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Research Report No. 140

STUDIES IN DYE-TRACING TECHNIQUES AND KARST HYDROGEOLOGY

By

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Water Resources Research Institute
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ABSTRACT

Information on fluorescent dyes used for water tracing and the results of six studies are reported. Optical brightener, direct yellow, fluorescein, rhodamine (WT), and other dyes are described and the procedures employed in their use in the field and in equilibration experiments are discussed. Three of the six studies consisted of investigations of the equilibration with passive detectors of three of the dyes. The absorption of optical brightener on fabric detectors was apparently linear with concentration and with immersion time, while detectors became rapidly saturated with direct yellow. Equilibrium of fluorescein on charcoal detectors with an elutriating solution was not achieved.

Several data processing tasks were performed, including the creation of a computer file for field data and the writing of programs to sort the field data and generate plotted maps, and to display the total fluorescence of samples. A fifth study was based on a series of dye traces into Royal Spring and Russell Cave Spring in the Inner Bluegrass Karst Region. Samples were collected with an automatic water sampler and the resulting flow velocity determinations combined with discharge data provided values at a number of aquifer parameters. The most interesting result was the very small value for depth of flow. A final study was of fracture traces identified on topographic maps and aerial photographs in the Inner Bluegrass Karst Region. It was found that while more such features were visible on the photographs, some were only apparent on maps.

Descriptors: Dyes*, Karst Hydrogeology*, Groundwater Basins, Dye Releases, Groundwater Movement, Groundwater Pollution, Aquifers, Karst, Limestone, Springs.

Identifiers: Inner Bluegrass Karst Region, Kentucky.

ACKNOWLEDGEMENTS

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DISCLAIMER

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A. INTRODUCTION

This is the second of two Completion Reports for Project B-064-KY, Hydrogeology of the Inner Bluegrass Karst Region, Kentucky: Water Tracing Studies, which was funded by the Office of Water Research and Technology, U.S. Dept. of the Interior. It includes the results of studies other than the water tracing and related investigations which were discussed in the first completion Report.

Because of the variety of topics discussed in this report, each has been written as a separate section with its own list of references, to allow individual distribution.

A1. Project Objectives

The objectives of the project were:

(a) To delineate, by qualitative and semi-quantitative dye-tracing techniques, major underground flow connections and groundwater divides in specific areas within the Inner Bluegrass Karst Region ("Area Studies").

The first Completion Report describes the results of work done to support this objective.

(b) To undertake quantitative dye studies of selected paths to determine hydrologic parameters ("Quantitative Traces").

The results of work done to support this objective is described in Section G of this Completion Report.

(c) To perform laboratory and field investigations to discover the most suitable dyes and dye-detector combinations ("Dye Investigations").

The results of work done to support this objective is described in Sections B,C,D, and E of this Completion Report.

(d) In support of these objectives, certain other tasks may be performed ("Other Work").

The results of work done to support this objective is described in Section F and H of this Completion Report.

B. WATER TRACING MATERIALS AND METHODS

J. Thrailkill

B1. Introduction

The dyes, equipment, and techniques used in the studies reported in later sections of this report are often similar, and they are largely discussed in this section to avoid later repetition, with the major exception being techniques employed in performing quantitative dye traces (Section G), which are discussed in that section. Some additional information on procedures utilized in the dye equilibration studies will be found in Byrd (1981) and Spangler (1982).

B2. Fluorescent Dyes

Table B1 lists pertinent data for the various dyes, and other information is discussed (by dye "type") in the sections that follow.

Batch	Type (1)	Dye (2)	Man. (3)	Sup. (4)	Form (5)	Purch Date	Quantity	Cost (6)
1	OB	CWS	AC	ACOT	L	6-76	128l(7)(300lb)	$1,78/l
2	DY	MBF	CG	MC	P	5-76	11.3kg (25lb)	12.79/kg
3	DY	MBF	CG	MC	P	6-77	22.7kg (50lb)	15.10/kg
4	AR	PAP	(8)	PP	P	(9)	(9)	(9)
5	DY	DBF	CG	CGDC	P	6-78	8.2kg (18lb)	(8)
6	DR	(8)	(8)	(8)	P	(10)	(10)	(10)
7	DY	MBF	CG	MC	P	1-79	22.7kg (50lb)	18.37/kg
8	DY	DBF	CG	KAC	P	1-79	11.3kg (25lb)	(8)
9	OB	CWS	AC	ACOC	L	1-79	128l(7)(300lb)	2.11/l
10	RH	RWT	DP	DPCD	L	1-79	9.86l(11)(25lb)	12.93/l
11	FL	FYD	(8)	PP	P	1-79	11.3kg (25lb)	13.27/kg
12	OB	PBS	(8)	MCC	L	4-80	97.8l(12)(250lb)	2.10/l
13	DY	MBF	CG	MC	P	5-80	34kg (75lb)	(8)

14	B2	TLW	(8)	CSC	P	8-81	22.7kg (50lb)	8.15/kg
15	DY	MBF	CG	MC	P	8-81	11.3kg (25lb)	27.00/kg

Notes:

(1) Project name and Society of Dyers and Colourists (1971) Generic Name ("GN") and Constitution Number ("CN"):

AR: Acid Red, GN Acid Red 52, CN 45100.
B2: Optical Brightener, GN Flourescent Brigntener 351, CN none.
DR: Disperse Red, GN Disperse Red 9, CN 60505.
DY: Direct Yellow, GN Direct Yellow 96, CN none.
FL: Fluorescein, GN Acid Yellow 73, CN 45350.
OB: Optical Brightener, GN Fluorescent Brigntener 28, CN 40622.
RH: Rhodamine, GN none, CN none.

(2) CWS: Calcoflour White ST Solution.
DBF: Diphenyl Brilliant Flavine 7GFF.
FYD: Pyla-Tel Fluorescent Yellow Dye.
MBF: Melodye Brilliant Flavine 7GFF.
PAP: Pyla-Tel Acid Pink Dye.
PBS: Phorwite BA solution.
RWT: Rhodamine WT.
TLW: Tinopal LPW.

(3) AC: American Cyanamid Co.
CG: CIBA-Geigy Corp.
DP: E.I. duPont de Nemours & Co.

(4) ACDT: Amer. Cyanamid Co., Dyes and Textiles Dept., Bound Brook, NJ 08805
ACOC: Amer. Cyanamid Co., Organic Chemicals Div.; Color, Textile, and Intermed. Chem. Dept.; PO Box 41316, Cincinnati,OH 45241
CGDC: Ciba-Geigy Dyestuffs and Chemicals Div., PO Box 11422, Greensboro, NC 27404

CSC: Chemical Solutions Corp., PO Box 35421, Houston, TX 77035
DPCD: E.I. DuPont, CD & P Dept., PO Box 360708M, Pittsburgh,PA 15250
KAC: Keystone (Standard Colors) Aniline and Chemical Co., 321 N. Loomis, Chicago, IL 60607.
MC: Melody Chemicals, Inc., PO Box 5424, Charlotte, NC 28205
MCC: Mobay Chemical Corp., Dyestuff Div., PO Box 385, Union, NJ 07083
PP: Pylam Products Co., Inc., 95-10 218th St., Queens Village, NY 11429

(5) L: Liquid
P: Powder

(6) Shipping not included.

(7) Density 1.06 gm/ml

(8) No record or unknown.

(9) Approximately 1 kg obtained from J.F. Quinlan in April, 1977.

(10) Approx. 50 kg obtained by J.W. Troester from unknown source in June 1978.

(11) Density 1.15 gm/ml

(12) Density 1.16 gm/ml

Table B1. Dye Data

B2a. Optical Brightener

This optical brightener (GN Fluorescent Brightener 28) was used by J.F. Quinlan in the Mammoth Cave area (Quinlan and Rowe, 1977) and was selected as a tracing agent in the Inner Bluegrass Karst Region on his recommendation. Although various batches were obtained from different suppliers, all were believed to have been produced by American Cyanamid Co., who has discontinued its manufacture. Batches 1 and 9 consist of 13.5%. brightener in a water solution (written communication from American Cyanamid Co.); the concentration of batch 12, although reportedly the same, is unknown. Batch 12 was also more difficult to dilute to low concentrations than batches 1 and 9. It is absorbed on cotton.

Chemical and other information on OB may be found in Society of Dyers and Colourists (1971). Reports on its lack of toxicity include no effect on rats following ingestion at up to 4 gm/kg of body weight (Amer. Cyanamid, 1960), 96-hour LC_{50} greater than 180 mg/l in fish (Amer. Dye Manuf. Inst., 1973), and no mutagenicity in mice (Lorlke and Machemer, 1975).

B2b. Direct Yellow

This yellow fabric dye (GN Direct Yellow 96) was first used by J.F. Quinlan (Quinlan, 1977). It is absorbed on cotton, and can be used in areas where the concentration of optical brightener in waters is too high for OB to be sued. It is manufactured by CIBA-GEIGY, and various lots were obtained from different suppliers. In powdered form, the concentration of dye is 20% (the remainder is probably NaCl). Prior to introduction, 1 kg was mixed with 10 liters of water and intermittently agitated for one or two days. This produced a suspension of the powder in the water which could be poured from the container. The solubility of the dye in cold water is low, and all of the dye was dissolved only after dilution with the water being traced. Insufficient agitation caused the powder to cake in the container.

Data furnished by CIBA-GEIGY Corp. indicates an acute oral LD_{50} of 23.1 glkg of body weight for rats and a 96-hour LC_{50} greater than

1000 mg/l for fish. The principal disadvantage of this dye is its cost, which, during the period from 1976 to 1981, more than doubled in price to $27/kg (Table B1). The longest trace (D48, 15 km) in the Inner Bluegrass Karst Region was conducted with 6kg of this dye (Thrailkill, et. al., 1982).

B2c. Fluorescein

Fluorescein is probably the fluorescent dye most widely used for water tracing. Supplied in powder form, it was usually dissolved in water prior to introduction. It is generally considered to have low toxicity; Smart and Laidlaw (1977) cite a 96-hour LC_{50} for rainbow trout of 1372 mg/l and state that it has been approved by the U.S. Food and Drug Administration for externally applied drugs and cosmetics.

B2d. Rhodamine

Rhodamine WT was approved for tracing into drinking water supplies by the Environmental Protection Agency in 1980 (P.J. Traina, written communication, 1980) and was so employed during the project.

B2e. Other Dyes

Acid Red was used for one trace. This dye (also termed Sulforhodamine B and Pontacyl Brilliant Pink B) has been employed as a water tracing agent and its use is discussed by Wilson (1968) and Smart and Laidlaw (1977). Although its toxicity is low it may be somewhat greater than the other dyes used in the study. Disperse Red was not used, and the second optical brightener (B2) was obtained for field use but has not yet been employed.

B3. Passive Detectors

Two types of cotton detectors were used to recover optical brightener and direct yellow, and charcoal detectors were used for fluorescein and the one acid red trace.

B3a. Surgical Cotton Detectors

Initially, detectors which had been utilized by J.F. Quinlan (1977) were used. These consist of a fist-sized wad of surgical cotton (Johnson and Johnson) suspended in the stream (usually the outflow of a spring). After removal, the cotton was vigorously rinsed under a jet of water in the lab, flattened into a pad, allowed to air-dry, and examined under a hand-held ultraviolet lamp at both 254 and 366 nm. The presence and degree of fluorescence was evaluated as strong (C), moderate (B), weak (A), or absent. Optical brightener imparts a blue-white, direct yellow a bright yellow, and direct yellow combined with an optical brightener background a chalky-white fluorescence.

Although surgical cotton detectors were used in a number of successful optical brightener and direct yellow traces in the project, and have been used by other workers (Smart, 1976; Quinlan and Rowe, 1977), they have a number of disadvantages. In rapidly flowing water, individual strands of cotton are washed away, with the result that after ten days or so in such an environment, only a small ball of cotton less than an inch in diameter remains. In turbid water, a great deal of mud will adhere to the cotton despite its being supported off of the bottom by a gumdrop (see Section B4 below), and in some springs the cotton decomposes rapidly, presumably due to algal growth.

Because very little water flows through the detector, only the outer part of the detector is dyed. During the rinsing and shaping process after removal, the outer portion is mixed with cotton from the interior, with the result that even a strong positive detector may show patches and streaks of fluorescence in non-fluorescing cotton, and a small amount of dye transferred to the detector during handling may easily produce a false positive. It was therefore necessary to take extensive precautions to avoid contamination.

Finally, although Smart (1976) had reported some limited success in quantitative evaluation of surgical cotton detectors using a filter fluorometer, there seemed to be no way of quantitatively evaluating the degree of fluorescence in the smaller sample compartment of a spectrofluorometer in view of the above factors, and a fabric detector was designed and utilized for all project traces performed after January

1, 1978.

