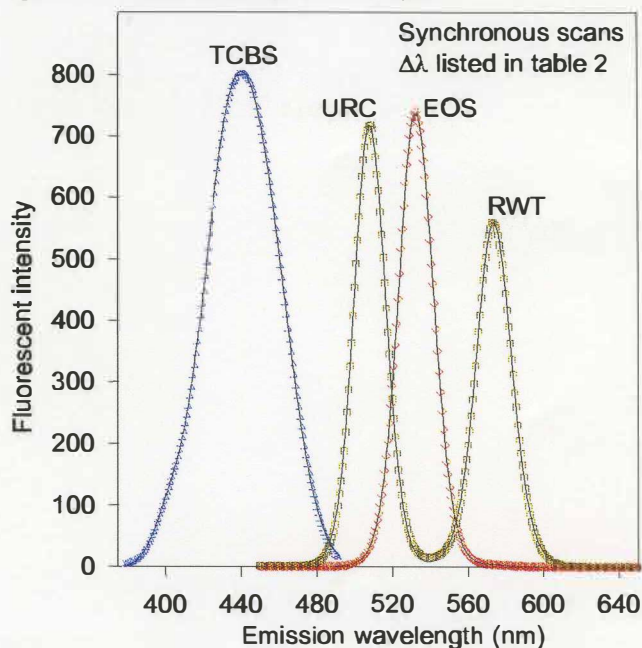


Figure 2. Fluorescent Spectra of Dyes



Results

Figure 3 summarizes the column experiment results. Each symbol in figure 3 represents a discrete data point derived from a single fluorometer scan. Chloride breakthrough exhibited the normal sigmoidal shape characteristic of saturated flow in a relatively homogenous porous medium, reaching $C = C_0/2$ at 1.0 pore volumes. URC and EOS were the earliest dyes to breakthrough, both reaching $C = C_0/2$ within 1.2 pore volumes. Optical brighteners were significantly retarded. RWT showed the characteristic stepped breakthrough attributed by Sabatini and Austin (1991) and Shiau and others (1993) to differing transport properties of two RWT structural isomers.

Retardation factors and distribution coefficients are listed in table 2. The complex breakthrough curve of RWT precludes the calculation of a single, meaningful value for its R_f , K_d and K_{oc} . An additional column experiment using a 1.0 pore volume input followed by flushing showed that sorption of TCBS to aquifer material is reversible. Over 94% of input dye mass was recovered within 15 pore volumes of flushing (results not shown).

The K_d values obtained for URC from this experiment are approximately 1 order of magnitude lower than the results of Sabatini and Austin, 1991 ($K_d = 0.05 \text{ cm}^3/\text{g}$) who used a very similar apparatus, porous medium and method. The source of this discrepancy is being investigated.

Conclusions

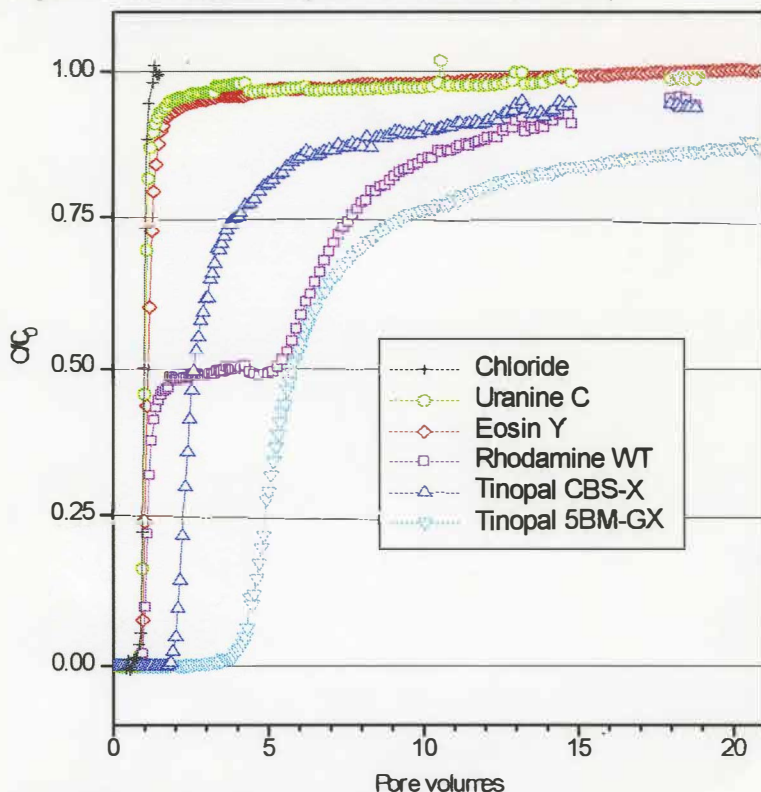
The breakthrough curve for EOS in this experiment was almost identical to that of URC. The symmetrical substitution of four Br atoms for four H atoms on the URC structure (see figure 1) does not appear to significantly affect the molecule's adsorption properties. EOS appears to be a good alternative to URC for tracer applications where retention on aquifer material is undesirable. EOS has the benefit of having a peak fluorescence emission wavelength higher than that of URC (see table 2 and figure 2). This characteristic reduces the potential for interference with naturally occurring fluorescent compound which tend to be concentrated at shorter green and blue wavelengths.

