

WATER TRACING IN TROPICAL REGIONS, THE USE OF FLUOROMETRIC TECHNIQUES IN JAMAICA

P.L. SMART and D.I. SMITH

Department of Geography, University of Bristol, Bristol (Great Britain)

Centre of Resource and Environmental Studies, Australian National University, Canberra, A.C.T. (Australia)

(Received September 4, 1975; accepted for publication October 11, 1975)

ABSTRACT

Smart, P.L. and Smith, D.I., 1976. Water tracing in tropical regions, the use of fluorometric techniques in Jamaica. *J. Hydrol.*, 30: 179–195.

Fluorescent dyes have been widely used in temperate latitudes for the tracing of karst groundwater. However, a review of the literature indicates that these tracers have been much less satisfactory in tropical karst areas, and are far less successful than *Lycopodium* spore tracing techniques.

Quantitative tests were carried out on six fluorescent tracers in a surface stream in central Jamaica. Tracer concentrations, measured using a Turner III filter fluorometer, were used in conjunction with discharge measurements to determine tracer losses under field conditions. Rhodamine WT and Lissamine FF proved to be the most successful dyes but Fluorescein also proved satisfactory under conditions with little direct sunlight. The optical brighteners Photine CU and Photine CSP showed large losses in the study reach. An underground test along a previously proven connection supported the findings of the surface tests. Two successful groundwater traces were completed in the North St. Catherine Basin, the first 30 km long using Rhodamine WT and the second over 14 km using Photine CU. The latter indicated that Photine CU was useful for the establishment of flow paths despite its relatively poor persistence.

The conclusions from these studies are that selected fluorescent dyes are suitable for water tracing in tropical limestone regions provided that a sensitive fluorometer is used for the analysis. The use of activated charcoal detectors is not recommended but the effects of suspended sediment and bacteria in the stream water are not thought to be limiting factors. A detailed comparison, including costings, of dye tracing and spore methods is also given.

INTRODUCTION

Fluorescent dyes have been extensively employed for the tracing of subterranean water in karst areas for over a hundred years. The majority of these studies were concerned with the establishment of connections between stream sinks and springs. Such tests relied upon a sufficiently high concentration of dye at the springs to allow visual detection. Some early attempts were made

to determine concentrations by colourimetric methods (Dole, 1906). Later work by Drew (1968a) used ultraviolet irradiation to improve the minimum detectability, but quantitative determinations of concentration were only possible after the application of spectrophotometric techniques (White, 1967). The recent development of sensitive filter fluorometers, suitable for field use, has allowed rapid quantitative analysis of dye concentrations as low as $0.01 \mu\text{g l}^{-1}$ for Rhodamine B (Feuerstein and Selleck, 1963; Wilson, 1968). The availability of such fluorometers has permitted the application of dye budgeting techniques to tracer tests (Brown et al., 1969; Atkinson et al., 1973). Other fluorescent dyes have also been introduced for water tracing in karst areas and include Rhodamine B, Rhodamine WT and Pyranine.

A REVIEW OF EARLIER TRACING WORK IN TROPICAL WATERS

All the methods outlined above have met with success in temperate karst areas. However, in tropical regions the relatively small number of tests using fluorescent dyes have not produced satisfactory results. There are two possible explanations, either the detection methods used to date have not been sufficiently sensitive or the dyes have a relatively poor survival rate in tropical waters.

Large quantities of Fluorescein have been used to establish connections visually in the Star Mountains of New Guinea by Verstappen (reported by Brongersma, 1963) and by Fincham and Ashton (1967) in similar studies in Jamaica. In the first case Fluorescein dye gave a positive result after 4 h for a trace of 16 km, while in the latter 19 kg of the same dye failed to establish a connection to possible resurgences from 2 to 35 km from the sink. The latter result confirmed earlier unpublished work by the Geological Survey of Jamaica in which comparable quantities of the dye failed to establish any underground connection. Fincham and Ashton (1967) also used activated charcoal detectors without success. Such detectors allow fluorescent dye to be adsorbed and eluted for subsequent analysis by laboratory methods (Dunn, 1957). This technique may allow the cumulative adsorption of low dye concentrations and thus enhance sensitivity beyond that obtained by the analysis of individual water samples (Zotter, 1963). In 1965 Fluorescein was also used in Jamaica by Brown (Brown and Ford, 1973), who reported one positive trace but had a similar lack of success using charcoal detectors. Subsequent detailed work on such detectors has demonstrated that they have poor success in natural waters because of competition from dissolved organic matter (Smart and Brown, 1975).

The apparent lack of success with Fluorescein as a tracer in Jamaica resulted in a search for alternative dyes. Fincham and Ashton (1967) experimented with the use of Rhodamine B and chemically-treated cotton hank detectors (Drew and Smith, 1969) but found that the colour change was obscured by a permanent brown pigmentation. Brown and Ford (1973) also used Rhodamine B in Jamaica but in conjunction with charcoal detectors. The analysis methods

were improved and included the determination of dye concentrations in the elutant by fluorometer. Unfortunately, the results again proved to be negative. They later successfully repeated the test using *Lycopodium* spores over a distance of some 12 km. More recently Day (1976) has used Rhodamine B and the chemical detection method for several positive traces over short distances, but no problems occurred with background contamination of the detectors.