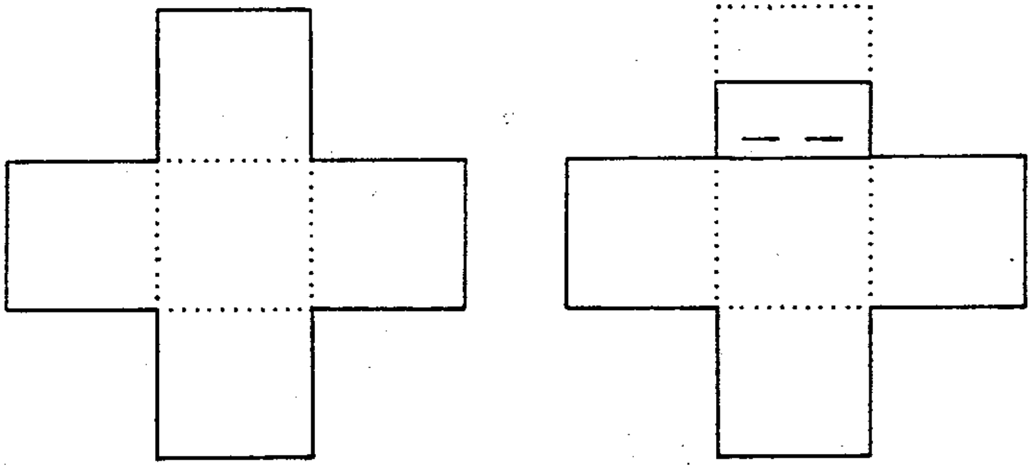
B3b. Fabric Detectors

The cotton fabric detectors are constructed from bleached mercerized combed 3.11 cotton broadcloth (Testfabrics, Inc., 419-A) which has not been treated with optical brighteners. The fabric is cut into cross-shaped pieces consisting of a 5 x 5 cm square with four arms of the same size attached. The side squares are folded toward the center and fastened with brass staples to form sleeves. Two squared C-shaped frame halves constructed of No.9 aluminum wire are inserted into the sleeves and the resulting detector and frame assembly is supported in the water by overlapping loops at the end of each frame half. Stages in the construction are shown in Figure B1.

The fabric detector is as subject to algal attack as the surgical cotton, and shows substantial decomposition after one week in some springs. In every other respect, however, the fabric detector is judged superior to the surgical cotton detector. Mud adheres to it less, it is more easily rinsed, and, if properly constructed, it shows little deterioration (except for algal attack) with time. Positive detectors exhibit a more even fluorescence and contamination from handling is more easily evaluated. Instrumental evaluation (see B5 below) is relatively simple.

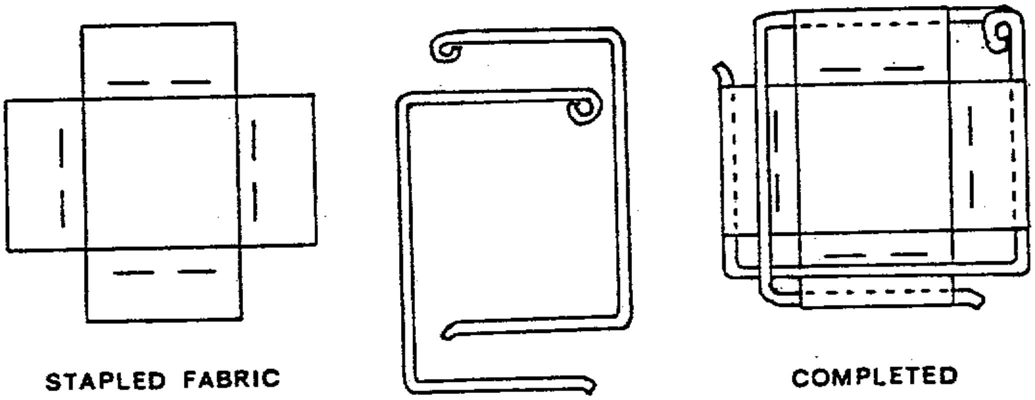
B3c. Charcoal Detectors

Charcoal detectors were used for the fluorescein traces and the one acid red Trace. The design and construction details varied somewhat from trace to trace, but the following is representative of the detectors used in the later traces. A 5 X 10 cm rectangle of plastic (nylon) screen (1.4 mm mesh) is rolled on a pencil to form a cylinder 10 cm long and 7mm in diameter with two layers of screen. One end is folded and fastened with a brass staple, 2 gm of fresh activated cocoanut charcoal, 6 to 14 mesh, is introduced, and the open end folded and stapled. It is supported in the water by a wire passed through one of the folded ends.



CROSS-SHAPED FABRIC

ARMS FOLDED IN HALF TOWARDS CENTER AND STAPLED



STAPLED FABRIC READY FOR FRAME

FRAME HALVES

COMPLETED DETECTOR

Figure B1. Stages in the construction of a fabric detector.

B4. Field Equipment and Techniques

Prior to introducing dye, detectors were placed in all springs, judged to be likely destinations of the dye. The number of such monitored springs was as high as 13 during initial investigation of an area, but averaged only 3 or 4 during later phases after some information had been gained on flow patterns. Before using optical brightener, the degree of background brightener in springs was also evaluated. Detectors were normally changed weekly.

Detectors (surgical cotton, fabric, and charcoal) are usually supported in the water using a "gumdrop" (Quinlan, 1977; Quinlan and Ewers, 1981), consisting of a wire arm embedded in a concrete base (approximately 1 kg). Quinlan's design was slightly modified by embedding two or more wires (No.9 galvanized steel) to provide both added strength and additional arms to support multiple detectors. Where there is insufficient depth (less than about 20 cm) to submerge a detector on a gumdrop, the detector is supported on a "hairpin" , a doubled length of No.9 galvanized wire whose free ends are thrust into the stream bottom sediment. Detectors are attached to a loop in the top of the hairpin and fabric detectors are supported vertically by passing the hairpin between the frame and the fabric. Both gumdrops and hairpins are attached to a point on the stream bank using light braided nylon cord.

B5. Laboratory Equipment and Techniques

B5a. Fabric Detectors

Fabric detectors mounted on the frame are returned from the field in individual plastic bags. While still on the frame, they are rinsed vigorously under a jet of tap water and allowed to air dry in a dark cabinet. They are removed from the frame, and, for visual determination of intensity, examined with a hand-held ultraviolet lamp at both 254 and 366 mm, and the intensity of dye fluorescence recorded as none, weak (A), moderate (B), or strong (C).

For instrumental evaluation, the four sleeves are trimmed from the central 5 x 5 cm square of the detector, which is then folded over a 2.5 x 3.5 cm piece of cardboard and fastened with a staple. The mounted detector is then inserted in a solid sample holder which fits diagonally into the 2.5 x 2.5 sample compartment of the spectrofluorometer. The sample holder consists of an aluminum plate 3.5 cm wide with a window 1 cm high by 2 cm wide cut in a position which is at 45° to both the excitation and emission beams of the spectrofluorometer. The mounted detector is held against the rear of the plate, and four positions can be examined by reversing and inverting the folded detector.

B5b. Charcoal Detectors

Experimental techniques were under development throughout the project, and no standard method was established. The following procedure was used for several detectors, however, and appeared to yield satisfactory results. The charcoal detector is rinsed in distilled water and placed in a 60 ml polyethylene bottle and 25 ml of elutriant added. The elutriant is one developed by P.L. Smart (J.F. Quinlan, oral communication) and consists of 32.5% ammonium hydroxide, 43.0% I-propanol, 24.5% distilled water (by volume). The bottle is agitated on a test-tube shaker for several hours and the elutriant evaluated for the presence of flourescein either visually, using the same scale as used for fabric detectors (see B4a above) or spectrofluorometrically.

B5c. Equilibration Systems

Two equilibration systems were constructed for use in studies of the equilibration of detectors to dye solutions (Sections C,D, and E). Because of the low concentration of dye in the solutions investigated (on the order of a few parts per billion) and the efficiency of the cotton fabric and charcoal detectors in removing dye from solution, a large volume is required to prevent the concentration from falling significantly during an experiment.

The larger equilibration system contained a measured volume of 231 liters in two large tanks containing approximately 100 liters each, and a smaller tank containing about 30 liters. The three tanks were interconnected with 11 mm (I.D.) hose, and water was circulated through the tanks with a variable-speed pump at a rate (monitored with a flow meter) of .25 l/min, yielding a turnover time of 15.4 hours.

Water temperature was monitored in the smaller tank by a thermistor and strip chart recorder. Two water driven magnetic stirrers were used to agitate the water in the smaller tank, which served as the reaction chamber and in which the detectors were suspended. Figure B2 shows the larger equilibration system.

A smaller equilibration system was used for most of the fluorescein experiments. It consisted of a single 30 l tank agitated by a water driven magnetic stirrer. It was located adjacent to the larger system, and was assumed to be at the same temperature.

B5d. Spectrofluorometric Examination

An Aminco SPF-125 S scanning spectrofluorometer (xenon lamp) connected to a 10-inch strip-chart recorder was used for the instrumental determination of fluorescence. Liquid samples were examined in standard 12.5 by 12.5 mm (O.D.) cuvettes which permit at least 80% transmission between 200 and 2600 nm. Standard procedure was to rinse the cuvette with a sample prior to filling, and to rinse with distilled water and immerse in 1:1 HNO_3 after use. A solid sample holder (described in B4a above) was designed for examination of fabric detectors.

All intensity readings were referenced to the fluorescence of uranium -doped glass block (Aminco J4-8916) to correct for variations in instrument response. Block fluorescence was measured at the excitation wavelength between 442 and 446 nm and the emission wavelength between 510 and 516 nm which gave the highest intensity at slits of 2mm excitation and 1mm emission.

Intensity readings (R) on both the reference block and a sample was determined by subtracting the meter or chart reading with the photomultiplier shutter closed from the reading when it was open. Usually two readings were taken for the block, three for each liquid sample,

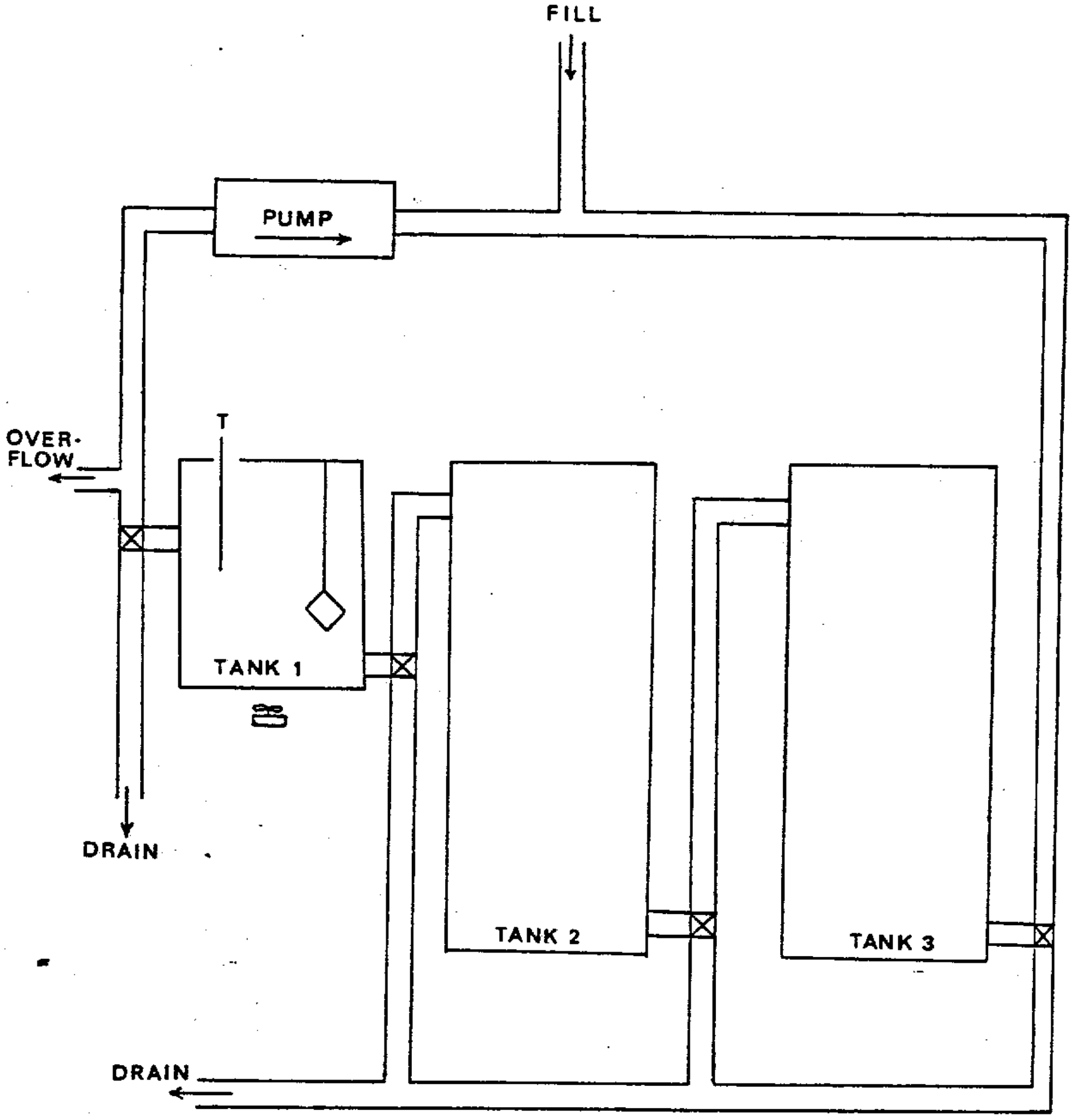


Figure B2. Schematic diagram of the larger equilibrium system.

and one for each solid sample. The mean of the block readings was divided by 100 to yield a correction factor (K) and the intensity (I) of a sample was determined by dividing the mean of the sample readings by K.