As stated by earlier authors, interpretation of RWT tracer test results requires an appreciation for its complex breakthrough pattern. In the absence of other tracer data the double stepped breakthrough of RWT could be misinterpreted as being indicative of multiple dye pathways.

TCBS and T5BM are potentially useful tracers. Although the detection of both dyes is subject to interference from other compounds, analytical developments can remedy that problem. A promising analytical improvement is discussed later in this paper. TCBS and T5BM are not distinguishable fluorometrically, ruling out

their concurrent use. However, their simple sigmoidal breakthrough curve and differing retardation factors means that they could be used for predicting the breakthrough of various retarded contaminants, with perhaps less ambiguity than RWT. The strong sorption characteristics of optical brighteners improves their utility as indicators of failing septic systems where the soil adsorption property may have broken down.

Figure 3. Soil Column Experiment Results Summary



COTTON DETECTION SYSTEM

While optical brighteners are readily detectable by fluorometry at the part per billion level in laboratory prepared solutions, problems exist with extending this method of analysis to field samples. A primary cause for concern is the presence of variable concentrations of naturally occurring organic compounds which fluoresce at similar wavelengths to optical brighteners in solution. Figure 4 is a synchronous fluorometer scan ($\Delta\lambda = 95 \text{ nm}$) which shows the spectra of both a pristine groundwater and a dilute solution of T5BM. These complications lead Alhajjar and others (1990) to conclude that optical brighteners are not suitable indicators of septic system impact on groundwater. These authors' limitation of their optical brightener data to filter fluorometer analyses on direct water samples demonstrated the ineffectiveness of wide-band groundwater fluorescence. Their work does not, as they assert, indicate that optical brighteners can not be used as tracers of septic system effluent.

Aley (1985) successfully used a detection system based on unbrightened cotton to identify sewage impacts on karst groundwater. Quinlan (1981) used optical brighteners as artificial tracers employing a similar cotton based detection system. The use of cotton detectors exploits the strong sorption affinity of optical brighteners for cotton. We are currently using a spectrofluorophotometer to analyze cotton detectors as part of a regional survey of septic system impact on domestic wells in southern Minnesota described by Spong and others (1995, this publication.)

The application of a dilute solution of T5BM to unbrightened cotton produces a characteristic peak in the fluorescence spectrum of the material at approximately 440 nm. Figure 5 is a synchronous fluorometer scan ($\Delta\lambda = 60 \text{ nm}$) which shows the spectra of unbrightened cotton and cotton doped with a dilute solution of T5BM. Note that the sharp peak at approximately 415 nm is present in both signals. TCBS and powder and liquid formulation domestic laundry detergents produced identical results (not shown). The cotton detection system is based on the recognition of the characteristic peak in the cotton spectrum at 440 nm after exposure of the cotton to waters containing optical brighteners. A sample is considered positive for optical brighteners when the characteristic peak is present.