After the findings of Fincham and Ashton (1967) and Brown et al. (1969), Drew (1969) experimented with a new fluorescent tracer, Pyranine (a green dye), which proved successful in three separate traces in Jamaica over distances of up to 3 km. One trace, employing 1 kg of dye, gave a markedly visible result after some 2 km of underground travel. The dye also appeared to be suitable for tracing in environments in which the content of the suspended sediment and organic matter were thought to be high (Drew, 1969). This verified the field properties of the dye outlined earlier by Reynolds (1966). Drew (1968b) noted that the elutriation technique is enhanced if a source of ultraviolet light, or better, a spectrophotometer is used for the laboratory analysis. In 1969 T.C. Atkinson, D.P. Drew and D.I. Smith (unpublished report to the Geological Survey of Jamaica, 1969) undertook further groundwater tracing in conjunction with the Geological Survey of Jamaica. This work was also based on the use of Pyranine with charcoal detectors and laboratory analysis using a scanning spectrophotometer. A number of tests were undertaken at various locations but with very limited success. Indeed, the only definite positive result was over a distance of less than 2 km using 9 kg of Pyranine. Attempts to use Rhodamine WT in conjunction with charcoal detectors and analysis by spectrophotometer also failed.

A study by Jordan (1970) describes the use of Rhodamine WT for subsurface water tracing in the karst of the Tertiary Lares Limestone in west central Puerto Rico. The work was undertaken to define groundwater flow directions at the sites of tailing disposal ponds for a projected copper mine. He conducted three successful traces, the longest of which was approximately 4 km with a travel time of some 4 days. A fluorometer was used for the detection of the dye but no details are given of the quantity of dye employed or the amounts recovered.

More recently blue fluorescent dyes, collectively known as "optical brighteners", have been used successfully in temperate latitudes for water tracing in karst areas (Glover, 1972). The dye is detected at the springs by means of cotton-wool detectors which, when positive, exhibit blue fluorescence under ultraviolet light. Gascoyne (1974) achieved some success with this technique in northern Venezuela. He reported a trace of 4 km in less than 14 days using 2 kg of Leucophor BS. Another optical brightener, Leucophor C, also proved successful in one short trace.

It is clear from the review given above that fluorescent dye tracers have met with limited success in tropical karst areas. Brown and Ford (1973, p. 632) state that "...conventional tracer dyes may not be appropriate for hydrologic

work in tropical areas” and T.C. Atkinson, D.P. Drew and D.I. Smith (unpublished report to the Geological Survey of Jamaica, 1969) comment that “...until the agents responsible for the failure of dyes as tracers in Jamaica have been discovered any further tracing should use a more reliable method”.

Lycopodium spore techniques, in contrast to the studies using fluorescent dyes, have been markedly successful in Jamaica. Brown and Ford (1973) report three positive traces over distances of 15–20 km using 14–35 kg of coloured spores. Drew (1969) describes a large number of traces, only one of which was unsuccessful, for distances of up to 6 km using quantities of spores varying between 1.0 and 20 kg. The work successfully defined the regional pattern of underground connections in the Maroon Town area and the Nassau Mountains. Day (1976) has used the technique to define spring catchments in the Brown’s Town area using small quantities of spores. The Joint Ground-water Project of the United Nations FAO—Jamaica Geological Survey has also established several sink to rising connections using this technique.

The purpose of the work described in this paper can be divided into three parts.

- (1) To evaluate fluorometric dye-tracing techniques in tropical waters.
- (2) To compare various fluorescent dyes for use in both quantitative and qualitative tracing.
- (3) To assess the relative merits of other successful tracing methods for application in water-resource studies in tropical karst areas.

TRACER TESTS AND RESULTS

A total of six fluorescent dyes were compared during this study which was undertaken in Jamaica during June 1975. These were the “orange” dye Rhodamine WT, the “green” dyes Pyranine, Fluorescein and Lissamine Yellow FF (hereafter Lissamine FF) and the optical brighteners Photine CSP and Photine CU. Lissamine FF and the Photine dyes have not previously been used for water tracing. Their properties are described in detail by Smart and Laidlaw (1976). References to the use of Rhodamine WT, Fluorescein and Pyranine are given in the first section of this paper and details of the suppliers and approximate costs of the dyes in Table I.

Dye analysis was undertaken using a Turner III filter Fluorometer fitted with a high sensitivity door and a far ultraviolet lamp. The fluorometer was calibrated for each dye using the filters listed in Table II with distilled water as the dilutant. Because of the strong dependence of Pyranine fluorescence on pH over the likely field range, this dye was calibrated using river water from the site of the investigation. The calibration was undertaken with the instrument at its normal operating temperature and individual samples were corrected for the variation of fluorescence with temperature using the method outlined by Feuerstein and Selleck (1963). The appropriate exponents are given in Table II. A detailed account of fluorometric analysis techniques is given by Wilson (1968).

TABLE I

Tracer availability and costs

Tracer	Price (£/kg)	Supplier in the U.K.
Photine CSP	2.50	Hickson and Welch Ltd., Castleford, Yorkshire
Photine CU	1.00 ^a	Hickson and Welch Ltd., Castleford, Yorkshire
Fluorescein LT	3.30	Brico Commercial Chemical Co., Ltd., 55-57, Glengall Road, London SE15
Lissamine Yellow FF	14.00	Brico Commercial Chemical Co., Ltd., 55-57, Glengall Road, London SE15
Pyranine	12.00	Bayer UK Ltd., Dyestuffs Division, Lester House, 1/13, Market Road, Richmond, Surrey
Rhodamine WT	6.90 ^a	DuPont (UK) Ltd., Dyestuffs Division, Church St., Altringham, Cheshire
<i>Lycopodium</i> spores	7.00 ^b	Brome and Schimmer Ltd., 7, Leather Market, London SE1

^a Of 20% solution.^b Subject to fluctuation.

TABLE II

Filter combinations and temperature correction exponents for the fluorescent dyes used

Dye	Primary filter ¹	Secondary filter ¹	Temperature exponent ² , n (°C ⁻¹)
Rhodamine WT	2 of 1-60 and 61	4-97 and 3-66	0.027
Fluorescein	36 and 1-56	55	0.0036
Lissamine FF	36 and 1-56	55	0.0020
Pyranine	36 and 1-56	55	0.0019
Photine CSP	7-37	98	0.020
Photine CU	7-37	98	0.012

¹ Numbers are those in the Kodak Wratten Filter Catalogue and Corning Colour Filter Glasses Catalogue.² For an equation of the form $F_s = F e^{-n(t_s-t)}$ where F_s is the fluorescence at standard temperature t_s , F is fluorescence at the sample temperature t , and n is a constant for the specific dye.

