

FLUORESCENT TRACERS - A TOOL FOR LANDFILL INVESTIGATION AND MANAGEMENT

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SUMMARY: The paper presents a three-stage framework for assessment of fluorescent dyes as tracers for use within Municipal Solid Waste (MSW) landfills. The value of tracer testing as a means of determining leachate behaviour and guiding leachate management strategies is explained. In the first stage, the fluorescence spectra of 27 leachates were compared with 30 fluorescent dyes, to find those dyes for which there was little interference from leachate. Fluorescein (Uranine), Eosin-Y and Rhodamine WT were selected. In a second stage, the dyes' resistance to biodegradation by anaerobes was tested. Fluorescein and Rhodamine resisted degradation but Eosin was moderately degraded. In the final stage, all three dyes were sorbed on shredded MSW, with results fitted to Freundlich isotherms. It was concluded that Rhodamine WT was the most suitable quantitative tracer, as modelling its behaviour would require only a single parameter to be fitted. Eosin would require parameters for linear sorption and degradation. Fluorescein was shown to be an excellent qualitative tracer.

1. INTRODUCTION

Landfill remains the prevalent means for end-of-use disposal of waste materials in the UK and globally. Under the European Union Landfill Directive modern landfills must be engineered to isolate the waste and resultant leachate from the surrounding environment, using natural geological materials and/or engineered low permeability liners. Active management and control, including leachate pumping and treatment, are required until such time as the landfill no longer presents a threat to human health or to the surrounding environment. The hydrological behaviour of liquids within landfills is generally uncertain and previous studies have demonstrated that leachate generation may be unevenly distributed and flow may follow preferential paths through the wastes (Johnson et al., 1998). This has implications for the efficient management of landfills, especially for control of leachate levels, for optimising the decay of putrescible materials and for flushing out potential contaminants (Barlaz et al., 2002). All these factors have a bearing on the time period required before the landfill no longer requires active management. Management strategies that are designed to shorten this period, such as regular flushing of leachate from the landfill, should be firmly based on evidence regarding the probable structure of flow within wastes and the dominant mechanisms of solute transport. Artificial tracer experiments are an important means of acquiring such evidence. Although they have so far only been applied to landfills in experimental situations, they have considerable potential for guiding landfill

management. In a typical experiment a tracer is added to leachate within the landfill, via boreholes or infiltration through the surface. Monitoring at other boreholes and/or outlet drains then shows whether the tracer can be detected as it moves in leachate through the waste. A specific flow regime may be imposed by pumping from some boreholes and recharging others, or the tracer may simply be allowed to follow the normal, undisturbed flow within the landfill. Experiments may be conducted on different scales, from a single borehole up to a whole landfill cell. Tracer breakthrough patterns at the various monitoring points (so-called *tracer breakthrough curves*, or plots of tracer concentration against time) can be matched against mathematical and numerical models of solute transport. These in turn provide insights that can be applied to devising better strategies for minimising the period for which landfills require active management.

Fluorescent organic dyes are used widely as tracers in natural systems on account of their high detectability and ease of assay by fixed-wavelength fluorometry (Flury and Wai, 2003, Mull et al., 1988). They have rarely been used in landfill studies because the deep colour and high fluorescence of dissolved organic matter (DOM) in many leachates present challenges to accurate measurement and the harsh ambient conditions may promote biochemical degradation (Smart, 1985, Blakey et al., 1998). Sorption on solid surfaces or biofilms is a further issue that must be understood for effective interpretation of tracer experiments.

In this paper the suitability of fluorescent dyes for use as tracers within landfills is examined in three stages that focus in turn on *detection*, *degradation* and *sorption*. In the first stage the fluorescent spectra of leachate samples were measured and compared with published fluorocentre data for 30 fluorescent dyes to demarcate regions of the spectrum in which there is minimum interference between them. Affordability and simplicity of preparation were also considered. Fluorescein (Uranine), Eosin-Y and Rhodamine WT were identified as potential tracers and routine procedures were developed to measure them in leachates. Results from the second and third stages show that the dyes were subject in varying degrees to degradation and sorption and that careful experimental design is needed to take account of these effects. Additional measurement problems affected Fluorescein, apparently arising from chemical changes in the leachate over time.