To allow comparison with the results of other laboratories, intensity determinations were made of quinine sulfate using ANSI/ASTM Standard Method E 578-76 (Table B2)

Concentration	Intensity
0	0.014
5	0.0674
10	0.112
20	0.204
50	0.577
75	0.725
100	0.898

Table B2. Concentration - intensity relationships for quinine sulfate. Excitation 350 nm, 2mm slit; emission 450, 1 mm slit, concentration units ppb .

B6. Dye Quantity, Discharge, and Distance Relationships

Relationships among visual detector intensity, dye quantity, discharge at the detection point, and distance (length of the trace) are shown in Fig. B3, B4, and B5 for optical brightener, direct yellow, and fluorescein, respectively. The data consist of all traces conducted with these three dyes, as listed in Thrailkill, et. al. (1982, Appendix 1). Note that the dye quantities are of dye as received.

In each diagram, the upper three histograms show the relationship between detector intensity and the ratio of dye quantity used and discharge at the detection point on a logarithmic scale. Because of the dilutive effect of large discharge, it would be expected that the most strongly dyed detectors (C) would be associated with large values of the ratio, the weakest detectors (A) from lower values of the ratio, and detectors evaluated as moderate (B) would result from intermediate values. Although distributions for optical brightener do suggest this (Fig. B3), those for direct yellow and fluorescein (Figs. B4 and B5) do not. The medians (M) of all three distributions show no systematic relationship.

The lower three histograms in each diagram show variations in detector intensity with the ratio of dye quantity and length of the trace. Here again there may be a weak relationship for optical brightener (Fig. B3) but little or none for direct yellow or fluorescein (Figures B4 and B5).

The reasons for the lack of correlation of detector intensity either with discharge or distance are not obvious. There are other factors which would be expected to influence detector response, including immersion time, temperature, water chemistry, and adsorption and dispersion of dye during the trace. Most of these, however, tend to be relatively constant for the various traces. Furthermore, although the visual evaluation scale is admittedly imprecise, its correlation with instrument intensities for optical brightener and direct yellow (see sections C and D) is good, and it is unlikely that detectors were grossly misevaluated.

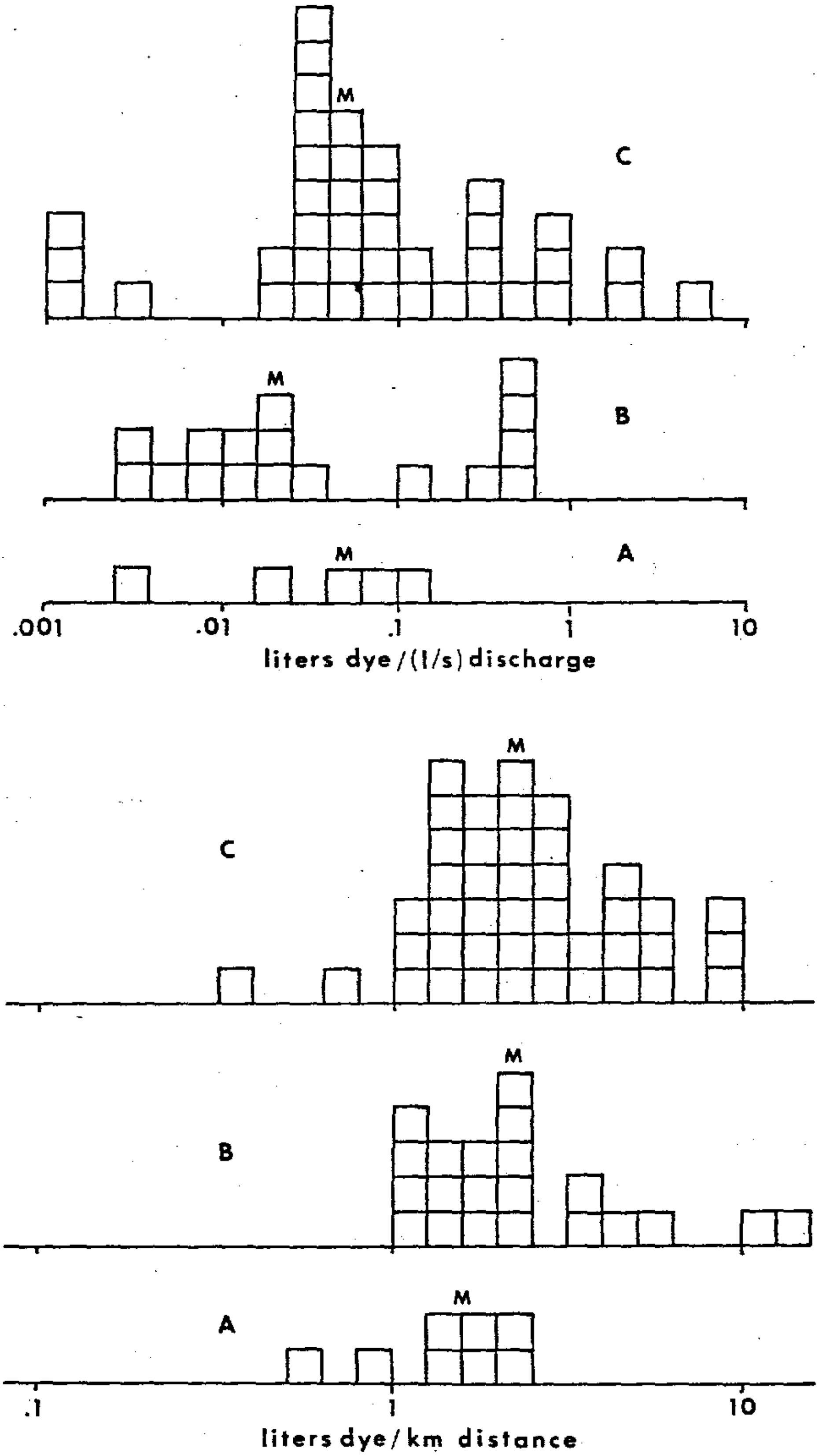


Figure B3. Optical brightener relationships. See text for discussion.

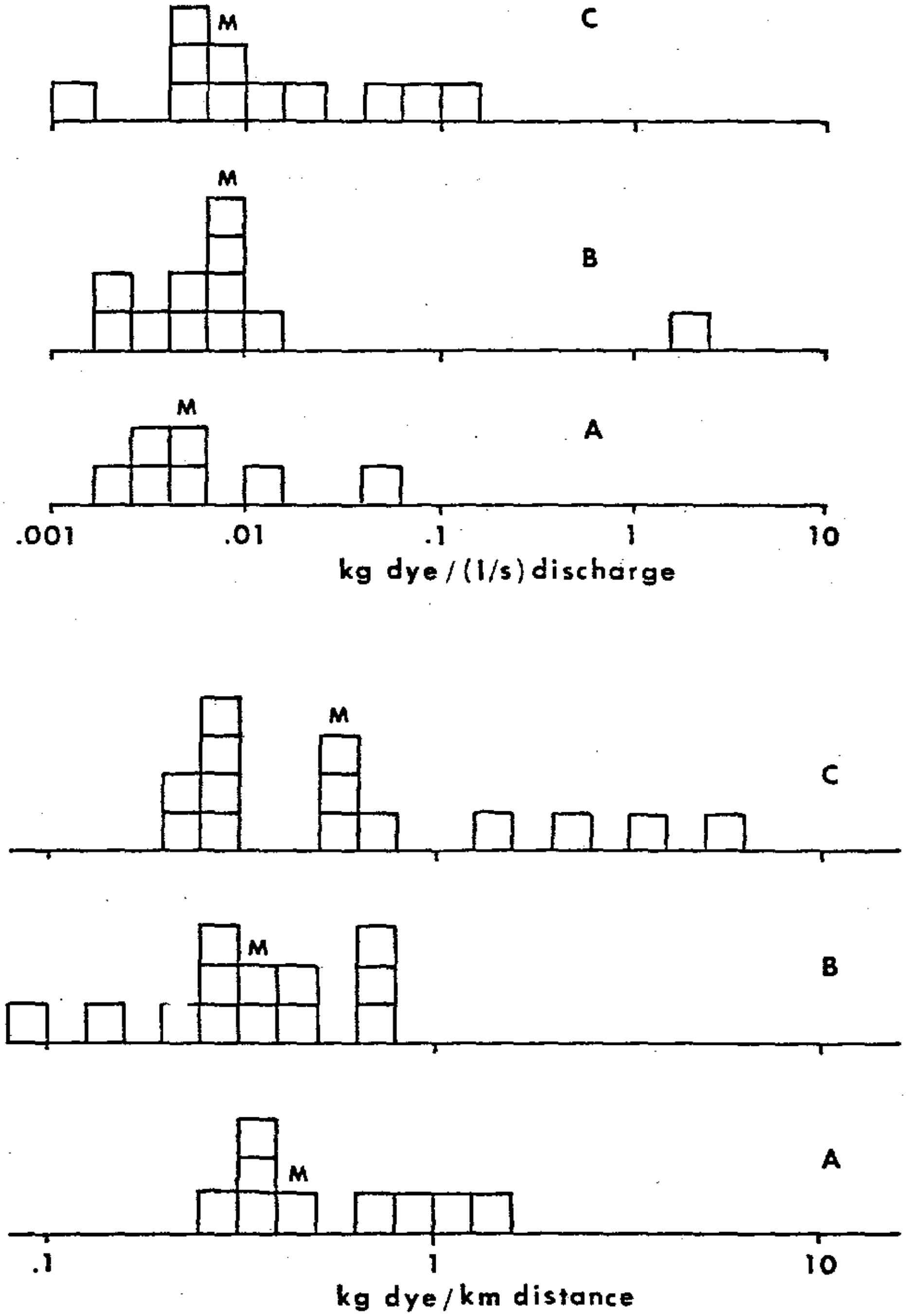


Figure B4. Direct yellow relationships. See text for discussion.

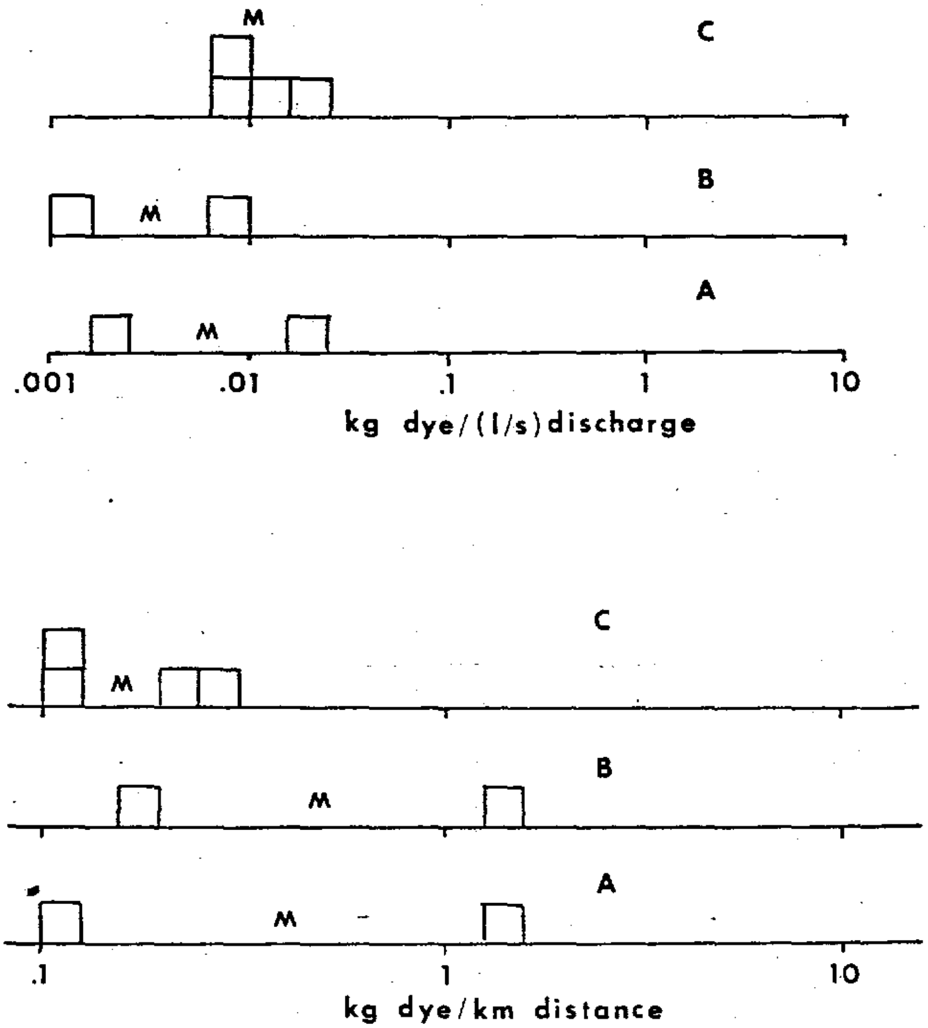


Figure B5. Fluorescein relationships. See text for discussion.