Surface recovery studies

In order to assess the extent of the loss of the various dyes under tropical conditions initial experiments were conducted in the One Eye River near Balaclava. This is totally fed by karst resurgences and can be considered comparable to underground conditions except that additional losses due to photodecomposition may occur in surface streams. The dyes were injected immediately downstream of the One Eye gauging station and sampled at Bridge 1, 1.25 km downstream, and at Bridge 2, 6.0 km from the injection point. Discharge was measured at both sampling sites using an Ott current meter.

Four separate tests were conducted, the first two (on June 4) with suspended sediment concentrations of less than 2 mg l^{-1} and the two remaining tests (on June 20) with values in the range $23\text{--}32 \text{ mg l}^{-1}$. The suspended sediment was measured using filtration through $0.45\text{-}\mu\text{m}$ membrane filters. At the higher concentrations the river was of a turbid, coffee colour and while no size analysis was undertaken it is thought that the proportion of the suspended sediment in the clay range was high.

The difference in river discharge between the two dates was small; on June 4 at Bridge 1 the discharge was 1.162 and at Bridge 2 $1.177 \text{ m}^3 \text{ sec}^{-1}$. On June 20th the discharges were 1.218 and $1.245 \text{ m}^3 \text{ sec}^{-1}$, respectively.

Table III presents the details of the four tests, including the calculated dye recoveries. This term is used for the mass of dye passing a sampling site and is calculated from the equation:

$$m = \int_0^{\infty} c Q dt$$

where: m is the mass of dye passing the sampling site; c is the concentration of the dye at time t ; and Q is the discharge at time t .

Fig. 1 illustrates the time—concentration curves for test 1 at Bridges 1 and 2 and is typical of the pattern exhibited in the other tests. It is apparent from Fig. 1 that there is an appreciable background fluorescence at both the Lissamine FF and Photine CU wavelengths. This is due to the difference in fluorescence between the distilled water used for calibration and the natural river water. The background figures for Rhodamine WT are very small in comparison to the other dyes used. The values of the background fluorescence in this and the other tests (see Table IV) exhibit the same ranges as are found for natural waters at temperate latitudes. Thus, if fluorometric techniques are employed, background fluorescence in tropical waters does not present any additional problems to those experienced in temperate latitudes.

The recovery values in Table III give an indication of the relative persistence of the dyes used. It is clear that there is little difference in recoveries between tests with high and low suspended-sediment concentrations. The maximum suspended-sediment concentration values encountered in these tests are

TABLE III

Dye recovery for surface tests

	Dye injected (g)	Recovery at Bridge 1 (as % of input)	Recovery at Bridge 2 (as % of input)
Test 1	100 Rhodamine WT	115.7	96.9
	562 Lissamine FF	101.9	106.0
	510 Photine CU	47.2	43.5
Test 2	813 Photine CSP	38.7	—
Test 3	80 Rhodamine WT	106.6	96.5
	580 Lissamine FF	102.4	102.0
	486 Photine CU	43.0*	62.0*
Test 4	8.0 Rhodamine WT	91.6	—
	320 Fluorescein	99.5	—
	918 Photine CSP	32.0*	—

Tests 1 and 2 less than 2 mg l^{-1} suspended sediment; tests 3 and 4 $23\text{--}32 \text{ mg l}^{-1}$ suspended sediment.

* Estimated values due to high and variable background fluorescence.

relatively low. However, Scott et al. (1969) have shown that there is little significant adsorption of Rhodamine WT until the suspended-sediment concentrations are well in excess of $1,000 \text{ mg l}^{-1}$. Concentrations of this magnitude have a low frequency in surface rivers and are unusual for karst resurgences. Petri and Craven (1971) report the successful completion of a surface trace with Rhodamine WT in the Big Blue River, Nebraska, in conditions with fine-grained suspended sediment concentrations of several thousand mg l^{-1} . Thus, from the evidence available it would appear that the loss of dye onto suspended sediment is a minor factor in considering the previous failures of dye tracers in tropical waters.

From Table III it can be seen that the optical brighteners exhibit high losses under the test conditions although Photine CU has consistently higher recoveries than Photine CSP. The losses may be due both to the adsorption onto naturally occurring organic substances and to the high photochemical decay rate of these compounds in dilute solutions (Smart and Laidlaw, 1976). The usefulness of these dyes for quantitative studies where a conservative tracer is required is therefore limited. However, they have some value for the establishment of point-to-point connections and travel-time studies.

The recoveries of Rhodamine WT, Lissamine FF and Fluorescein are well within the experimental error of the methods used. The errors are estimated as $\pm 5\%$ for dye volumes and weights, $\pm 5\%$ for discharge measurement and a $\pm 1\%$ instrumental error for dye concentrations. In addition, there may be appreciable variation in background fluorescence during the passage of the dye pulse which will affect the blue and green fluorescent dyes more than the orange. It would appear that Lissamine FF exhibits similar or slightly better persistence than the established tracer dye Rhodamine WT. The performance of Fluorescein