Figure 4. T5BM Detection in Direct Solution

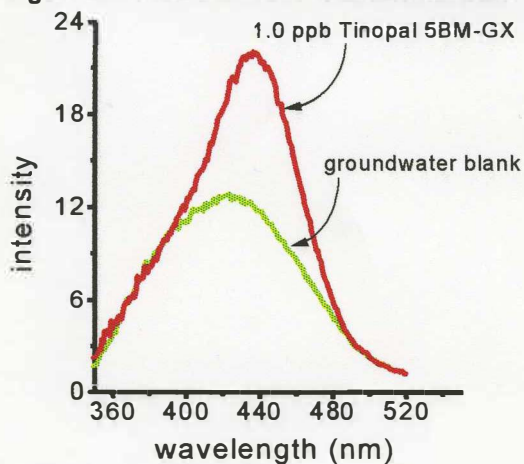
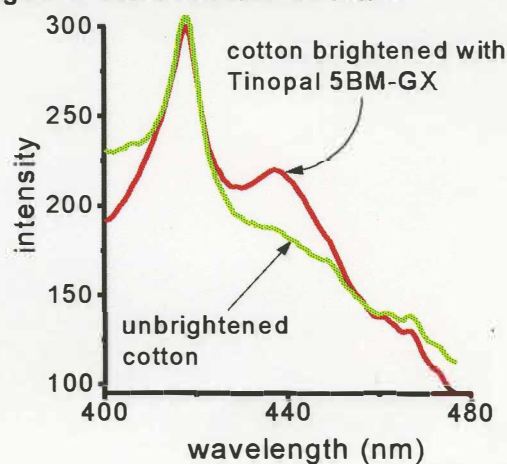


Figure 5. T5BM Detection on Cotton

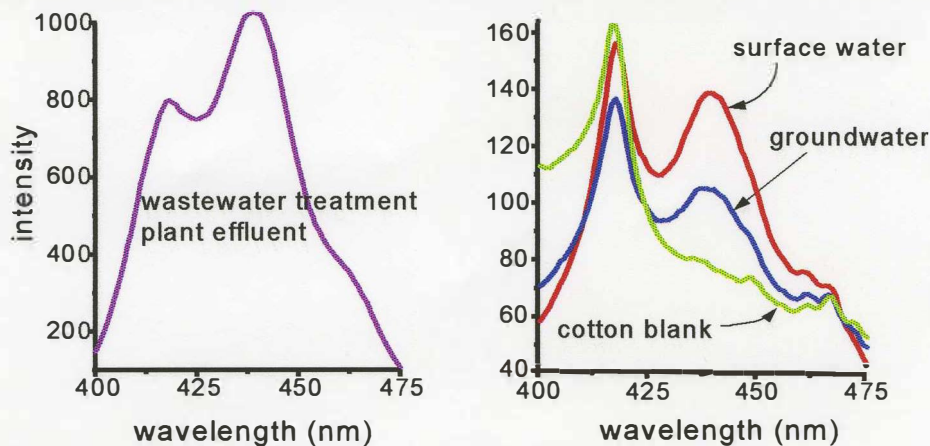


Results

Optical brighteners have been detected in a variety of water environments. Spong and others (1995, this publication) summarize the results of a regional survey of optical brighteners in shallow water table aquifers. Figure 6 contains some typical positive sample scans. All of the spectra in figure 6 are synchronous scans ($\Delta\lambda = 60$ nm) of cotton samples. Note that the graph on the left side of figure 6 (cotton after exposure to the effluent stream of a waste water treatment plant) has a much larger y axis, indicating a greater degree of brightening.

Long term exposure of the cotton to a supply of the sample water (of the order of weeks) is typically required (see Spong and others, 1995). While increasing exposure time improves the chance of detection by allowing more of the sample water supply to encounter the cotton detector problems arise with bacterial colonization, mineral precipitation and cotton fiber loss. These phenomena tend to lead to heterogeneous brightening of the cotton surface, requiring multiple scans of various parts of each sample and restricting the cotton detection method to a qualitative positive/negative determination.

Figure 6. Example Fluorescence Spectra of Cotton Samples Positive for Optical Brighteners



NOVEL POLYETHERSULFONE DETECTION SYSTEM

This section of the paper describes our investigation into an improved detection methodology for optical brighteners. Syringe tip filter capsules are frequently used to remove suspended solids in the preparation of water samples for dissolved species analysis. One material used in the construction of such filters is polyethersulfone (PES). PES filters appear to selectively absorb optical brighteners.

The Acrodisc⁴ (AD) and Acrodisc PF (ADPF) products both use PES as a filtration medium. Both products are housed in a 25 mm diameter modified acrylic housing, having an effective filtration area of 2.8 cm² (Gelman, 1994). The AD model that we tested has a 0.45 μm PES filter. We also used the ADPF which utilizes a 0.2 μm PES filter preceded by a 0.8 μm PES prefilter. Our investigation of the AD and ADPF filters consisted of three separate series of experiments:

⁴ Acrodisc and Acrodisc PF are registered trademarks of Gelman Corporation, Ann Arbor, Michigan, USA.