2. MATERIALS AND METHODS

2.1 Leachates

Twenty-seven leachate samples were obtained from site operators at 12 municipal solid waste (MSW) sites from across the UK over a period of 2 years. The sites and the cells from which the leachates were extracted varied in age and were representative of the varied waste streams that have been landfilled over several decades. The samples were supplied in sealed 1L bottles and stored at $\sim 4^{\circ}\text{C}$. Measurements were made within 2 days of receipt.

2.2 Fluorescence measurements on leachates and dyes

Fluorescence spectra were collected using a Varian Cary Eclipse fluorescence spectrometer operated at 20°C . Samples were serially diluted using ultra-pure water (Milli-Q) prior to measurement to avoid inner-filtering effects which could arise due to the dark colour and high fluorescence intensity of the raw leachate (Ohno, 2002). The intensity of the first Raman line for water was measured daily at 348nm and was used to monitor instrument performance and to standardise all collected data (Baker and Curry, 2004).

Three-dimensional (3D) spectra of the leachates were obtained by measuring successive emission spectra at 5nm intervals across the range 200 to 800 nm and using excitation wavelengths spaced at 10nm from 200 to 600 nm. The resulting spectra were then merged into an excitation-emission matrix and processed using SigmaPlot 2007 (SPSS Inc.) to generate contour maps of the fluorescence intensity (e.g. Figure 1a).

When measuring solutions containing dyes of known fluorescence properties, synchronous fluorescence scans were used. Spectra were collected by simultaneously scanning the excitation and emission wavelengths across the 400 to 600 nm range with constant wavelength differences $\Delta\lambda=20\text{nm}$.

2.3 Dye degradation under anaerobic conditions

The resistance of each dye to biodegradation under the anaerobic microbial conditions widely present within a landfill was investigated. In these experiments 500 ml of a test leachate was spiked with 25 ml of active sewage sludge from an anaerobic digestor. The seeded leachate was then placed in an anaerobic cabinet with an atmosphere composed of 90% N₂, 5% CO₂, 5% H₂ (Coy Laboratory Type A Vinyl anaerobic chamber, Wolflabs, England) for 4 days to allow the system to acclimatise. Experimental control vessels prepared in an identical manner were sterilized by autoclaving at 121°C for 15 minutes prior to placement in the anaerobic cabinet. The stock solution of tracer dye to be investigated was also prepared and stored under anaerobic conditions. To mark the start of the experiment, the vessels were spiked with the dye stock solution and immediately sealed using OMNI multi-way pressure valves. The bottles were retained in the anaerobic cabinet for the entire experiment duration with occasional manual agitation to ensure mixing of the contents. Over a period of 13 weeks samples were collected from each vessel and analysed for the fluorescence intensity of each dye. Samples were subsequently stored at 4°C under dark conditions to limit further microbial degradation and photo-degradation.

2.4 Dye Sorption

Equilibrium sorption experiments were conducted to determine dye sorption onto a whole, shredded MSW waste composed of paper 28.9%, plastics 9.3%, textiles 1.7%, glass 0.9%, fines (< 20 mm) 33.1% and miscellaneous coarse material 26.1%. A test leachate in amber bottles was spiked with the tracer dye and added to a known mass of the shredded MSW. The bottles were sealed and agitated by rolling until equilibrium was achieved. After 7 days the bottles were stood upright and allowed to settle. The supernatant liquid was sampled to measure the dye concentration remaining in solution. The ratio of solid (waste) to liquid (dye-leachate solution) is a parameter known to affect the measured sorption of solutes in general (EPA, 1992). Six values of this ratio in the range from 1:4 to 1:65 were used and the results expressed in the form of conventional isotherm plots of dye mass sorbed per unit mass of waste versus dye mass in solution per unit volume of leachate.