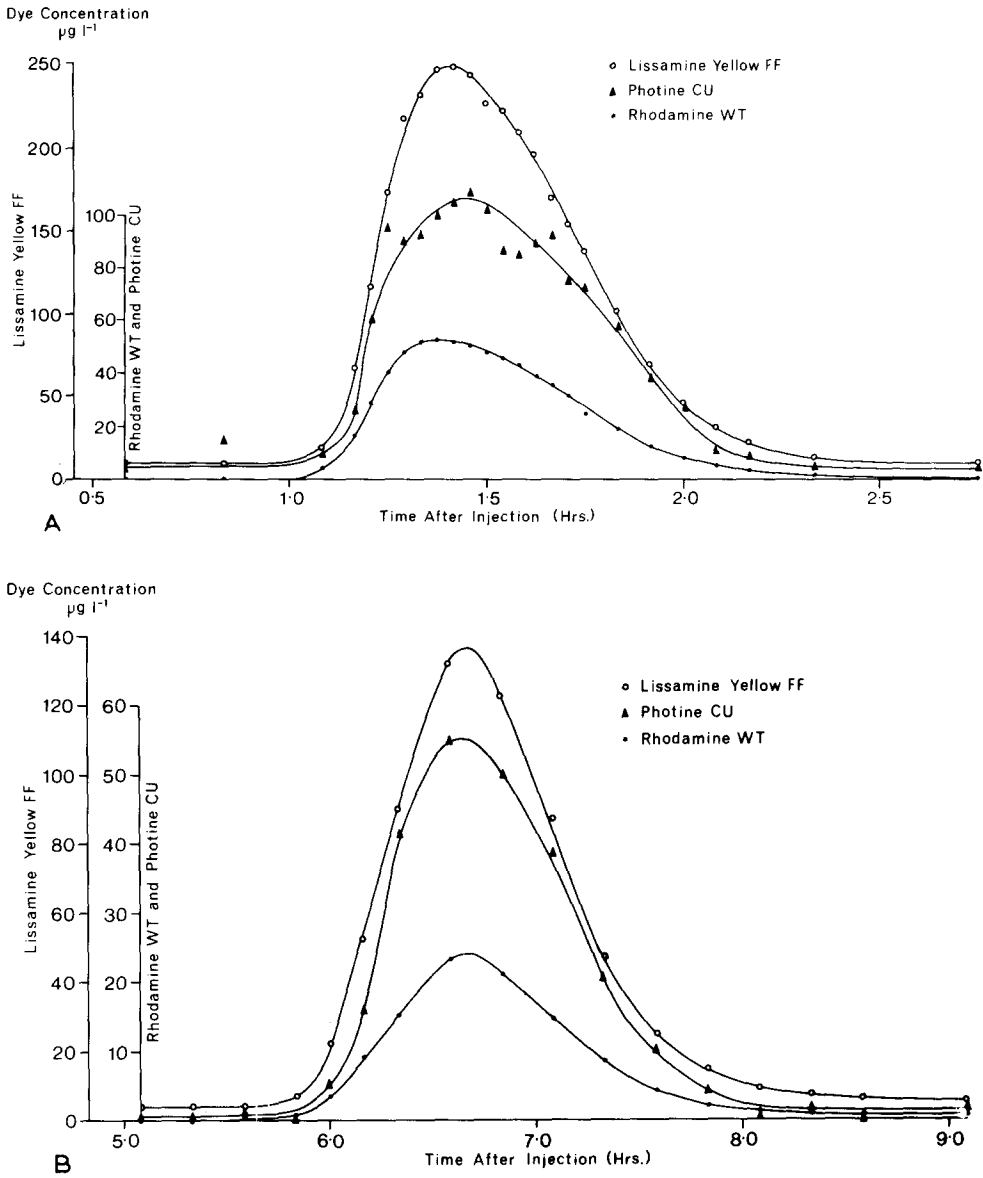


Fig. 1. Time—concentration curves.
A. For test 1 at Bridge 1.
B. For test 1 at Bridge 2.

TABLE IV

Background fluorescence and concentration (all values in $\mu\text{g l}^{-1}$) of positive samples for the North St. Catherine's Basin sampling sites

Site	N	Photine CU		Fluorescein		Rhodamine WT		Positive samples
		mean	S.D.	mean	S.D.	mean	S.D.	
Moona Spring	11	6.5	11.3	2.3	1.6	0.005	0.007	—
Tulloch Spring	12	21.6	14.7	2.6	2.3	0.012	0.024	—
Pear Tree Bottom	8	12.0	6.5	4.6	3.0	0.010	0.014	Rh. WT 0.55, 1.38
Laughlands Gt. River	6	21.7	15.4	5.7	3.8	0.010	0.017	Rh. WT 1.52, 0.02
Roaring River	7	15.8	18.9	3.5	4.0	0.012	0.025	Rh. WT 0.04, 0.18
Cave River	4	23.1	28.5	5.2	6.7	0.029	0.042	—
Ocho Rios	3	4.5	5.3	1.4	1.9	0.016	0.030	—
Dunn's River	4	4.9	3.6	1.7	0.4	0.008	0.020	—
Jericho Well	16	1.2	11.6	1.5	1.9	-0.010*	0.008	—
Worthy Park Sink	8	20.5	4.9	6.6	1.6	0.020	0.010	—
Pedro River	7	23.4	15.8	7.5	2.4	0.030	0.010	—
Crofts River	7	24.9	9.6	6.2	1.2	0.014	0.010	—
Black River	14	23.7	9.8	7.4	3.7	0.040	0.120	Ph. CU 91.0
Riverhead Moneague	7	85.4	14.9	21.0	3.3	0.100	0.014	—

N = Number of samples; Rh. WT = Rhodamine WT; Ph. CU = Photine CU; S.D. = standard deviation.

* Indicates a fluorescence less than that of the distilled water used for calibration.

is good though the test was conducted under cloudy daylight conditions in order to reduce photodecomposition which is much more rapid under direct sunlight (Feuerstein and Selleck, 1963). There was a significant difference between the high and low concentration runs for Rhodamine WT (tests 3 and 4 at Bridge 1, Table III). This was not explained by variations in background or instrumental effects and may indicate that dye losses are relatively more important for low dye concentrations, i.e. dye loss does not occur on a simple percentage basis.