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C. RESPONSE OF FABRIC DETECTORS TO OPTICAL BRIGHTENER

P.E. Byrd and J. Thrailkill

C1. Introduction

Optical brightener was first used as a water tracing agent in Great Britain (Crabtree, 1970; Glover, 1972) and their first use in the United States was by Quinlan (Quinlan and Rowe, 1977). The most comprehensive discussion available is by Smart (1977), which became available at about the time the present project was proposed. Smart conducted both laboratory and field experiments with four different optical brighteners and both surgical cotton and fabric detectors. His results suggested that quantification of their behaviour is possible, and that further work was warrented.

The experiments described below were conducted with Fluorescent Brightener 28 (Society of Dyers and Colourists, 1971) which was extensively employed in the field aspects of the study (Thrailkill et. al., 1982). Two batches of this dye were used, termed Dye 1 and Dye 12, which are described in more detail in section B. A description of the apparatus and methods used will also be found in Section B. Some additional discussion of the study is in Byrd (1981). A brief discussion of a computer mapping at the fluorescent spectra of optical brightener on fabric detectors will be found in Section F3.

C2. Optical Brightener in Solution

Fluorescent Brightener 28 exhibits a broad emission peak centered at about 420 nm when excited at 335 nm (Fig. C1). It is detectable at concentrations as low as 1 ppb (I = 0.0144, 2mm excitation slit, 1 mm emission slit).

C2a. Standard Solutions

Initially, standard solutions were prepared with tap water, because

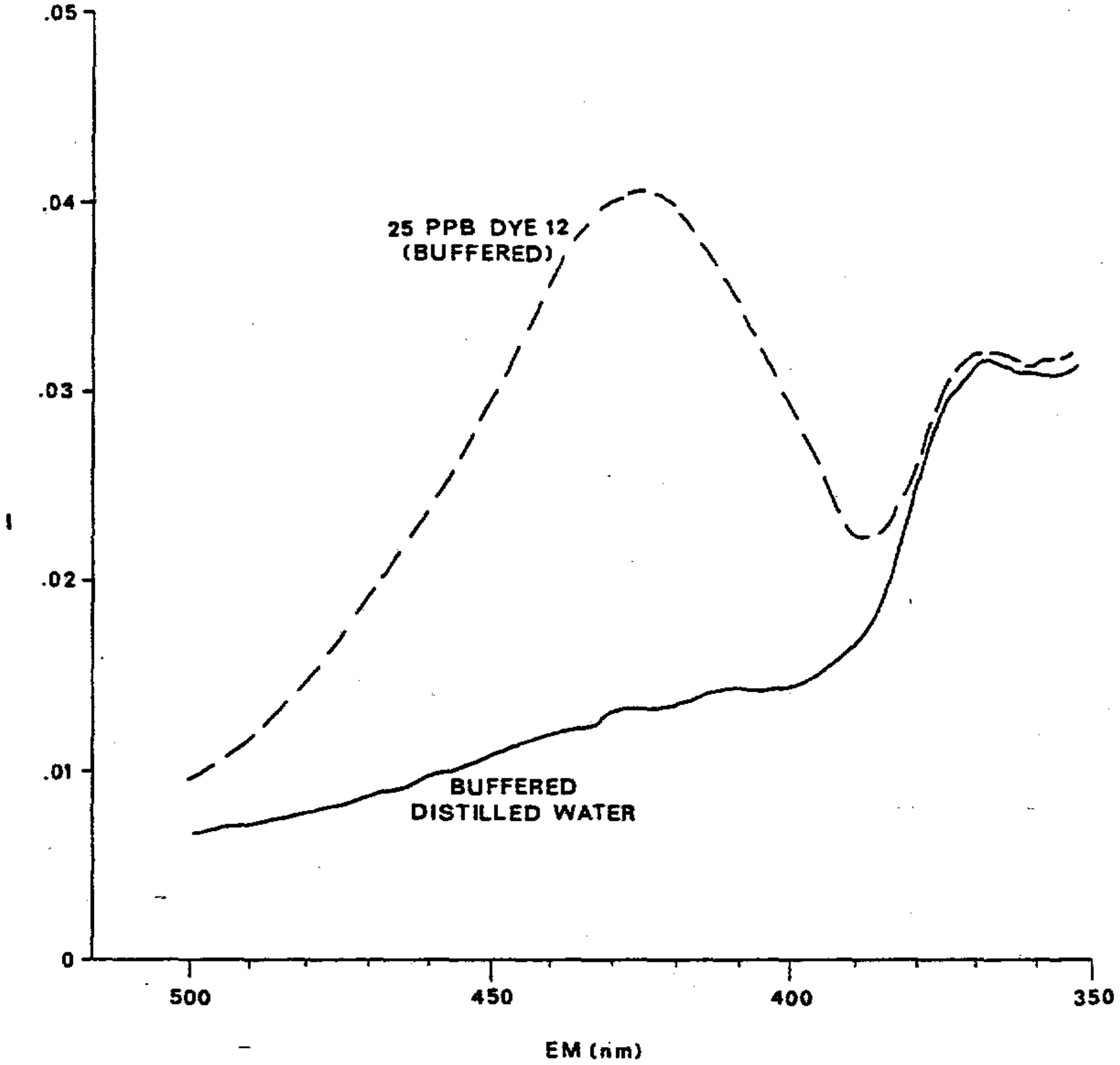

Figure C1. Emmission spectrum of optical brightener in solution. Buffer is 1mM $NaHCO_3$. Excitation 335 nm, 2mm slit; emission scan, 1mm slit.

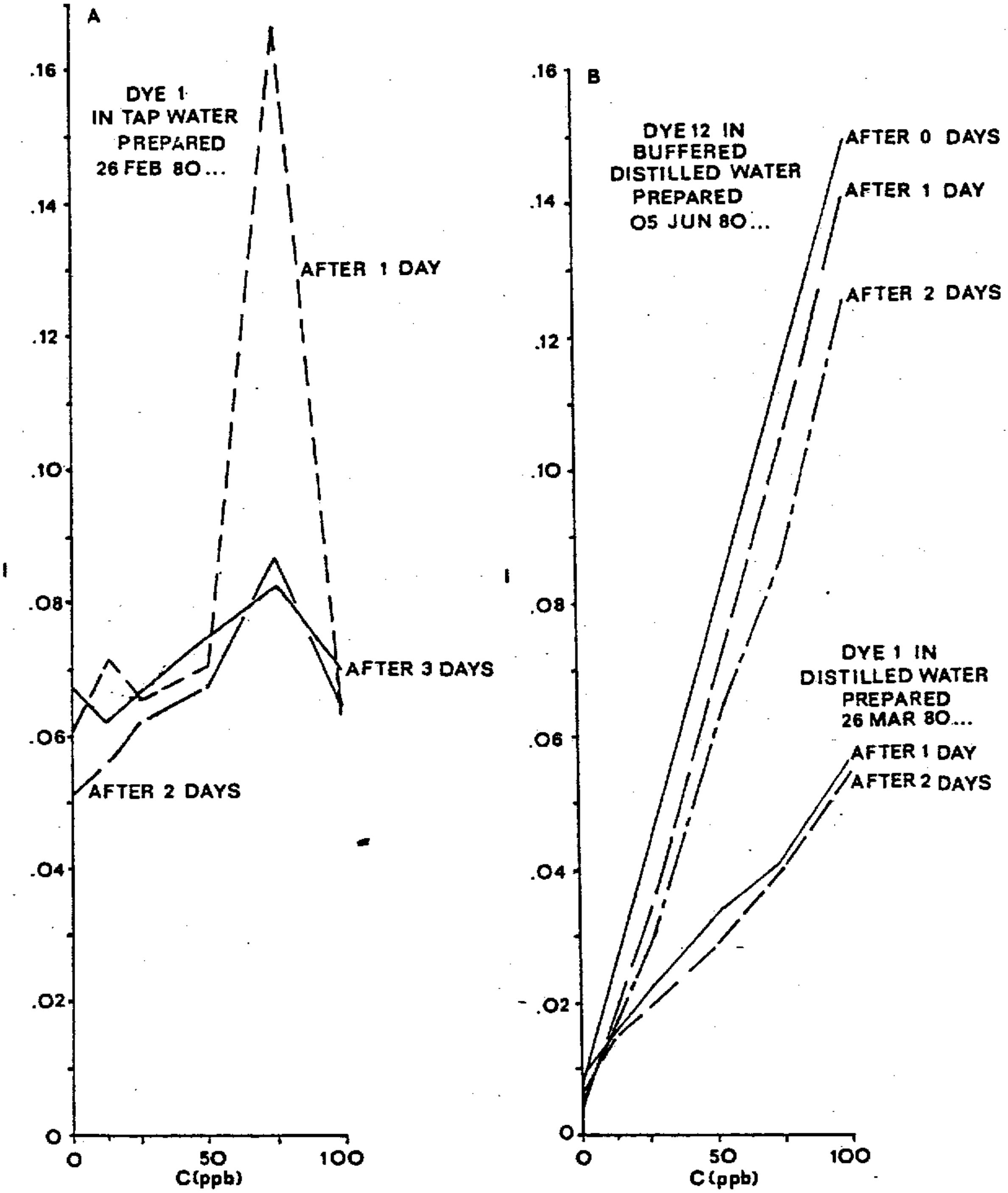

Figure C2. Optical brightener working curves. Excitation 335 nm, 2mm slit; emission 335 nm, 2mm slit; emission 420 nml, 1mm slit.

of its similarity in major dissolved species to the groundwater of the region. The working curves obtained, however, were not only non-linear but exhibited erratic changes as the solutions aged (Fig. C2). It was concluded that residual chlorine present in tapwater was affecting fluorescence. Smart and Laidlaw (1976) had reported a similar effect for other dyes.

Standard solutions prepared with distilled water were much more linear and showed smaller, and more consistent changes with age of the solutions, but fluorescent intensity was low (Fig. C2). This was suspected to be caused by the low pH of distilled water in equilibrium with atmospheric CO_2. Smart (1976) reported that the fluorescence of some of the optical brighteners he examined decreased slightly at a pH below 7. Also, it was thought that raising and buffering the pH might at least partially control the variations in apparent concentration in the equilibration system (see C3 below).

Standard solutions were buffered with $NaHCO_3$ to a concentration of 1 mM, which raised the pH to 8.1, which suggests the equilibrium PCO_2 of the laboratory of about 1.3×10^{-3} atm, which is a reasonable value. This pH is probably also representative of the groundwater of the region. Standard solutions so buffered were used for all subsequent work. They showed a much higher intensity than unbuffered distilled water, and a systematic decline in intensity with solution age (Fig. C2), although some of this effect may have been due to the exhaustion of the supply of the first batch of dye, referred to as Dye 1 (see C1 above), and adoption of the second batch (Dye 12) at the same time the standard solutions began to be buffered. Although both batches had Fluorescent Brightener 28 as the active ingredient, the concentration of this active ingredient in Dye 12 was unknown. Also, the other constituents of Dye 12 (also unknown) apparently differed from those of Dye 1. Dye 12 was significantly more difficult to dilute, requiring more vigorous and longer agitation. In the experimental work, the standards used corresponded (in dye batch and buffering) to the equilibrating solution.

C2b. Equilibration System

As described in Section B, the large equilibration system in which the detectors were exposed to dye consisted of three tanks connected with tubing. Two problems arose with the system during the study. First, although prior to an experiment the entire system was flushed with distilled water until no dye from previous runs was detectable, and dye was added to the tanks in proportion to their volume, samples taken from the three tanks during an experiment showed substantial intensity differences when the make-up distilled water was unbuffered (Fig. C3). In addition, the fluorescent intensity, and hence the apparent concentration of optical brightener, was on the order of 3 or 4 times the nominal concentration determined from the amount of due introduced and the volume of the system. This difference is also shown in Fig. C3, where the intensity curve for the nominal concentration is derived from a standard prepared at the time the due solution was made up in the equilibration system.

It was thought that both the heterogeneity and enhancement of fluorescent intensity in the equilibration system might be due to variations in pH, as discussed above. Buffering the system with $NaHCO_3$ (see C2) did reduce both the intensity differences between tanks and the increase in overall fluorescent intensity substantially (Fig. C3) but did not eliminate it.

Although tank 1 of the equilibration system in which the detectors were suspended was equipped with magnetic stirrers, substantial but inconsistent differences in intensity of detectors in various positions in the tank were found. In earlier experiments (OB-A and OB-B), four detectors were exposed for each time interval, and four positions were read on each detector (see Section B). The coefficient of variation of the four readings from one detector (about 8%) was about the same as the coefficient of variation of the means of the four detectors. In later experiments, therefore, only one detector was exposed for each time interval.