3. RESULTS AND DISCUSSION

3.1 Fluorescent characterisation of leachates

The 3D EEM spectra compiled for the 27 leachate samples showed up to 5 recurring centres of fluorescence that have all been widely recognised in the literature. Not every leachate sample displayed all five centres. The fluoro-centres match the classification of fluorescence regions

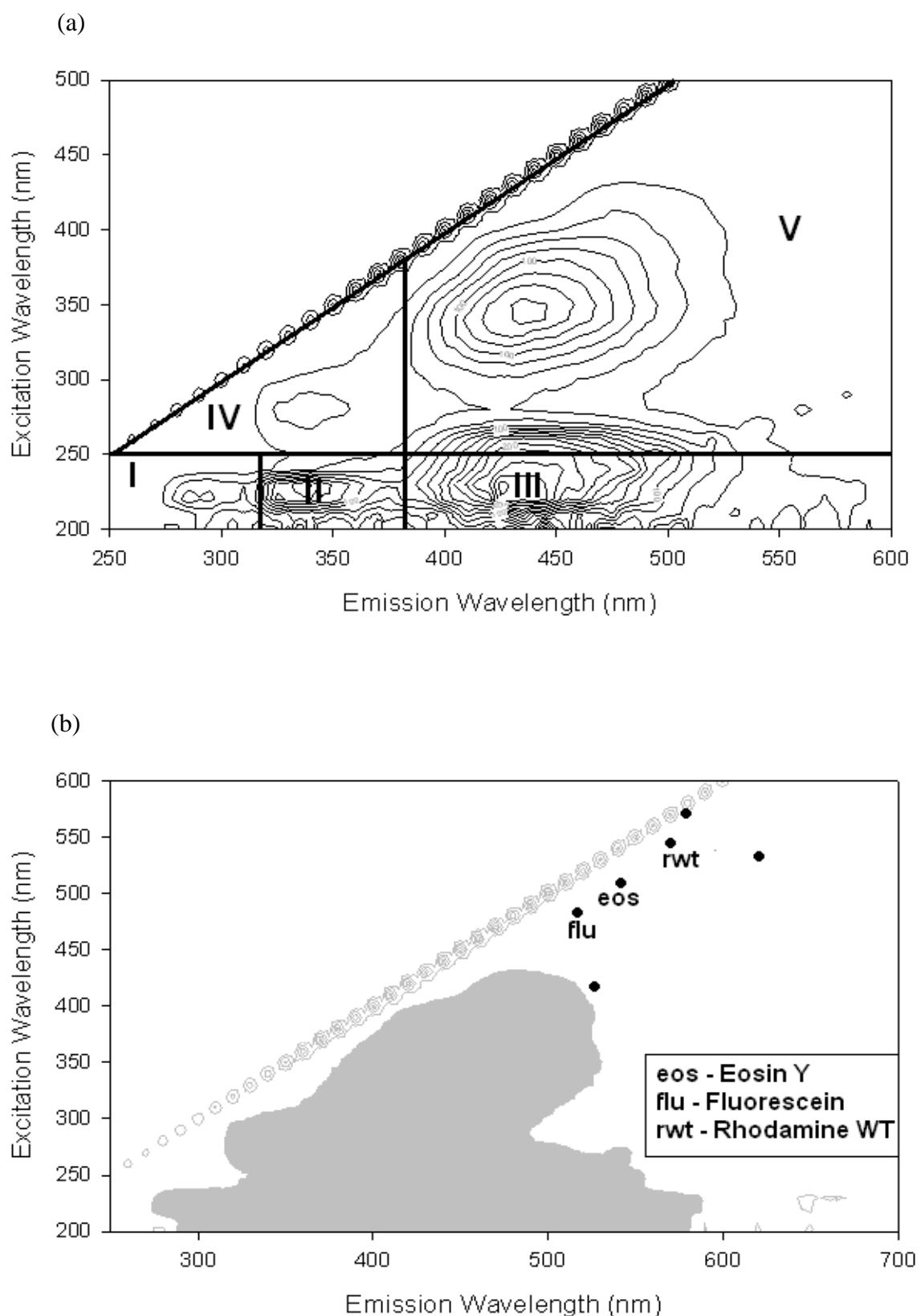


Figure 1: Excitation-Emission Matrix of a sample leachate, (a) showing main fluorophore regions and (b) location of possible tracer dye species relative to the major fluorescence regions.

defined by Chen et al. (2003) as indicative of dissolved organic matter (DOM). Humic-like, fulvic-like and protein-like fluorescence centres were all present (Figure 1**Error! Reference source not found.a**).

Region I, demarcated by $\text{Ex}<250\text{nm}/\text{Em}<330\text{nm}$ is generally indicative of tyrosine-like protein fluorescence (Yan et al., 2000) and was the least common fluoro-centre observed in the samples. Regions II and IV contain tryptophan-like protein fluorescence (Baker and Inverarity, 2004, Saadi et al., 2006). They were present in varying proportions in most samples. Region III, bounded by $\text{Ex}<250/\text{Em}>380\text{nm}$, is typical of fulvic-like fluorescence (Saadi et al., 2006, Parlanti et al., 2000) and was present in all samples. Similarly the humic-like fluorescence associated with Region V, $\text{Ex}>280\text{nm}/\text{Em}>380\text{nm}$, (Yan et al., 2000) was present in all samples.

3.2 Selection of tracers

The generated contour profiles of the test leachates were used to create a generic leachate 'footprint' on which the peak coordinates (Em/Ex) of 30 fluorescent dyes were plotted (six examples are shown on Figure 1b). Dyes which did not encroach or overlap with the leachate footprint were short-listed and further assessed for ease of preparation