Underground recovery studies

The successful surface tests were followed by an experiment to confirm the persistence of three of the dyes for an underground trace. The 5 km long connection, previously established by Brown and Ford (1973), between Hectors River Sink and the One Eye River (also known as Coffee River) was used for this test. Brown and Ford used 14 kg of Fluorescein to establish this connection and the dye appeared at the resurgence after 42–48 h, and visible colour persisted for 10 days. The trace was repeated using 0.40 kg Rhodamine WT, 2.03 kg Pyranine and 2.92 kg of Photine CSP. The discharge at Hectors River Sink was $0.257 \text{ m}^3 \text{ sec}^{-1}$ and that at the resurgence fell gradually during the test from 0.792 to $0.651 \text{ m}^3 \text{ sec}^{-1}$.

The curves of concentration against time for the three dyes at the One Eye River sampling site are illustrated in Fig. 2. The time of arrival of the peak concentration was 31 h after input and was identical for all three dyes. The recoveries were calculated to be 108.5% for Rhodamine WT, 63.0% for Pyranine and approximately 14.0% for Photine CSP. As in the surface tests Rhodamine WT proved to be very satisfactory. Pyranine showed considerable losses, which may be partially due to a difference in the pH of the river during the test and that used for the dye calibration. This pH dependence provides a severe limitation to the use of Pyranine for quantitative studies in both temperate and tropical waters.

There are problems with the interpretation of the time—concentration curve for Photine CSP. Although the background concentrations varied in an irregular fashion, between 50 and $12 \mu\text{g l}^{-1}$, over the four days of the test, a peak in concentration is discernable. The same problem was experienced to a lesser extent in the surface tests (see Fig. 1) and applies to both the optical brighteners used. A factor that may be responsible for some of the variation in the background fluorescence for these dyes is the use in the area of cold-water detergents which contain a considerable quantity of optical brightener. For “Cold Power”, a liquid detergent commonly used for the washing of clothes, the concentration of optical brightener is approximately equivalent to a 4% solution of Photine CSP or 2% solution of Photine CU. However, a more significant factor was thought to be an increase in the blue fluorescence which occurred over a period of several days when samples were left standing prior to analysis. This did not significantly affect the orange wavelength. The samples were normally analysed

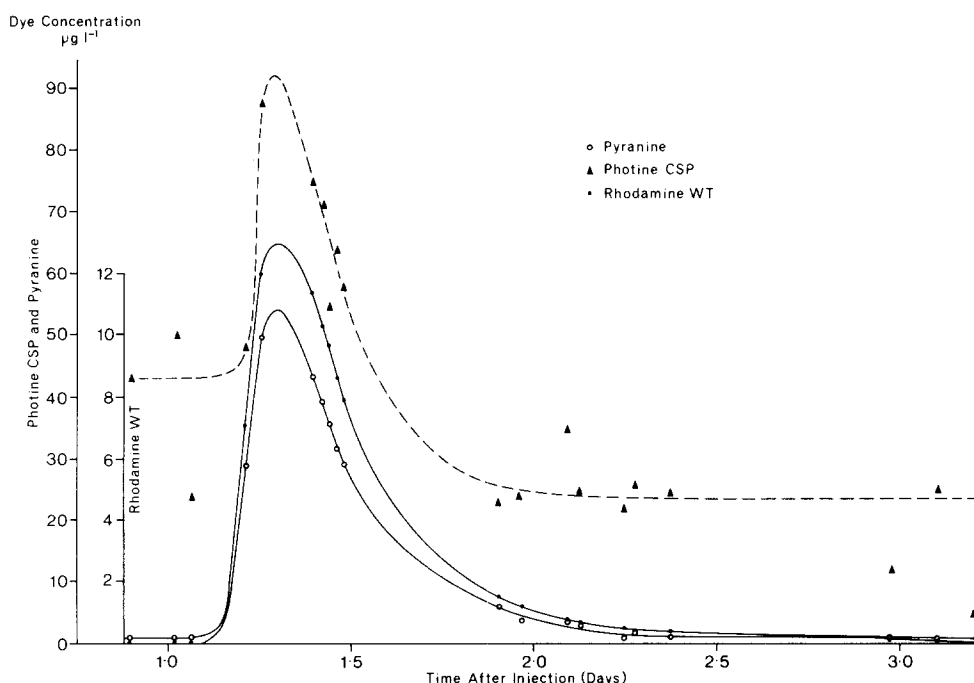


Fig. 2. Time—concentration curves for the Hectors River test at the One Eye River sampling site.

within one or two days of collection. Analysis of a limited number of samples stored for some weeks gave extremely high blue-fluorescence values and the samples smelt of hydrogen sulphide. This may indicate a chemical or, more likely, microbiological modification, the details of which are unknown. It is not established if this effect is limited to tropical waters. Thus it is necessary to analyse samples containing optical brighteners as soon as possible after collection.

The underground dye recovery test supports the results obtained in the surface tests and indicates that fluorometric dye-tracing techniques are viable in tropical waters.