Experiment #1 (Dye scavenging efficiency of PES): Dye solution mixtures used for earlier column experiments (see table 2) were used to test the degree to which PES filters remove fluorescent dyes and optical brighteners from solution. In each experiment 3 ml of dye mixture solution was forced through an AD filter with a single-use 3 ml syringe directly into a 3 ml acrylic fluorometer cuvette. A 1 ml air purge was used, in accordance with the filter manufacturer's instructions, to remove liquid held on the filter by surface tension. The solution which had passed through the PES filter was analyzed and compared with an unfiltered (U) dye sample. The method of dye solution analysis was identical to that described in the "sorption behavior" section, above. To investigate the effect of filtration through an inert medium a 1.0 μm pore size glass fiber (GF) filter was also evaluated. Each dye/filter combination was tested in triplicate.

Experiment #2 (Relationship between sorbed mass and fluorescence): The solid sample holder of the fluorometer allows the analysis of materials such as the PES filter medium. In a series of experiments a known mass of dye was applied to individual ADPFs using the syringe method described above, with the addition of a 9 ml deionized water rinse. After exposure the filter casing was broken open, and the filter medium removed. The fluorescent emission spectrum of the filter medium was measured between 380 nm and 525 nm, holding an excitation wavelength of 370 nm. Five samples were examined for photodegradation during analysis. After an initial scan samples were allowed to remain in the path of the fluorometer excitation beam (set at 650 nm) for approximately 2 minutes, and then reanalyzed. This time frame brackets the normal period which would be allowed to lapse between placing the sample in the fluorometer and initiating the emission scan.

Experiment #3 (Effect of natural background organic compounds): A sample of lake water containing no optical brighteners, but relatively rich in natural organic compounds was filtered through ADPF. This experiment was conducted to measure the degree to which naturally occurring organic compounds might adhere to the PES medium and interfere with optical brightener detection.

Results

Figure 7 graphically displays the results of experiment 1. The x axis reflects the three treatments given the dye mixtures: unfiltered (U), glass fiber filtered (GF) or polyethersulfone filtered (PES). The connecting lines are a visualization aid only and have no physical interpretation. Box height at each x axis interval indicates the variability encountered in triplicate analyses. Figure 7 shows that while over 80% of both optical brighteners passed through the GF filter no TCBS or T5BM was detectable after passing through the PES filter. URC and RWT concentrations were slightly reduced by PES filtration. EOS was reduced to approximately 40% of unfiltered concentration. The GF filtered URC samples had an apparent concentration of 105% relative to unfiltered samples. This is possibly due to the removal of iron colloids and/or microscopic calcite laths. These particles were observed in the unfiltered groundwater and may slightly obscure the fluorescence of unfiltered direct dye samples.