and costs. Fluorescein, Eosin-Y and Rhodamine WT were the three finally selected as they are readily available, easy to prepare and have all been used widely as tracers in ground and surface waters. Other fluorescent dyes that have similar spectral characteristics (e.g. Pyranine, Lissamine Yellow, sulforhodamines) were not investigated beyond this stage because their spectra overlap with one or more of these three.

3.3 Dye Degradation

Measurements of dye fluorescence intensity in the biodegradation culture vessels were normalised with respect to the measured Raman peak (Figure 2). All dyes showed a progressive decrease, with the greatest reductions being observed within the first 7 days. This initial loss of intensity also occurred in the control vessel and was attributed to sorption onto the microbial matter present. Subsequently the measured dye intensities for Rhodamine WT and Fluorescein reached a state in which levels fluctuated around a constant value, without any further downwards trend. This suggests that degradation did not affect these two dyes. Eosin-Y showed the greatest overall reduction, a 60% decrease over the experimental period. Unlike the other dyes Eosin showed a continuing downward trend in the post-sorption period, which we attribute to degradation.

It was also observed that throughout the experimental duration the control vessels, in particular the autoclaved control, showed similar or greater losses than the active culture vessels, suggesting that the observed losses were not solely a result of biodegradation but due to other factors including adsorption to the surfaces of the lysed bacterial matter produced as a result of autoclaving. This may partly explain the variability in measured intensity as dye losses were not permanent but fluctuated as they were bound to and released from the interacting surfaces produced by live and dead bacteria.