Catchment delimitation in the North St. Catherine Basin, Jamaica

The northern boundary of the North St. Catherine Basin is located in an area of karst topography developed on the massive facies of the White Limestone. Rivers flow from the impermeable strata of the Central Inlier sink at the margin of the White Limestone; three such rivers are the Pedro River, the Crofts River and the Savanna River (see Fig. 3). Several smaller streams drain Lluidas Vale, which is a totally enclosed depression with an area of some 30 km² floored, in part, by impermeable alluvial deposits. The only active sink at the time of

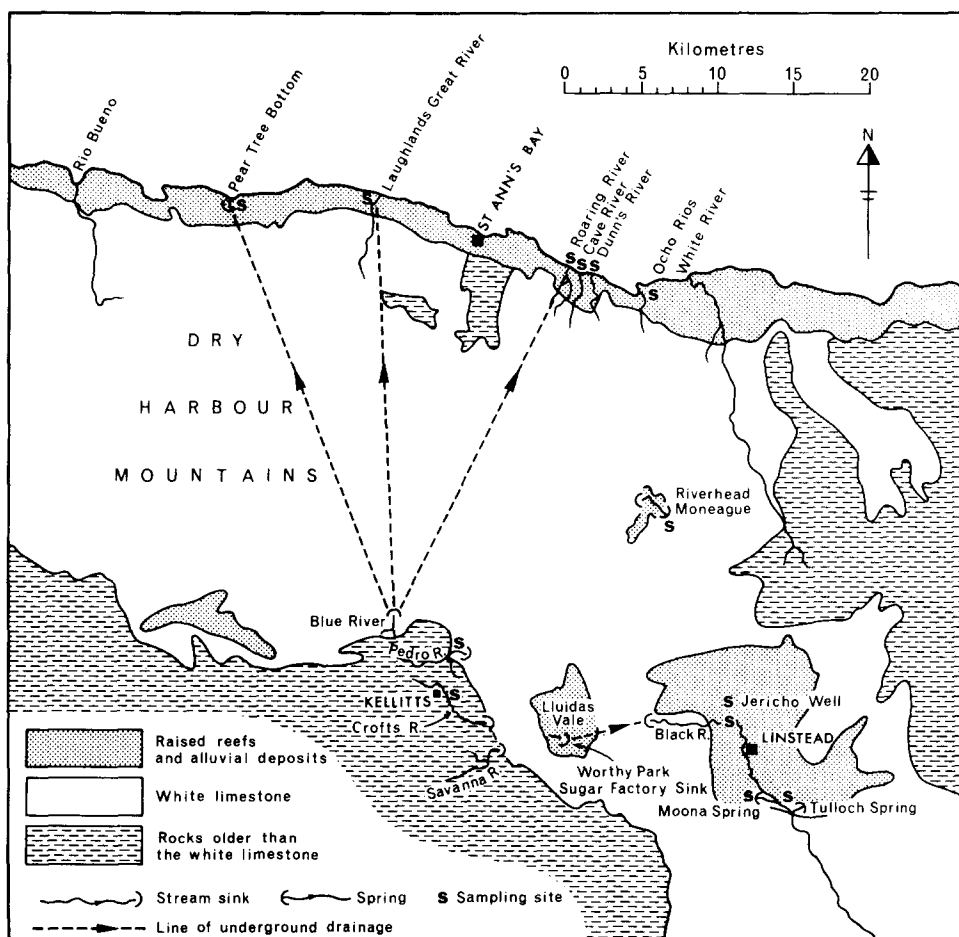


Fig. 3. Map of the geology, sampling sites and underground connections in the North St. Catherine Basin.

the test was at the Worthy Park Sugar Factory with a discharge of some 10 l sec^{-1} . No surface streams are found on the White Limestone of the Dry Harbour Mountains, but in localities where the underlying Yellow Limestone outcrops small streams may develop. The Blue River, 4.5 km to the northwest of Kellitts, is an example of this type with a discharge at the time of the test of less than 5 l sec^{-1} .

It is a necessary part of water-resource evaluation to delimit catchment boundaries. In karst areas this is difficult as groundwater and topographic divides often do not coincide. Indeed, the northern divide of the North St. Catherine Basin cannot be defined on topographic evidence as it is situated in an extensive area of closed karst depressions of the cockpit type. The Blue River is therefore of particular interest as it is one of the few streams in the Dry Harbour Mountains.

Tracers were injected at the Pedro River Sink, the Worthy Park Sugar Factory Sink and the Blue River Sink using 9.0 kg of Fluorescein, 2.2 kg of Photine CU and 3.2 kg of Rhodamine WT, respectively. All possible resurgences, both to the north and south of the Dry Harbour Mountains, were sampled. The sites are shown on Fig. 3. For convenience the sites on the north coast were sampled where the discharge from the springs crossed the main road; similarly the Black River was sampled some 8 km downstream of the actual rising. Samples were collected from fourteen resurgence sites and from a pumping well in the White Limestone at Jericho which had an abstraction rate of 50 l sec^{-1} . Cotton-wool detectors were also used at the majority of the sampling sites following the procedure outlined by Glover (1972) for the detection of optical brighteners. Water samples of 15 ml volume were collected daily from the southern sites for the first week of the test and at three-day intervals for those on the north coast. Subsequent sampling for all the sites was at approximately three-day intervals; sampling ceased after four weeks. The cotton-wool detectors were changed in conjunction with the collection of the water samples.

No positive results were obtained for the Fluorescein injected at the Pedro River Sink. If the dye had reappeared at the Black River sampling site, thought to be the most probable, photodecomposition over the 8 km of surface river flow was likely to have severely reduced the dye concentration. An earlier trace from this site described by Fincham and Ashton (1967) using 19 kg of Fluorescein also failed to establish any connection, though the work was undertaken before the development of fluorometric techniques.

A positive trace was obtained for the Photine CU from the Worthy Park Sugar Factory Sink to the Black River sampling site near Linstead, a total distance of 14 km. The dye first arrived at the sampling site 8 days after injection and was just detectable in the next sample collected three days later. This result was confirmed by a positive detector recovered 8 days after injection, other detectors were negative.

The Rhodamine WT dye from the Blue River Sink reappeared at three sites on the north coast, namely Pear Tree Bottom, Laughlands Great River and Roaring River. The maximum concentrations at these sites were 1.38, 1.52 and $0.18 \mu\text{g l}^{-1}$, respectively, compared to the mean background values of 0.01, 0.01 and $0.012 \mu\text{g l}^{-1}$ shown in Table IV. The first positive samples at all three sites were recovered 16 days after dye injection; they were still positive two days later but had returned to the background values after a further three days. The distances travelled by the dye which reappeared at the positive sites were from 26 to 30 km, measured as straight-line distances; the larger part of the route was underground. Because of the sampling interval employed it is not possible to calculate exact dye recoveries.