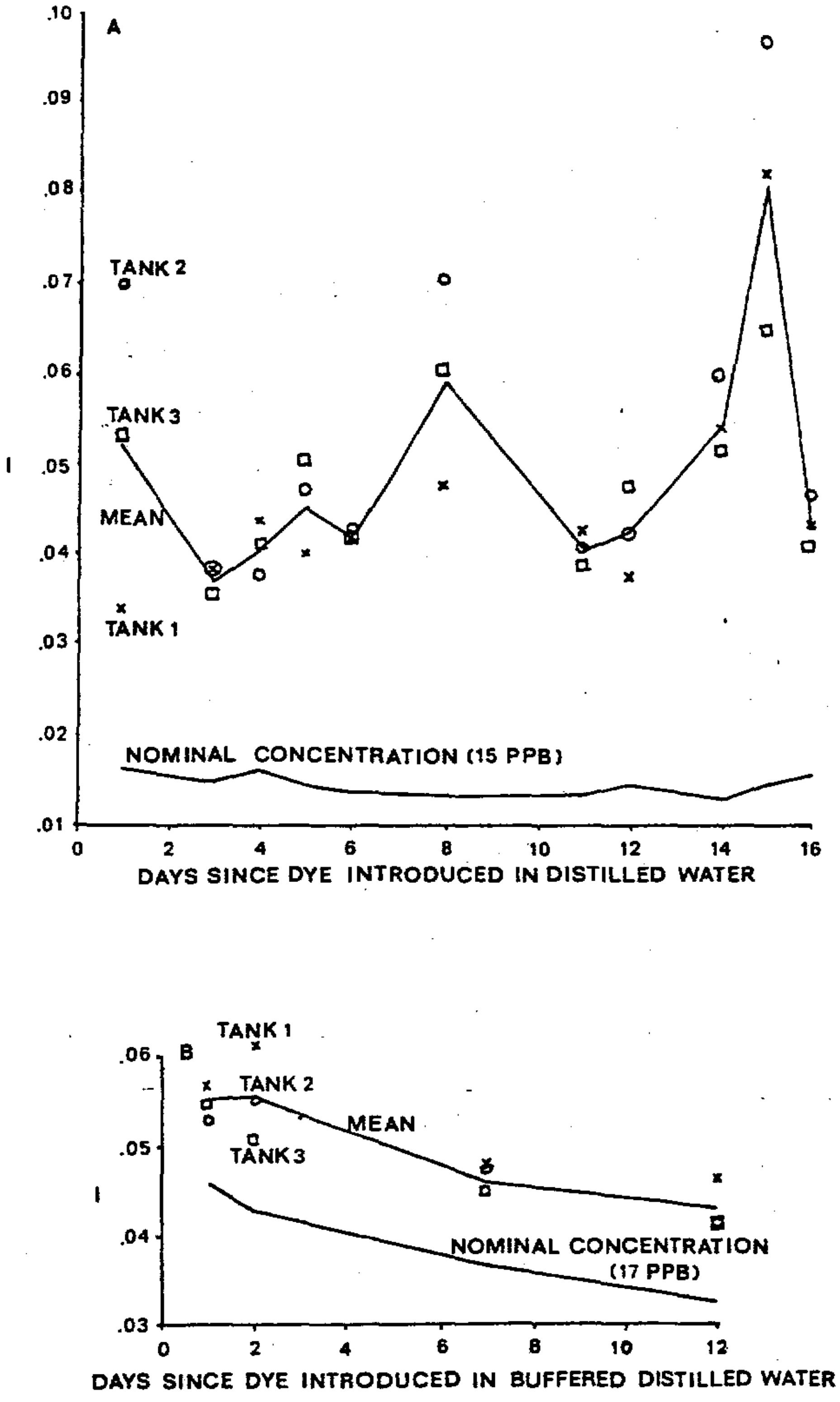

Figure C3. Changes in optical brightener intensities in equilibration system with time. Excitation 335 nm, 2mm slit; emission 420 nm, 1mm slit.

C3. Detector Response

When absorbed on the detector, Fluorescent Brightener 28 produces the highest emission at an excitation wavelength of 385-390 nm, which produces a peak at 430 nm at higher intensities and a shoulder at 425 nm on the side of the reflection peak at lower intensities (Fig. C4, solid line). When excited at 435 nm the emission peak is at 420 nm and, although usually of lower intensity, is clearly separated from the reflection peak (Fig. C4, dashed line). For this reason, detectors were evaluated at this excitation and emission wavelength, which is the same as that used for dye in solution (see C2).

C3a. Immersion Time and Temperature

Results of the five equilibration experiments (all of which were conducted with Dye 12) are shown in Table C1, and the relationship between detector intensity and immersion time are presented in Fig. C5. Experiments OB-A and OB-D were conducted at nearly the same dye concentration (15 and 17 ppb, respectively). In view of the large uncertainties, a line was drawn so as to pass within the 95% confidence intervals and an intensity of 40 at zero time, which was the average intensity of a detector which had not been exposed to dye. The line for both experiments OB-A and OB-D was the same ($I = 40.0 + 17.6T$).

Experiments OB-B and OB-C were conducted with a dye concentration of 25 ppb, but the slopes of the fitted lines were quite different (OB-B: $I = 40.0 + 25.0T$; OB-C: $I = 40.0 + 12.0T$), and it was not possible to fit the 5-day detector in experiment OB-B, since it showed essentially the same intensity as the detector immersed for 4-days (Fig. C5). It is likely that this is due to the detector becoming saturated after 4 days. The difference in slope for the two experiments is ascribed to the difference in temperature; a heating failure in the laboratory during the experiment OB-C resulted in an average temperature of 10° C, as opposed to about 20° C during experiment OB-B. Further investigation is required before this explanation is conclusive, however, especially since a similar heating failure near the end of experiment OB-D does not appear to be reflected in the detector intensities

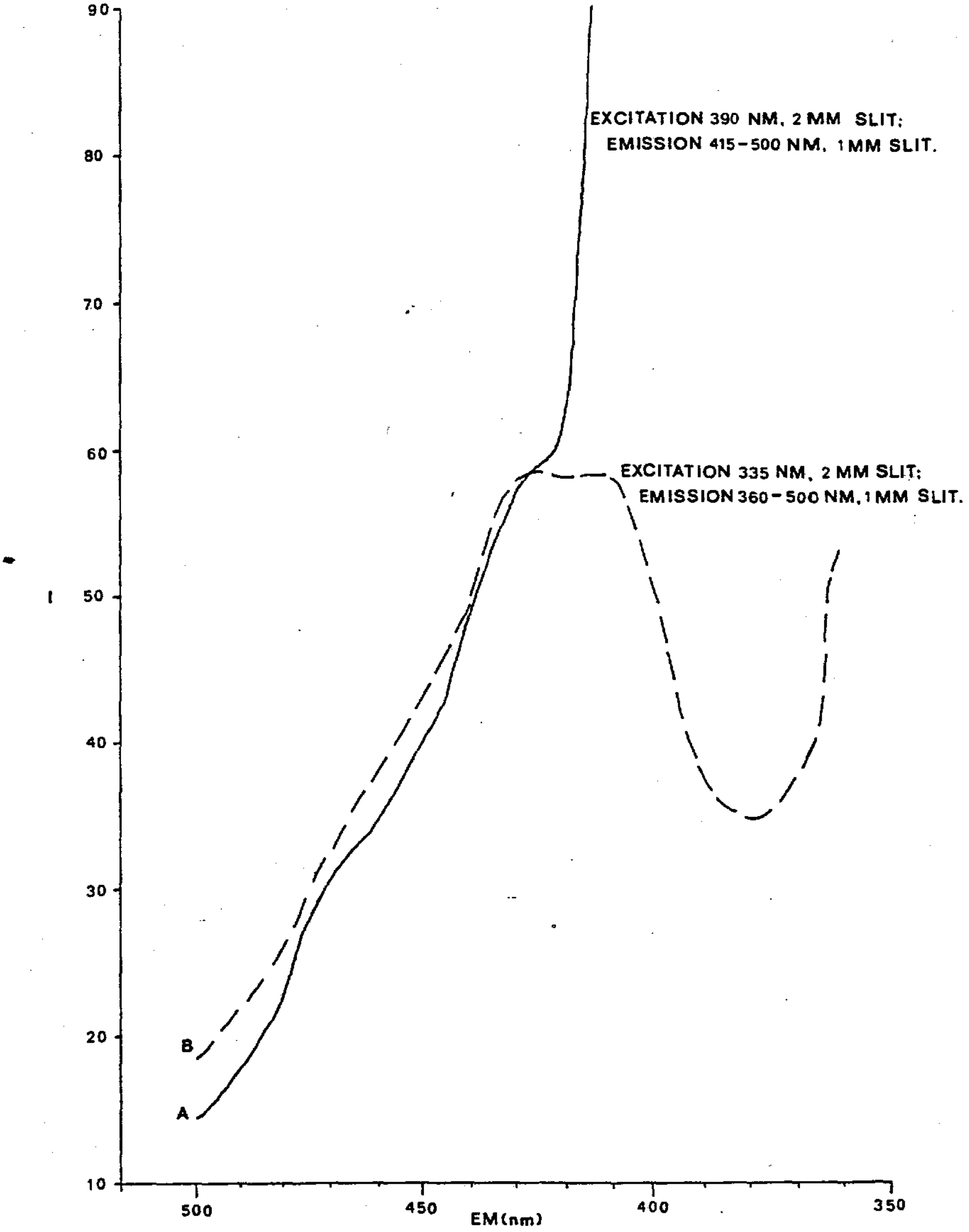

Figure C4. Emission spectra of optical brightener on fabric detector immersed 5 days in 25 ppb (Dye 12).

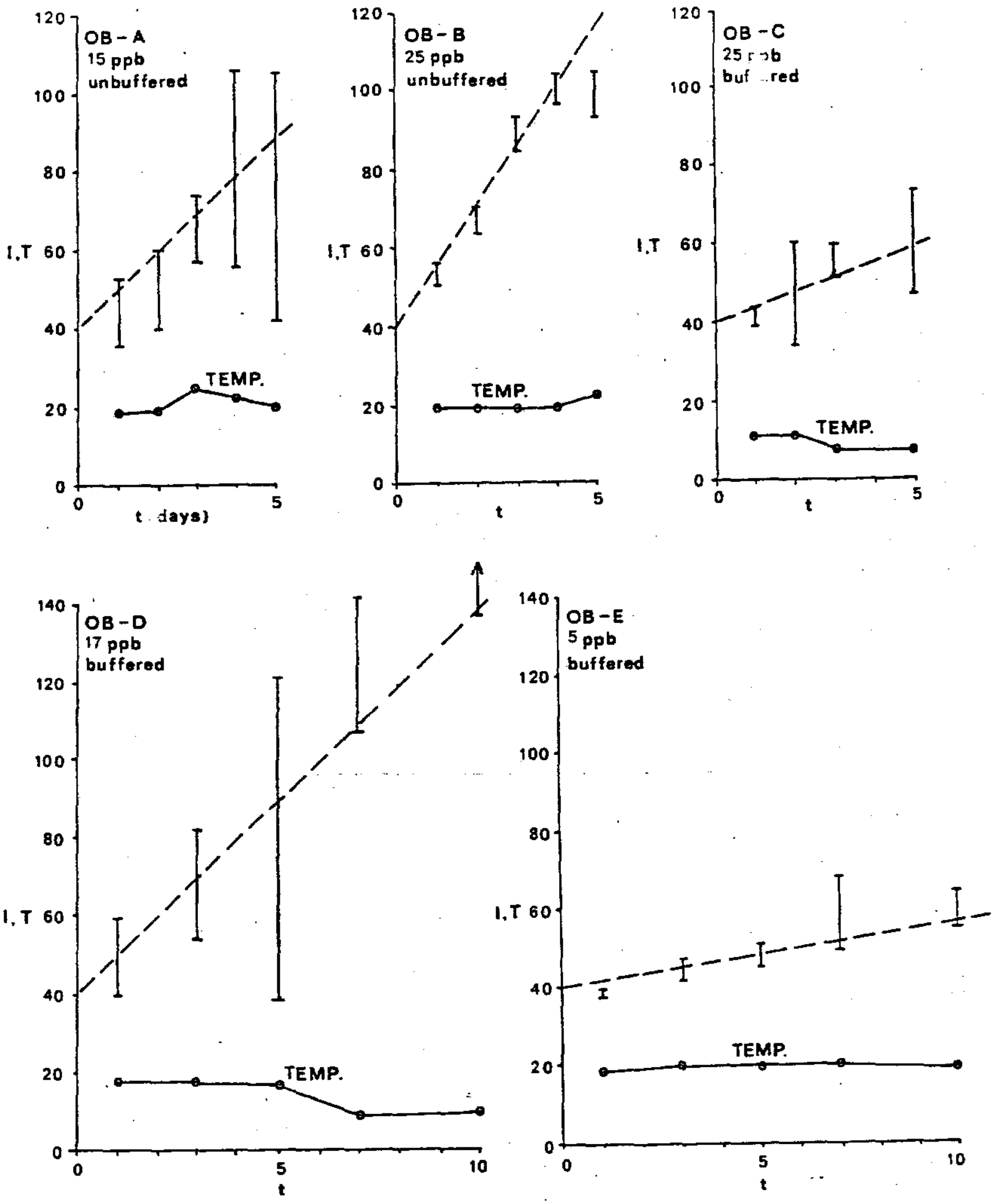

Figure C5. Changes in detector intensity with immersion time and temperature. Error bars indicate 95% confidence intervals.