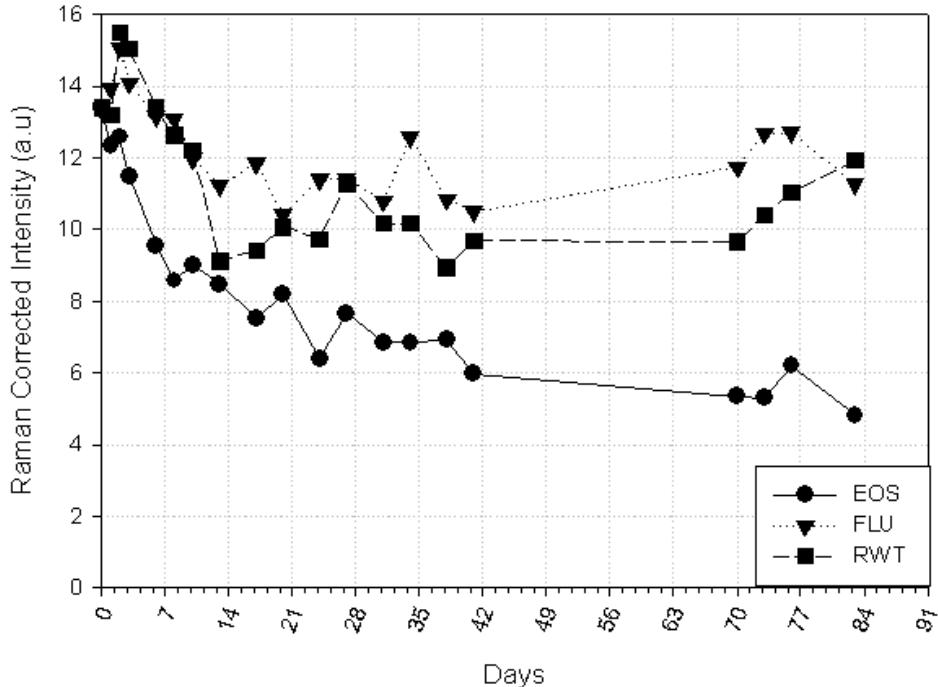


Figure 2: Anaerobic biodegradation results for selected dyes.

3.4 Dye sorption

Batch sorption experiments were conducted on the three dyes to determine the potential losses which could arise as a result of interaction with landfill waste. The concentration of sorbed dye was determined using the mass balance of the initial dye concentration in solution relative to that remaining at the end of sorption.

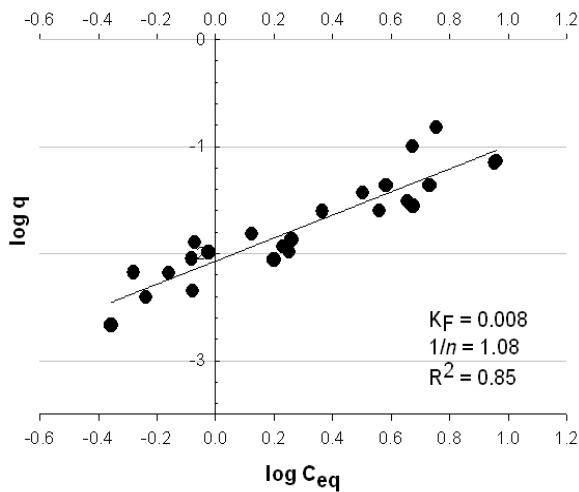
A preliminary experiment showed that apparent sorption equilibrium was attained by all three dyes in less than 7 days. Given that this period was much shorter than the duration of the degradation experiments, it was assumed that all losses in the sorption batches were directly attributable to sorption onto the waste. The results were fitted by linearised Freundlich and Langmuir isotherm equations using least-squares regression. On the basis of calculated correlation coefficients, the Freundlich isotherm provided the best fit.

The Freundlich isotherm equation is based on a conceptual model in which uptake capacity of the sorbate is infinite and the sorbent surface is heterogeneous.