DYE TRACING IN THE TROPICS

The work reviewed and reported suggests that the following conclusions can be drawn.

(1) Water tracing using fluorescent dyes in the tropics is extremely unreliable without the use of a suitable fluorometer. In particular the activated charcoal detector method suffers from severe limitations.

(2) Variations in background fluorescence present no greater problem in tropical waters than those in temperate latitudes.

(3) Adsorption onto suspended sediment appears to be of little significance except, perhaps, under conditions of very high sediment concentration.

(4) The high recovery values obtained in the experiments indicate that for the most suitable dyes adsorption and biodegradation are not significant. Optical brighteners are, however, susceptible to adsorption onto naturally occurring organic matter.

(5) For quantitative work Rhodamine WT and Lissamine FF are the most reliable, but in general orange dyes are preferable to green or blue dyes because of the low background fluorescence.

(6) For qualitative work, e.g. the establishment of point-to-point connections, optical brighteners provide an acceptable third dye for simultaneous tracing.

A comparison of methods for karst water tracing in the tropics

There are four groups of commonly used water-tracing techniques, namely those employing radioactive, bacteriological, particulate or chemical tracers. To our knowledge, the first two have not been used in tropical karst areas. Both require a high degree of technical competence and may present problems in obtaining official permission for their use. The only viable particulate tracer utilises coloured *Lycopodium* spores, and has been widely and successfully used in the tropics as described in the earlier section of this paper. Of the chemical techniques fluorescent dyes are the only tracers suitable for widespread application because of their very high detectability per unit weight. The relative merits of *Lycopodium* and dye-tracing methods are summarised in Table V.

The largest single cost in tracing work is that of the time and transport involved in the collection of samples. Thus, it is advantageous if several input sites are traced simultaneously. By using coloured *Lycopodium* spores up to six individual input sites may be traced in one experiment, whereas it is only possible to use three fluorescent dyes simultaneously due to the filter overlap in distinguishing between orange, green and blue emission. Furthermore, the cumulative nature of spore collection by means of plankton nets allows a larger sampling interval, and hence less-frequent visits, than the collection of water samples used in dye methods. However the difference in the method of collection precludes any satisfactory quantitative analysis of *Lycopodium* recovery which would be necessary to fully analyse the network characteristics of the system. Automatic water samplers can be used for dye tracers and have the advantage of obtaining a large number of samples without the necessity for frequent visits.

The laboratory determination of the tracers after collection is also a major

TABLE V

Comparison of *Lycopodium* and fluorescent-dye tracer techniques

<i>Lycopodium</i> spores	Fluorescent dyes
(1) limited to a maximum of six simultaneous inputs	(1) limited to three simultaneous inputs
(2) requires only periodic sampling	(2) requires frequent sampling
(3) sampling requires the use of special plankton nets	(3) sampling requires no special equipment and is possible using an automatic water sampler
(4) qualitative	(4) quantitative
(5) cost of capital equipment (microscope, centrifuge) moderate	(5) cost of capital equipment (fluorometer) high
(6) cost of non-capital equipment (nets, glassware, etc.) high	(6) cost of non-capital equipment (glassware) low
(7) pre-treatment to colour spores time consuming and moderately expensive	(7) no pre-treatment required
(8) post-collection treatment, time consuming	(8) no post-collection treatment
(9) analysis time consuming and requires skilled personnel	(9) analysis straightforward and fast, requires no skilled personnel
(10) immediate field analysis not possible	(10) immediate field analysis possible
(11) cost of tracers moderate	(11) cost of tracers moderate
(12) unaffected by water chemistry and pollutants	(12) perhaps detrimentally affected by water chemistry and pollutants
(13) affected by high sediment concentrations	(13) affected only at extremely high sediment concentrations

consideration. In the case of dyes a large capital outlay is required to purchase a fluorometer (approximately £ 1,500, all prices based on 1975 U.K. figures), but the actual analysis is straightforward and rapid. The time for an individual determination is less than one minute and therefore large numbers of samples may be analysed. Furthermore, the fluorometer may be used in the field allowing instantaneous determination of samples which permits continual re-assessment of the sampling programme. This is not possible for the *Lycopodium* spore technique. For spores the laboratory equipment needed consists of a good quality microscope and centrifuge facilities. The analysis itself is extremely time consuming and requires a skilled technician. In addition lengthy pretreatment is necessary to dye the spores. For detailed accounts of the *Lycopodium* methods see Maurin and Zötl (1959) and Drew and Smith (1969).

The costs of the tracers are broadly comparable for longer underground tests, though for smaller tests dyes have the advantage. For the Blue River Sink trace, described above, the cost of the Rhodamine WT was some £ 120 and that estimated for *Lycopodium* spores would have been £ 140. However, the dyes suitable for qualitative work, i.e. Fluorescein and the optical brighteners are considerably cheaper. The availability and costs of dyes are given in Table I. In some situations where heavily polluted waters are to be traced the survival of coloured *Lycopodium* spores may exceed that of fluorescent dyes; conversely

where very slow or diffuse flow occurs the reverse may be true. A further limitation on the use of the *Lycopodium* technique occurs when very high sediment concentrations are encountered, which can either overload the collection nets or cause problems in separating the spores from the large amounts of sediment trapped in the nets. However, for straightforward sink to rising connections in karst areas there is little to choose between the persistence of the two tracers.