Experiment:	OB-A	OB-B	OB-C	OB-D	OB-E
Dates:	5-21 Jun 80	22 Jul-3 Aug 80	5-10 Jan 81	6-15 Feb 81	9-18 Mar 81
C (ppb):	15	25	25	17	5
Solution:	unbuffered	unbuffered	buffered	buffered	buffered
	I (T)	I (T)	I (T)	I (T)	I (T)
Exposure Days					
1	43.9±8.5 (18)	52.9±2.9 (19)	41.2±2.4 (11)	44.0±4.9 (17)	38.0±0.6 (18)
2	50.0±10.1 (19)	67.3±2.7 (19)	47.7±13.5 (11)	--	--
3	64.9±8.5 (24)	89.1±4.3 (19)	56.3±4.0 (8)	67.6±14.3 (17)	44.2±2.5 (19)
4	80.0±24.8 (22)	100.0±3.7 (19)	--	--	--
5	72.9±31.5 (20)	99.8±4.5 (22)	60.7±13.8 (8)	79.4±41.2 (16)	47.5±3.1 (19)
7	--	--	--	124.4±16.9 (8)	58.3±9.1 (19)
10	--	--	--	136+ (9)	58.4±4.5 (18)

Table C1. Results of equilibration experiments with optical brightener. Dye 12 in distilled water. Uncertainties are 95% confidence intervals. All intensities I are at 335 nm excitation, emission peak near 420 nm, 2 mm excitation slit, and 1mm emission peak. Figures in parentheses are temperatures (C).

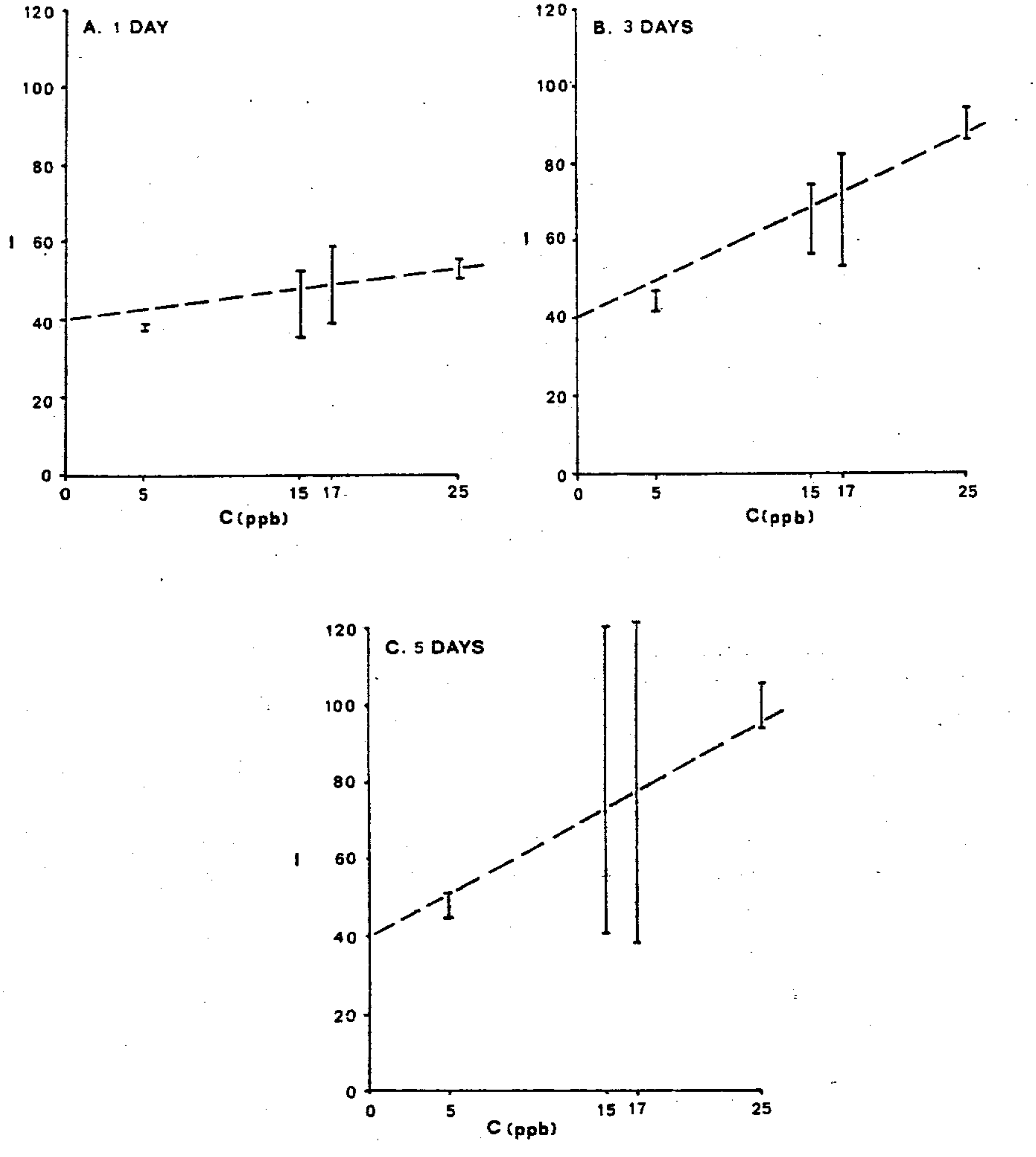

Figure C6. Detector intensity versus concentration working curves. Error bars indicate 95% confidence intervals.

(Fig. C5).

C3b. Dye Concentration

Excluding experiment OB-C, the one, three, and five day intensities are plotted versus concentration on Fig. C6, and a line was fitted to each plot as nearly as possible to pass through the 95% confidence intervals and an intensity of 40 at zero concentration. The slopes and intercepts of the lines are: $I = 40.0 + 0.53\ C$ for one day of immersion; $I = 40.0 + 1.9\ C$ for three days; and $I = 40.0 + 2.2C$ for five days. Note that the fitted line does not pass through the 5 ppb concentration at one and three days, suggesting the working curve flattens out at low concentrations, as would be expected. Also, the one-day 5 ppb values have an intensity slightly lower than the value of 40 taken as the blank intensity, indicating the range in values of the blank among detectors.

C3c. Instrumental Versus Visual Intensities

As discussed in Section B, evaluation of fabric detectors used in optical brightener traces in the field portion of the project (Thrailkill, et al., 1982) was by visual assessment using a hand held ultraviolet lamp. Although it is planned to evaluate field detectors instrumentally in future investigations, this was not possible during the project because the instrumental techniques were still being developed during the final phases of the field work.

Visual evaluation of detectors was on a simple scale of negative or weak (A), moderate (B), or strong (C) fluorescence. A selection of detectors used in the equilibration experiments was also evaluated instrumentally, with the results shown in Table C2.

C4. Conclusions

As with any experimental study in which a developed methodology does not exist, difficulties were encountered which, even though

Instrumental	Visual	Instrumental	Visual
38.0	Negative	67.6	B
41.2	"	71.1	"
44.0	A	79.4	"
44.2	"	81.1	"
47.5	"	90.1	C
56.3	"	96.7	"
58.4	"	101.2	"
60.7	"	110.4	"
64.0	"	124.4	"
67.4	B	136+	"

Table C2. Comparison of instrumental and visual intensities

partially or largely overcome, limited the validity of earlier experiments and make their results difficult to compare to later findings. These included, but were not confined to, problems in establishing working curves, in maintaining constant composition in the equilibration system, ambient temperature changes, and changing dye batches.

Despite these difficulties, however, the findings of the study suggest that quantitative results are obtainable from passive detectors in water tracing results using optical brightener. Especially encouraging is the linear or near-linear relationship between detector intensity and both dye concentration and detector immersion time. The dye hydrograph that emerges during a trace resembles a discharge hydrograph (see Section G), and this dual-linearity promises to provide a method for integrating it, allowing dye-recovery volumes to be estimated.

It is difficult to compare the findings of the study with those of Smart (1976), since different optical brighteners were used and experimental conditions were not the same. One noteable difference, however, was that his conclusion that fabric detectors reach saturation in less than one hour was at variance with the greater than 3 day saturation times determined in this study. The fact that his detectors were responding to concentrations as high as 180 ppb during a dye pulse may accound for this apparent discrepancy. Unless dye concentrations of this magnitude may confidently be expected in field studies, it seems likely that too-frequent detector changes, in order to more precisely establish travel times, may result in a trace not being detected.

In summary, it is believed that the study results, while not definitive are encouraging enough so that such equilibration experiments should be continued under conditions of more active agitation, to reduce concentration heterogeneities, and controlled temperature. Furthermore, because dyes used in the polyethylene containers may have contributed to the apparent fluorescent enhancement, other materials should be investigated.

C5. References

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Quinlan, J.F., and D.R. Rowe, 1977. Hydrology and water quality in the Central Kentucky Karst: Phase I. University of Kentucky Water Resources Institute, Research Report No.101, 93p.

Smart, P.L., 1976. The use of optical brighteners for water tracing. British Cave Research Association Transac., V.3, p. 62-76

Society of Dyers and Colourists, 1971. Colour Index, 3rd ed., 6411p.

Thrailkill, J., L.E. Spangler, W.M. Hopper, Jr., M.R. McCann, J.W. Troester, and D.R. Gouzie, 1982. Groundwater in the Inner Bluegrass Karst Region, Kentucky. Univ. of Kentucky Water Resources Research Inst., Res. Rept. 136, 136p.

D. RESPONSE OF FABRIC DETECTORS TO DIRECT YELLOW

P.E. Byrd and J. Thrailkill

D1. Introduction

Direct yellow (Direct Yellow 96, Society of Dyers and Colourists, 1971) was first employed by J.F. Quinlan in the Mammoth Cave area of Kentucky (Quinlan, 1977). No previous work on its adsorbancy on cotton detectors for the purpose of evaluating water traces is known. Two batches of dye, termed Dye 2 and Dye 5 were used (see Section B for a detailed description). Information on apparatus and methods will be found in Section B, and some additional discussion of the study is in Byrd (1981).

D2. Direct Yellow in Solution

Direct yellow (both Dye 2 and Dye 5) in solution exhibited a broad emission peak from 430 to near 530 nm when excited at 395 nm. It is detectable at an emission wavelength of 490 nm at concentrations as low as 1 ppb (I= 0.0055, excitation slit = 2 nm, emission slit - 1 mm). Emission scans of various concentrations are shown in Fig. D1.

D2a. Standard Solutions

The preparation of 1000 ppm stock solutions of direct yellow dye was difficult, requiring up to 30 minutes of agitation or overnite storage, due to the tendency of the powdered dye to cake. Working curves using both buffered and unbuffered distilled water were quite linear and showed a decline in fluorescence with age, similar to optical brightener (Fig. D2).

Two batches of dye were used (Dye 2 and Dye 5), and solutions of the latter were made up using buffered distilled water. This confounding of effects makes it impossible to state whether the differences in working curve slope are due to differences between dye batches or due

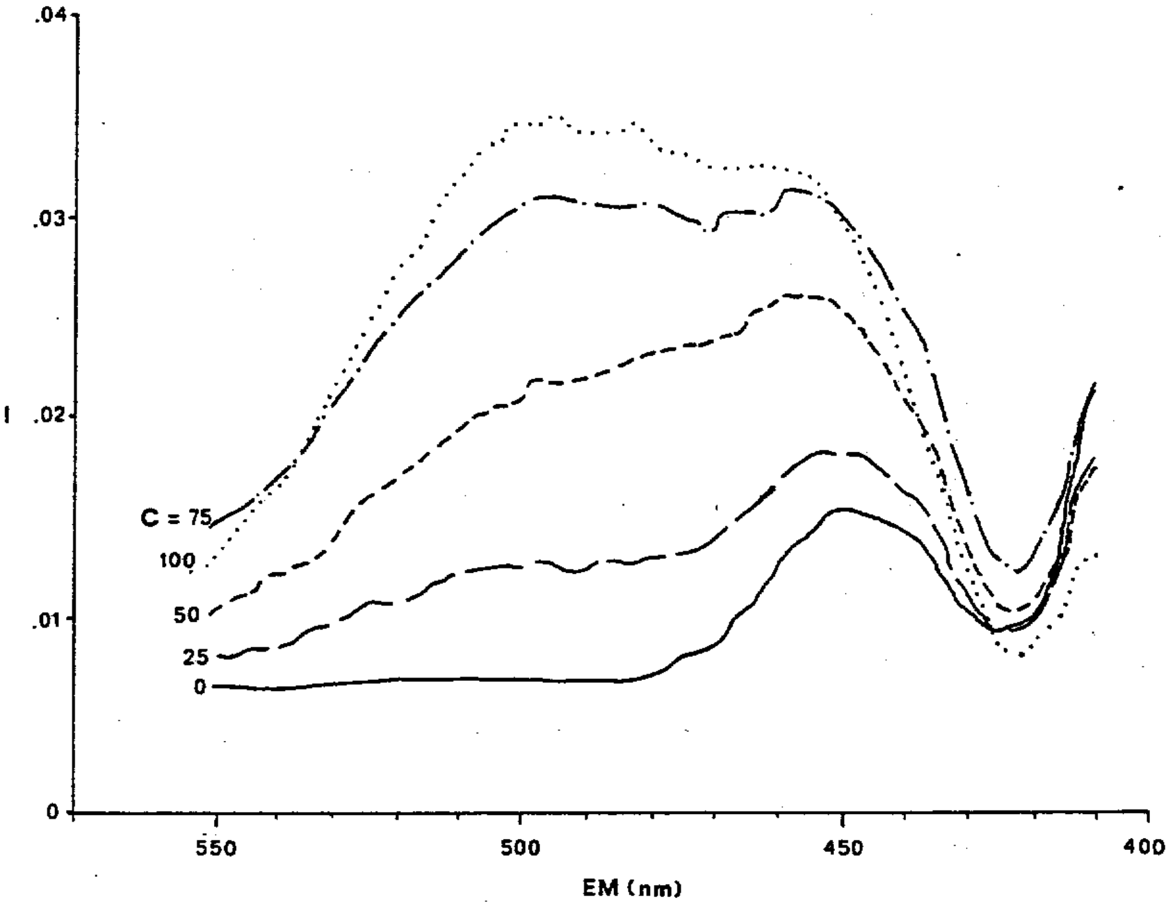

Figure D1. Emission spectra of various concentrations of direct yellow (in ppb) in solution. Buffer is 1mM $NaHCO_3$. Dye 5; excitation 395 nm, 2mm slit; emission scan, 1mm slit.