Figure 7. Sorption to Filter Media

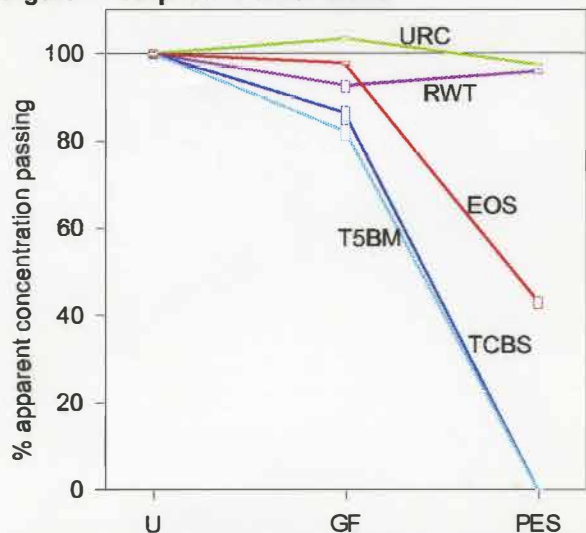


Figure 8. Tinopal 5BM-GX on Polyethersulfone

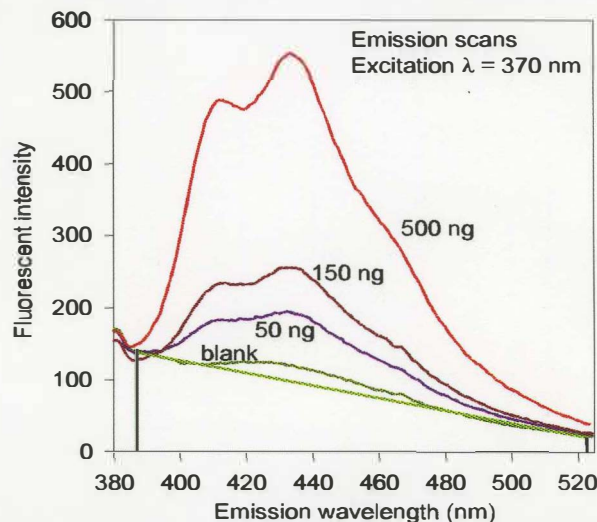


Figure 8 contains the fluorescence spectra of PES media with various masses of T5BM sorbed. A double peaked signal, which increases in area with increased sorbed dye mass, is evident. The main peak is at 434 nm with a secondary peak at 414 nm.

Figure 9 is a plot of emission scan peak area versus sorbed mass for TCBS and T5BM. Peak area was calculated by numerical integration of the fluorometric emission scan signal between 388 nm and 525 nm followed by the subtraction of the underlying trapezoid (see fig. 8). The complex nature of solid phase fluorescence spectra precluded area integration with the non-linear curve fitting procedure described above for direct solution analysis. The linear best fit for T5BM is described by the function: $\text{mass (ng)} = [\text{peak area (fluorescent intensity} \cdot \text{nm)} -$

667.9] / 55.18. The constant in this equation (667.9) represents the best estimate of the portion of the peak area attributed to unexposed "blank" PES.

In figure 9 vertical lines connect samples which were analyzed immediately and those which were allowed to remain in the fluorometer excitation beam. Significant photodegradation is evident for T5BM, especially at higher concentrations. No degradation was observed for TCBS. The TCBS curve is steeper than the T5BM indicating more media brightening per mass of brightener sorbed. These observations are in accordance with the manufactures specifications.

Figure 10 summarizes the results of experiment #3. The lower box compares the emission scan spectra of the organic rich lake water before and after it was passed through the PES filter. The fluorescent signature is essentially unchanged which indicates no significant removal of fluorescent compounds by the filter. Note that the vertical scale of the lower part of figure 10 is much more expanded than that of figure 8 or the upper part of figure 10. The upper box compares the emission spectra of two PES filters, one exposed to the lake water and the other to deionized water. The lake water produced no significant enhancement on the PES filter compared to organic free deionized water. The same experiment comparing optical brightener free groundwater with deionized water produced identical results (not shown.)

Figure 9. Tinopal Calibration Curves

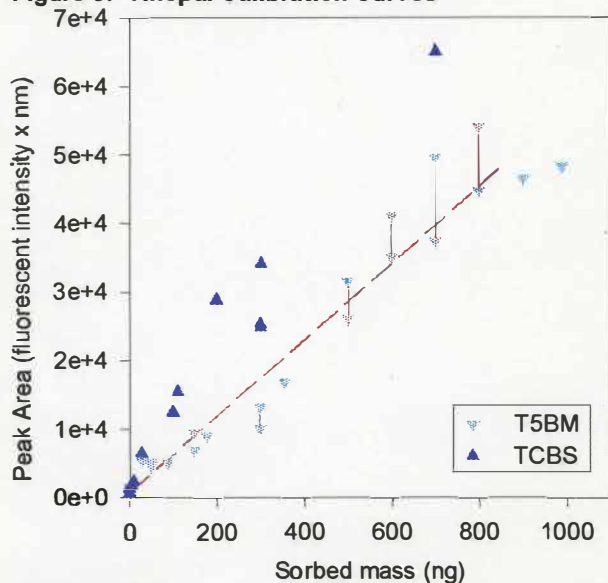
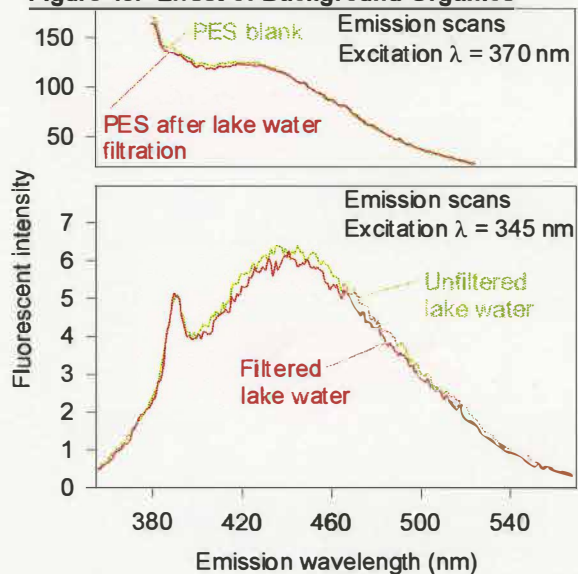