It can be concluded that for broad water-resource reconnaissance studies in karst areas *Lycopodium* methods should be used. This assumes that suitably skilled personnel are available to undertake the laboratory analysis and that the number of sampling sites is limited. In the case of the North St. Catherine Basin study with fifteen sampling sites sampled for four weeks the analysis would have been excessive. Where quantitative information is required fluorometric dye techniques are essential.

ACKNOWLEDGEMENTS

Financial assistance towards the cost of the travel and equipment was provided by a research grant from the Natural Environment Research Council. Assistance in Jamaica was provided by the Director and Staff of the Water Resources Division of the Ministry of Mining and Natural Resources, particularly by Michael White who was directly concerned with the field programme. Hickson & Welch Ltd. of Castleford, advised on the selection of optical brighteners and donated those used in the study.

At the time the work was undertaken both authors were on the Staff of the Department of Geography at the University of Bristol, and the Department afforded much assistance in a variety of ways. Dr. S.T. Trudgill of the University of Sheffield, gave much valuable assistance in the field.

We would like to express our sincere thanks to all these institutions and individuals without whose help the work would not have been possible.

REFERENCES

- Atkinson, T.C., Smith, D.I., Lavis, J.J. and Whitaker, R.J., 1973. Experiments in tracing underground waters in limestones. *J. Hydrol.*, 19: 323–349.
- Brongersma, L.D., 1963. *To the Mountains of the Star*. Doubleday, New York, N.Y., 318 pp.
- Brown, M.C. and Ford, D.C., 1971. Quantitative tracer methods for investigation of karst hydrological systems. *Trans. Cave Res. Group G.B.*, 13(1): 37–51.
- Brown, M.C. and Ford, D.C., 1973. Caves and groundwater patterns in a tropical karst environment: Jamaica, West Indies. *Am. J. Sci.*, 273: 622–633.
- Brown, M.C., Wigley, T.L. and Ford, D.C., 1969. Water budget studies in karst aquifers. *J. Hydrol.*, 9(1): 113–116.
- Day, M., 1976. The morphometry and hydrology of some Jamaican karst depressions. *Earth Surface Processes* (in press).
- Dole, R.B., 1906. Use of fluorescein in the study of natural waters. *U.S. Geol. Surv., Prof. Pap.*, 160: 73–85.

- Drew, D.P., 1968a. A review of the available methods for tracing underground waters. *Proc. Br. Speleol. Assoc.*, 6: 1–20.
- Drew, D.P., 1968b. Tracing percolation water in karst areas. *Trans. Cave Res. Group G.B.*, 10(2): 107–114.
- Drew, D.P., 1969. Water tracing. In: D.I. Smith (Editor), *Limestone Geomorphology; a study from Jamaica*. *J. Br. Speleol. Assoc.*, 6(43/44): 96–110.
- Drew, D.P. and Smith, D.I., 1969. Techniques for the tracing of subterranean drainage. *Br. Geomorphol. Res. Group, Tech. Bull.*, 2, 36 pp.
- Dunn, J.R., 1957. Stream tracing. *Mid-Appalachian Region Natl. Speleol. Soc. Bull.*, 2: 7.
- Feuerstein, D.L. and Selleck, R.E., 1963. Fluorescent tracers for dispersion measurements. *Proc. Am. Soc. Civ. Eng., Pap.*, 89(SA 4): 1–21.
- Fincham, A. and Ashton, K., 1967. The University of Leeds hydrological expedition to Jamaica, 1963. *Trans. Cave Res. Group G.B.*, 9(1): 1–60.
- Gascoyne, M., 1974. Hydrological investigations in northern Venezuela. *Trans. Br. Cave Res. Assoc.*, 1(3): 169–179.
- Glover, R.R., 1972. Optical brighteners — a new water tracing reagent. *Trans. Cave Res. Group G.B.*, 14(2): 84–88.
- Jordan, D.G., 1970. Water and copper-mine tailings in karst terrain of Rio Tanama Basin, Puerto Rico. *U.S. Geol. Surv. (Caribbean District), Open File Rep.*, 18 pp.
- Maurin, V. and Zötl, J., 1959. Die Untersuchung der Zusammenhänge unterirdischer Wasser mit besonderer Berücksichtigung der Karstverhältnisse. *Steirische Beitr. Hydrogeol.*, N.F., 1/2, 184 pp.
- Petri, L.R. and Craven, J.L., 1971. Dilution helpful in measuring fluorescence of samples containing much sediment. *U.S. Geol. Surv., Water Res. Div. Bull.*, Aug–Sept., 1971: 24–25.
- Reynolds, E.R.C., 1966. The percolation of rainwater through soil demonstrated by fluorescent dyes. *J. Soil Sci.*, 17(1): 127–132.
- Scott, C.H., Norman, V.W. and Fields, F.K., 1969. Reduction of fluorescence of two tracer dyes by contact with fine sediment. *U.S. Geol. Surv., Prof. Pap.*, 650-B: 164–168.
- Smart, P.L. and Brown, M.C., 1975. The use of activated carbon for the detection of the tracer dye Rhodamine WT. *Proc. 6th Int. Congr. Speleology, Olomouc, Czechoslovakia* (in press).
- Smart, P.L. and Laidlaw, I., 1976. A comparison of fluorescent dyes for water tracing. (In press.)
- White, W.B., 1967. Modifications of fluorescein dye groundwater tracing techniques. *Steirische Beitr. Hydrogeol.*, N.F., 18/19, pp. 151–158.
- Wilson, Jr., J.F., 1968. Fluorometric procedures for dye tracing. In: *Techniques of Water Resources Investigations of the U.S. Geological Survey, Book 3, Applications of Hydraulics*, Ch. A12, pp. 1–31.
- Zotter, H., 1963. Stream tracing techniques and results: Pocahontas and Greenbrier Counties. *Bull. Natl. Speleol. Soc.*, 21(10): 136–142.