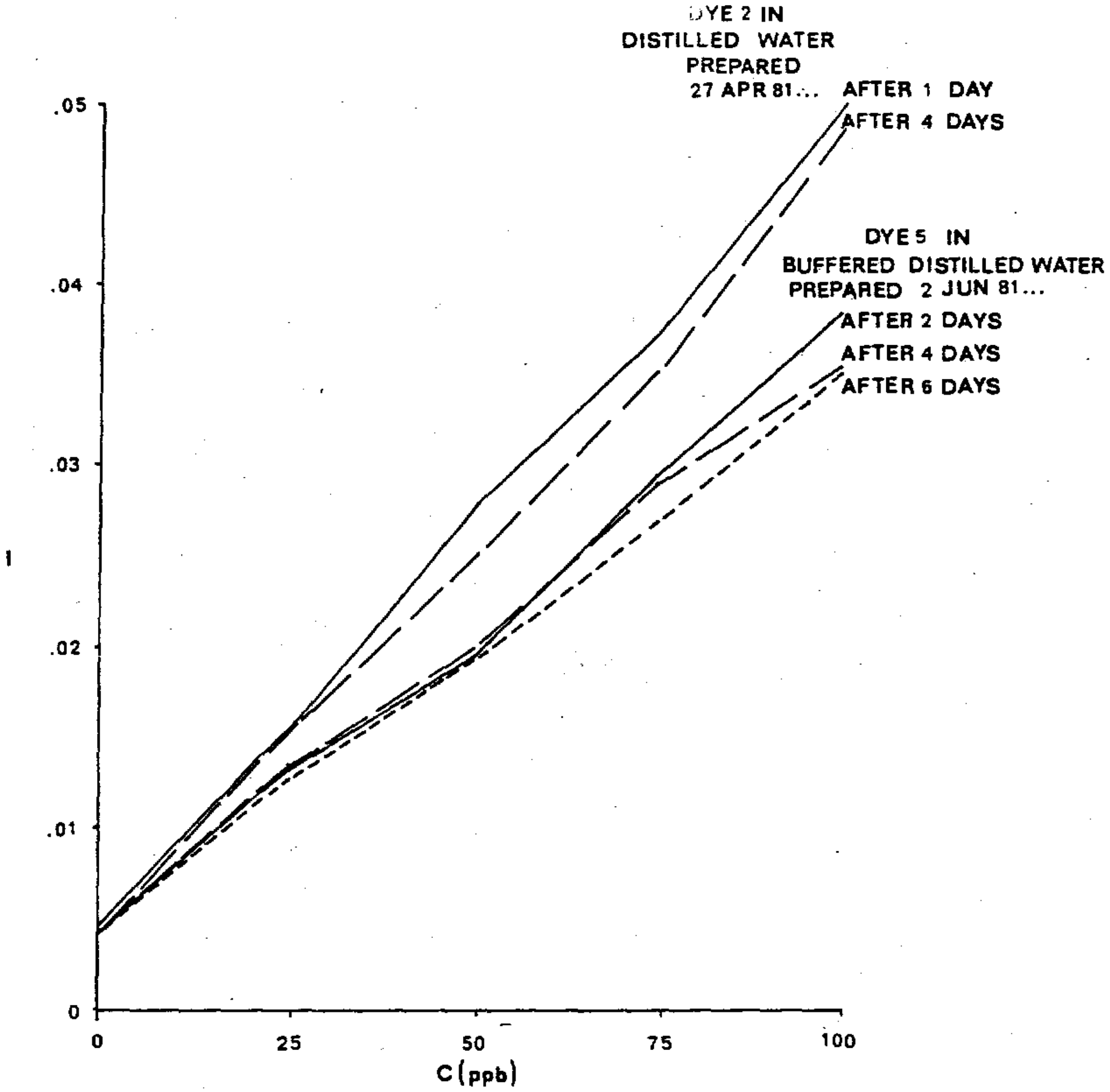

Figure D2. Direct yellow working curves. Excitation 395 nm, 2mm slit; emission 490 nm, 1 mm slit.

to the higher pH of the solution buffered with 1mM $NaHCO_3$ (Fig. D2). Note also that both buffered and unbuffered distilled water showed a blank intensity of about .004.

D2b. Equilibration System

Direct yellow solutions in the equilibration system exhibited the same phenomena as did optical brightener solutions. Although the system was thoroughly flushed prior to the initiation of an experiment, and dye was introduced into each of the three tanks in proportion to its volume, monitoring during an experiment showed substantial heterogeneities in the system and an apparent dye concentration higher than that which would result from the amount of dye introduced. The heterogeneity decreased with time, suggesting that the solution was becoming better mixed, and the enhancement was substantially less with buffered distilled water, indicating pH to be a major factor (Fig D3).

D3. Detector Response

On a fabric detector, direct yellow showed a broad emission peak from 440 to 480 nm when excited at 395 nm. This peak was superimposed on the side of the reflection peak, and was difficult to evaluate at low concentrations. When examined at reduced slit widths (1 mm excitation and 0.2 mm emission), a small peak is visible at 475 nm (Fig. D4). This peak was found on all detectors examined regardless of whether they had been exposed to dye, and was designated the "fabric peak". Because of its ease of identification and proximity to the center of the direct yellow peak, detector intensity was evalauted at this wavelength.

Results of the three equilibration experiments are given in Table D1, and Fig D5 shows plots of the detection intensity with time. The three experiments failed to provide significant data on detector intensities relative to exposure time, concentration, or temperature. Although the mean intensity of the undyed fabric is 0.44, there is some variation (which was not systematically investigated), and because it is not possible to instrumentally evaluate a detector prior to its

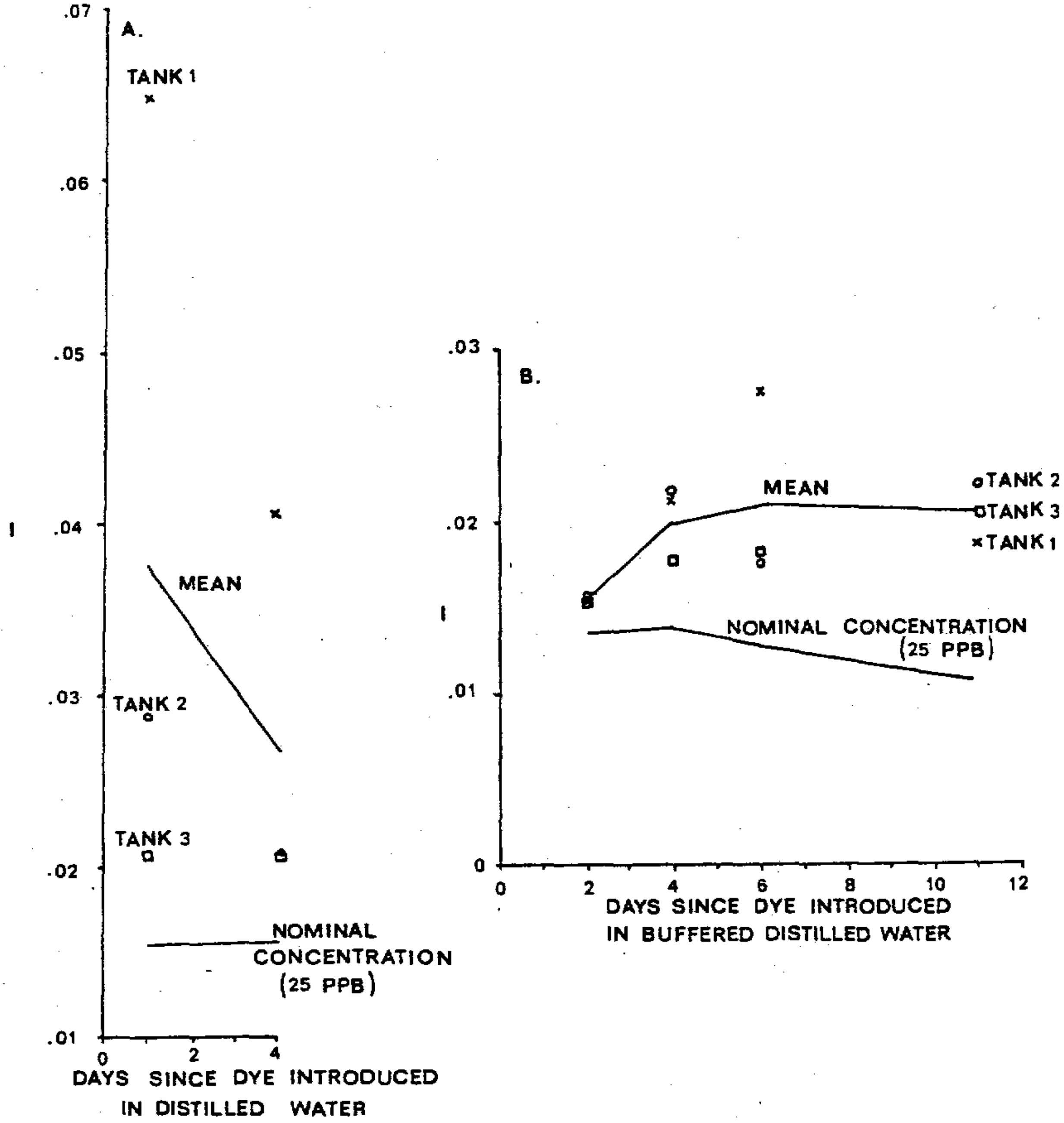

Figure D3. Changes in direct yellow intensities in equilibration system with time. Excitation 395 nm, 2 mm slit; emission 490 nm, 1 mm slit.