Figure 10. Effect of Background Organics



Conclusions

PES filters quantitatively sorb optical brighteners from solution without simultaneously sorbing at least some naturally occurring organic compounds. We speculate that the mechanism responsible for the binding of optical brighteners to PES is related to the sulfonate functional groups present on both Tinopal compounds (see figure 1). T5BM is prone to photodegradation during fluorometric analysis when sorbed to the PES medium at higher concentrations. The phenomenon appears to be less important at lower concentrations.

Naturally occurring organic compounds in a lake water and groundwater sample did not interfere with optical brightener detection using PES filter media.

SEPTIC SYSTEM TRACER APPLICATIONS

The detection methodology described above was used to analyze samples obtained from two instrumented septic systems located in rural southern Minnesota. The systems, identified here as A and B, were constructed in October, 1994 in heavy clay-till soils where shallow water table conditions generally prevail. Both systems are equipped with a curtain tile to locally depress the water table beneath the drain field. The system A drain field is situated in a topographically flat area. System B has a gravity fed drain field installed on a moderate slope. Both systems receive input from single family dwellings.

Water quality in and around the drain field is sampled through a series of lysimeters located at 30.5 cm, 61 cm and 91.5 cm (1, 2 and 3 feet) below the drain field pipes. Additional samples were obtained from the drain field influent. The optical brightener data discussed below come from a single sample set collected March 27, 1995. Other water quality parameters were recorded but are not discussed here.

For each sample between 36 ml and 72 ml of water were passed through and ADPF in the field. Filters were refrigerated in darkness until being broken apart and having the PES filter medium subjected to fluorometric analysis. Fluorometric spectra with discernible peaks in the region characteristic of optical brighteners were

analyzed by the methodology described above. Peak areas were converted to an equivalent T5BM mass with the linear regression formula. Sorbed mass was converted to concentration based on known sample volume.

Results

Peaks were visually noted to be very similar in shape to the T5BM emission signatures (fig. 8.) Optical brighteners were detected in five of the six lysimeter samples and one of the two septic system influent samples (see table 3.) The practical detection limit appears to be approximately 0.1 ppb T5BM equivalent, corresponding to the smallest discernible peak in the sample emission spectra of this sample set. The very brief presentation of this field data is used only to demonstrate that optical brighteners can be detected in field situations by the methodology outlined above. This technique is a component of ongoing research at these and other instrumented septic systems.

Table 3. Optical Brightener Concentrations (ppb T5BM equivalent)