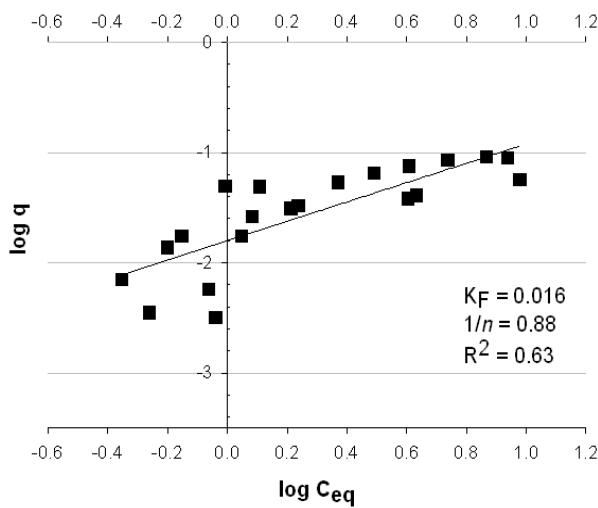
$$q = K_F * C_{eq}^{1/n} \quad \text{or} \quad \log q = \log K_F + \frac{1}{n} \log C_{eq}$$

q is the sorbate uptake of the dye (mg/g), C_{eq} is the final equilibrium concentration of dye in solution (mg/L), K_F is the Freundlich sorption constant and n is a constant that expresses the degree of curvature in the isotherm graph when plotted arithmetically. By contrast, the Langmuir isotherm is based on a surface containing a finite density of homogeneous sites. The better fit of the Freundlich model confirms that binding of dyes occurs onto more than one type of site, which may be due to the heterogeneity of the waste surfaces present. Scatter in the data precludes more complex models from consideration.

(a) Eosin



(b) RWT



(c) Fluorescein

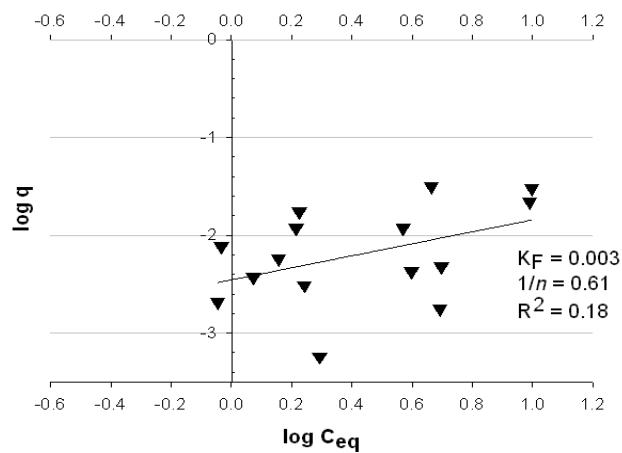


Figure 3: Freundlich isotherms for (a) Eosin, (b) RWT and (c) Fluorescein.

A comparison of the fitted isotherms reveals differences in sorption behaviour between the three dyes. The coefficient K_F represents the amount of dye sorbed when the solution is of unit concentration, and is thus a measure of relative susceptibility of each dye to sorption on the

surfaces of the waste used in the experiment. Despite the large scatter in the data for Fluorescein (c)

(c) Fluorescein

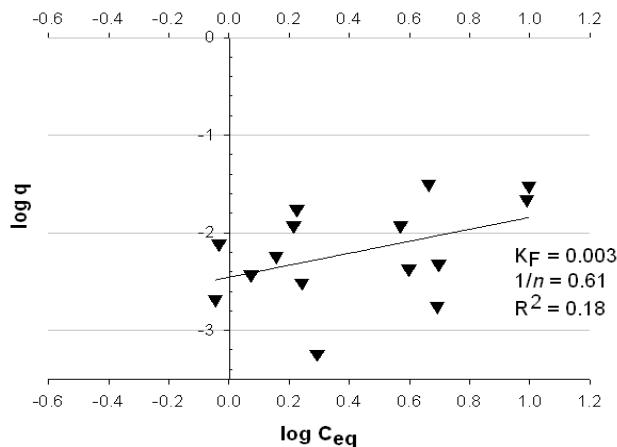


Figure 3c) it is clearly the least sorbed of the three tracers on the substrates provided by the waste sample. Rhodamine WT and Eosin show roughly similar sorption once scatter is taken into account, although there is a two-fold difference in fitted values of K_F . The coefficient $1/n$ (sometimes called the linearity constant) indicates how the partitioning relationship between the bound and free dye changes as the concentration in the solution is altered. A value of $1/n$ close to unity indicates that the isotherm is linear and suggests that sorption sites on the solid phases always present a large excess over the dye molecules available to fill them. Eosin has a fitted value of $1/n = 1.08$, indicating that the proportion of dye in bound form increases slightly as overall dye concentration in the system rises. This may be due to competition between different types of site, with some types only becoming occupied when dye is present at high concentration. Rhodamine WT, with $1/n = 0.88$ also shows slight non-linearity, but with the bound form becoming relatively less important at high concentration, perhaps because some or all types of site are becoming filled to a significant extent at high dye concentrations. However this could also depend on the relative proportion of isomer species present, as previous work by Vasudevan et al (2001) showed that the para-isomer of Rhodamine WT sorbed more than the meta-isomer.

Fluorescein has a strongly non-linear value of $1/n \approx 0.6$, although the scatter in the data for this dye is large compared with any trend. One possible cause of this scatter is that *enhanced* intensity values were sometimes measured during the sorption tests. The exact source of the additional fluorescence was not determined, but following a series of additional tests (to be reported elsewhere) it is believed it may derive from compounds present in the waste.

4. CONCLUSION

An ideal tracer would be simple to assay in a leachate matrix, show negligible bio-degradation under landfill conditions, and be non-sorbing (or at least show simple, predictable sorption behaviour). All three dyes fulfil the first of these criteria to the extent that they are all easily *detectable* against the background fluorescence of leachate. Fluorescein shows little biodegradation and the least sorption, making it potentially the best tracer of the three for landfill work. However the problems of quantitative measurement and scattered data that occurred in the

present study may also occur in the field. We conclude that while fluorescein may have value as a field tracer it should be used with caution. Its non-linear sorption isotherm would require fitting two parameters, K_F and n , to account for sorption in any field situation, while the scatter of data in the present study precludes precise constraints on possible values for such parameters. Fluorescein could certainly be used as a tracer of flow paths, however, and as a guide to breakthrough times even if intrinsic uncertainties affecting measurement were to preclude its use as a fully quantitative tracer.

Eosin and Rhodamine WT can both be measured quantitatively in a leachate matrix, without the interferences that affect Fluorescein. Both are sorbing tracers that have almost linear sorption isotherms, suggesting that $1.1 \geq 1/n \geq 0.9$ or $1/n = 1$ might be adopted as constraints on best-fit values for this parameter when fitting solute transport equations to breakthrough curves from field tests. Eosin exhibits mild biodegradation under landfill conditions, which implies that at least one extra parameter would have to be incorporated into modelling of field results. Though the half-life of Eosin in the present tests could in principle be estimated, we have refrained from this because of the difficulty of separating degradation from other effects that influenced both the experimental batches and the controls. For Rhodamine WT however, biodegradation appears to be small and within the scatter of the experimental data.

We conclude that Rhodamine WT is the most suitable among the three dyes tested for use as a quantitative tracer in landfill. Solute transport models fitted to breakthrough curves should include a term for linear sorption, but could probably neglect non-linear sorption and degradation. As Eosin is degradable, models used to fit breakthrough curves would have to incorporate a first-order decay term as well as a linear sorption term. Fluorescein should only be used as a quantitative tracer with circumspection. However, if there is good reason to believe that measurement problems can be avoided or overcome in any given field situation, it is potentially the nearest of the three to an ideal tracer as it shows little tendency to bio-degradation and the least sorption. Nevertheless, modelling the effects of sorption would require two parameters to account for its non-linear isotherm.

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