System	Influent	30.5 cm	61 cm	91.5 cm
A	8.4	0.3	1.6	3.2
B	<0.1	<0.1	0.8	0.1

REFERENCES

- Alexander, S.C., S.J. Fay, E.C. Alexander Jr., and J.A. Green. 1993. Groundwater tracing in southern Minnesota karst using fluorescent dyes (poster). Amer. Geophys. Union 1993 Fall Annual Meet., Dec. 6-10, 1993, San Francisco, Cal. Eos, Trans. Amer. Geophys. Union, vol. 74, no. 43, Oct. 26, 1993/suppl. p.286 (abs)
- Aley, T.J. 1985. Optical brightener sampling; a reconnaissance tool for detecting sewage in karst groundwater. Hydrological Science and Technology Short Papers. v.1, no.1, p45-48
- Alhajar, B.J., G. Chesters, and J.M. Harkin. 1990. Indicators of chemical pollution from septic systems. Ground Water. v.28, no.4, p559-568.
- Ciba. 1987. Fluorescent whitening agents product information sheets. Ciba-Geigy Corp, Greensboro, NC
- Everts, C.J., R.S. Kanwar, E.C. Alexander, Jr., and S.C. Alexander. 1989. Comparison of tracer mobilities under laboratory and field conditions. Journal of Environmental Quality. v.18, no.4, p491-498
- Everts, C.J. and R.S. Kanwar. 1994. Evaluation of rhodamine WT as an adsorbed tracer in an agricultural soil. Journal of Hydrology. v.153, p53-70
- Freeze, R.A. and J.A. Cherry. 1979. Groundwater. Prentice Hall Inc., Englewood Cliffs, NJ
- Gelman. 1994. Product Catalog. Gelman Sciences Inc. Ann Arbor, MI
- Sabatini, D.A. and Austin, T.A. 1991. Characteristics of rhodamine WT and fluorescein as adsorbing ground-water tracers. Ground Water. v.29, no.3, p341-349
- Shiau, B-J, D.A. Sabatini, and J.H. Harwell. 1993. Influence of rhodamine WT properties on sorption and transport in subsurface media. Ground Water. v.31, no.6, p913-920
- Smart, P.L. and I.M.S. Laidlaw. 1977. An evaluation of some fluorescent dyes for water tracing. Water Resources Research. v.13, no.1, p15-33
- Spong, R.C. 1995. Optical brightener screening for sewage contamination of water table aquifers in southeastern Minnesota, USA. International Association of Hydrogeologists, XXVI International Congress, Edmonton, Alberta, Canada. June, 1995 (this publication.)
- Quinlan, J.F. 1981. Hydrologic research techniques and instrumentation in the Mammoth Cave region, Kentucky. In: GSA Cincinnati '81 Field Trip Guidebooks. v.3, p457-506. (Ed: T.G. Roberts.) American Geological Institute, Washington, DC

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BIOGRAPHICAL SKETCHES

Steffan R. Fay

Steffan Fay received his Bachelor of Science degree in Geology from Imperial College of Science, Technology and Medicine, University of London, UK. in 1990. Between 1990 and 1993 Mr. Fay was employed as a hydrogeologist with Barton & Loguidice, P.C. Consulting Engineers in Syracuse, New York, USA. Mr. Fay is currently enrolled in a Masters degree program at the Department of Geology and Geophysics, University of Minnesota, USA, where his interests focus on ground water contaminant fate and transport, laboratory analytical techniques and field hydrogeology teaching. Mr. Fay was awarded a fellowship by the National Ground Water Association in 1994 to study the transport behavior of selected fluorescent organic chemicals in natural porous media.

Ronald C. Spong

Ronald C. Spong is the project manager for the two-year, state-funded study entitled "Optical Brighteners: Indicators of Sewage Contamination of Groundwaters". He is Environmental Supervisor of the Water and Land Management Section, Dakota County (Minnesota) Environmental Management Department. He has 21 years full-time regulatory experience in public and environmental health and 7 years part-time consulting experience, including well and water supply sanitation, waste water treatment, solid and hazardous waste management, groundwater contamination and remediation, and karst hydrogeology. He holds a Baccalaureate degree in biology and chemistry, 1972, and is a MPH candidate in environmental health, both from the University of Minnesota.

Scott C. Alexander

Scott Alexander is a Junior Scientist working with Dr. E. Calvin Alexander, Jr. at the University of Minnesota. Scott and Calvin have been working on the dating of groundwaters in Minnesota for the past ten years. They have used fluorescent dyes, chemical tracers and environmental isotopes to date waters on the time scales of hours to tens of millennia.

E. Calvin Alexander, Jr.

Calvin Alexander received a BS in Chemistry from Oklahoma State University in 1966 and a PhD in Chemistry from the University of Missouri at Rolla in 1970. After 3 and 1/2 years post-Doctoral research in Physics at the University of California, he joined the Geology and Geophysics Department at the University of Minnesota in 1973. He is currently a sabbatical visiting Professor at the University of Auckland in New Zealand.

The central theme of Dr. Alexander's research interests is the rate of movement of fluids in hydrogeology. This research includes the use of isotopic techniques (tritium, carbon-13, and stable oxygen and hydrogen isotopes) and inadvertent tracers (pollutants, pesticides, and nutrients) to measure fluid flow or residence times on time scales ranging from months to tens of thousands of years. Much of his current work involves the use of artificial tracers such as fluorescent dyes and anions to measure fluid flows on time scales of minutes to years. His initial interests in karst hydrology have expanded into a range of non-Darcian phenomena such as preferential flow in soils, and flow in fractured and granular media. He is also interested in how the results of recent hydrogeologic research can be incorporated quickly and effectively into public policy questions of non-point source pollution, Best Management Practices, and Well Head Protection Regulations.