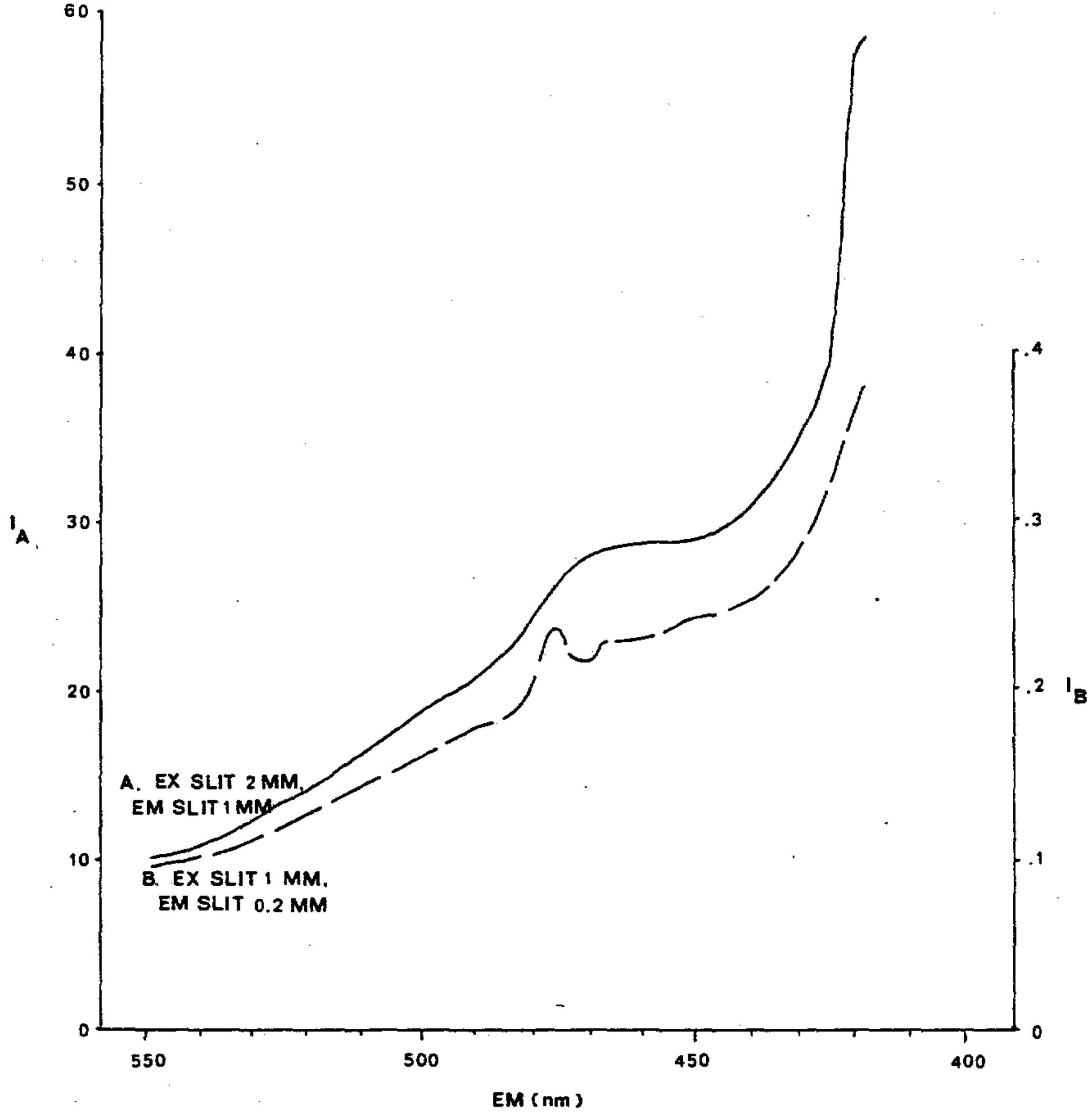

Figure D4. Emission spectra of direct yellow on fabric detector immersed 7 days in 25 ppb (Dye 5). Excitation 395 nm.

Experiment:	DY-A		DY-B		DY-C	
Dates:	29 Apr-8 May 81		4-13 Jun 81		19-29 Jul 81	
C (ppb):	25		25		17	
Solution:	unbuffered		buffered		buffered	
Dye:	2		5		5	
	I	(T)	I	(T)	I	(T)
Exposure Days						
1	.39 ±.14	(19)	.52±.09	(20)	.52±0	(22)
3	.47 ±.05	(19)	.52±.02	(19)	.46±.02	(21)
5	.44 ±.03	(19)	.49±.03	(20)	.49±.11	(21)
7	.39 ±.08	(19)	.49±.02	(21)	.47±.04	(21)
10	.37 ±.08	(18)	.47±.02	(21)	.46±.08	(21)

Table D1. Results of equilibration experiments with optical brightener. Uncertainties are 95% confidence intervals. All intensities I are at 395 nm excitation, 1mm slit; approximately 475 nm emission (at "fabric peak"), 0.2 mm slit. Figures in parentheses are temperatures (C).

being placed in the equilibration system (see Section B), it is likely that some of the variation in intensity shown on Fig. D5 is due to initial intensity variation of the detector. This is almost certainly true for experiment DY-A, since the mean intensity of all detectors was less than 0.44.

The uncertainties indicated in Table D1 and Fig. D5 are 95% confidence intervals derived from examination of 4 locations on a single detector. Except for the 1 day detector in experiment DY-C, they are all large. Inspection of the data, however, allows some very tentative observations to be made. It seems likely that saturation was reached in all experiments very rapidly, probably by the first day, and that later variations may have been due to the detectors being exposed to higher or lower dye concentrations due to heterogeneities in the system. The lower intensities in experiment DY-A may have been caused by the lack of solution buffering, the use of Dye 2 rather than Dye 5, and/or the slightly lower temperatures. No explanation is offered for the apparent lack of difference in intensities between experiment DY-B

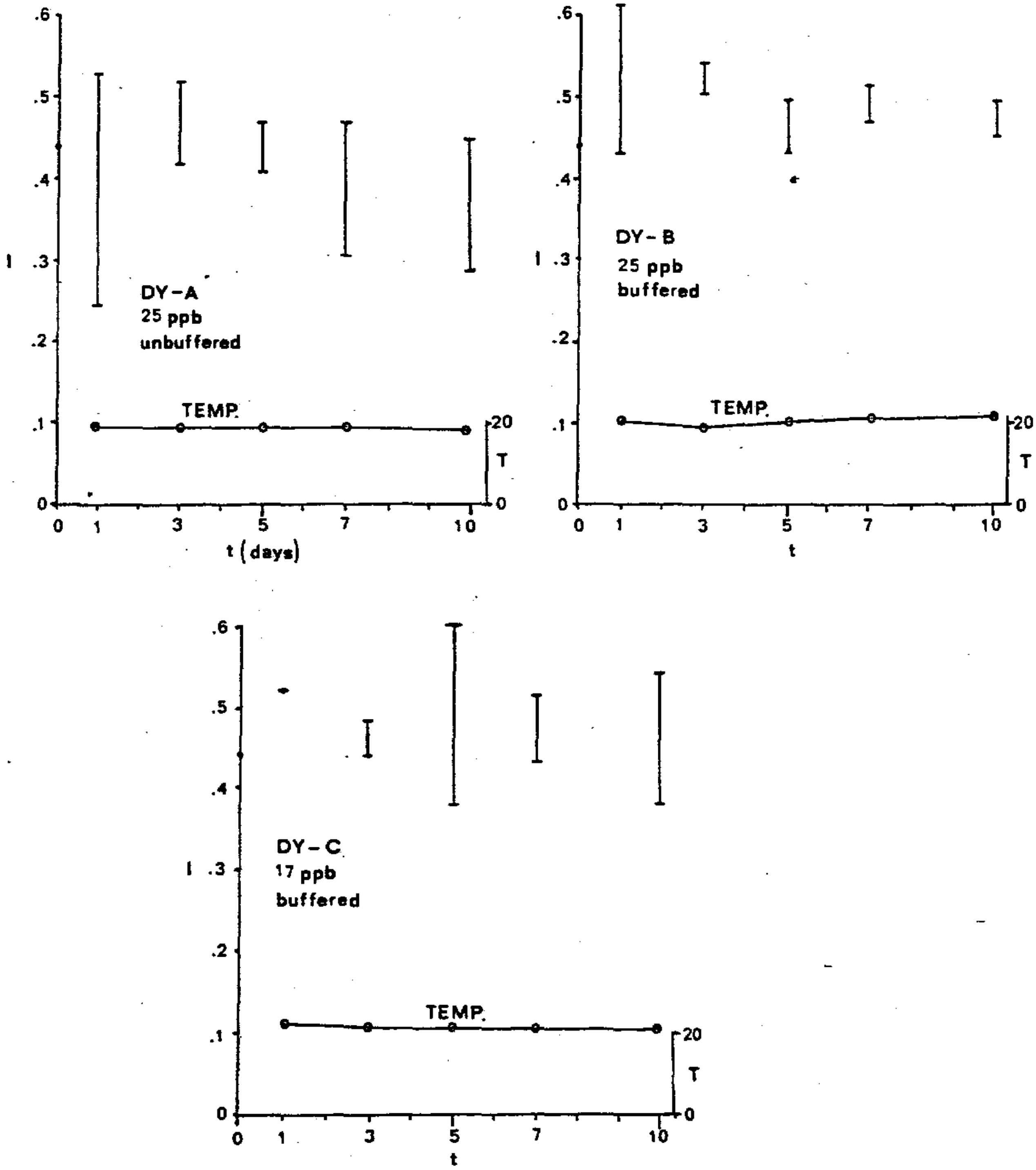

Figure D5. Changes in detector intensity with immersion time and temperature. Error bars indicate 95% confidence intervals.

at 25 ppb (mean intensity 0.49) and experiment DY-C at 17 ppb (mean intensity 0.48).

All of the detectors showed a weak (A) visual intensity, including those from experiment DY-A whose mean instrumental intensity was less than that of the undyed fabric.

D4. Conclusions

The experiments with direct yellow must be considered even more preliminary than those with optical brightener (Section C). No firm relationships between dye concentration, immersion time, or temperature can be drawn from the data obtained. It appears that the response of detectors to the dye is rapid (much more so than to optical brighteners) and that both pH and temperature are factors. There is no evidence that instrumental evaluation extends to lower concentrations than visual evaluation.

At present, direct yellow is the only due known to be detectable on cotton in the presence of optical brightener. If its use in this application continues, further equilibrium experiments should be undertaken with temperature control, improved stirring to homogenize the system, and attention to the influence of container materials, as discussed for optical brightener (Section C). In addition, further investigations should be conducted on its spectra and on the blank corrections which should be applied.

D5. References

Byrd, P.E., 1981. The effects of two water tracing agents on passive cotton dye detectors. University of Kentucky, M.S. Thesis, 51p.

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E. RESPONSE OF CHARCOAL DETECTORS TO FLUORESCEIN

L.E. Spangler, K.R. Pogue, and J. Thrailkill

E1. Introduction

Fluorescein (Acid Yellow 73, Society of Dyers and Colourists, 1971) has probably been used for water tracing longer (Dole, 1906) and more extensively than any other fluorescent dye. There is a very extensive literature on its use and detection by visual, instrumental, and passive detectors. Dunn (1957) described a technique for detecting the passage of dye by immersing a packet of activated charcoal, and the method has been widely used.

Because fluorescein was employed in a few water traces in the field portion of the project (Thrailkill, et. al., 1982; also see Section B), some investigations were conducted into designing a suitable detector and procedure to evaluate these traces, inasmuch as no standard method exists. A description of the equipment and procedures used is in section B. Some additional discussion of portions of the study is in Spangler (1982).

E2. Fluorescein in Solution

Fluorescein (Acid Yellow 73) in solution in distilled water shows a well defined emission peak at 500 to 510 nm when excited at about 480 nm. During the detector equilibration studies described below, the substantial depression of fluorescent intensity by the low pH of distilled water was only beginning to be appreciated, and satisfactory working curves relating intensity and concentration were not obtained.

Other than an exploration experiment in the large equilibration system, all equilibration experiments were conducted in the single tank system (see Section B). It was found that intensity of a dye solution made up with unbuffered distilled water increased nearly 2.5 times in 5 days. Buffering the solution to approximately 8.1 with 1 mM $NaHCO_3$

stabilized the intensity markedly, but a steady increase in intensity of about 1% per day continued. The same increase of fluorescent intensity in the buffered solution also took place in uncolored polyethylene and clear glass containers stored in darkness.

E3. Detector Response

Detectors consisting of charcoal encased in packets of screen were immersed in the tank for various time intervals and then placed in an elutriating solution, agitated for various time intervals, the elutant decanted, and the fluorescent intensity determined instrumentally. A number of experiments were conducted with various types of packets, screen material, and elutriating solutions before adopting the following standard (see also Section B). The detector is constructed of a 5 x 10 cm rectangle of nylon screen (1.4 mm mesh) rolled on a pencil to form a cylinder 10 cm long and 7 mm in diameter with two layers of screen. One end is folded and fastened with a brass staple, 2 gm of fresh cocoanut charcoal is introduced, and the open and folded end stapled. After exposure to dye, the detector is rinsed in distilled water and placed in a 60 ml polyethylene bottle and 25 ml of elutrient added. The elutrient used was developed by P.L. Smart (J.F.Quinlan, personal communication) and consists of 32.5% NH_4OH, 43.0% 1-propanol, and 24.5% distilled water (by volume). The bottle is agitated on a test-tube shaker for varying periods, and the elutriant decanted and evaluated instrumentally (and/or visually).

Prior to establishing this standard, it was found that there was no evidence that removing the charcoal from the detector affected the results significantly. Some early detectors were constructed of aluminum screen, but the alkaline elutriant reacted with the aluminum to produce a green solution which interfered with at least the visual determination of the presence of fluorescein. In addition to the elutriating solution described above, experiments were conducted with both 5% KOH - 95% ethanol and 5% NaOH-95% ethanol. No consistent differences were found in the behaviour of the three elutriants, and the "Smart solution" was adopted, primarily due to the difficulty of obtaining ethanol. As might be expected, one design feature that did significantly affect results was the number of layers surrounding the charcoal, with more layers tending to reduce the contact of the charcoal with the dye solution, resulting in less fluorescein being adsorbed.

The results of one experiment designed to investigate the relationship between detector immersion time in the system, elutriation time, and fluorescent intensity of the elutriant is presented in Table El. It will be noted that there is apparently rapid dye adsorption during the first day, but that dye continues to be adsorbed during later days. Elutriation of the dye is very rapid, and that the dye concentration in the elutriant falls with time after the first day.

	Elutriation Time (days)		
Immersion Time (days)	1	2	3
1	1.04	0.64	0.37
2	1.57	1.29	0.65
3	2.30	1.53	0.96
4	2.70	1.84	1.24

Table El. Elutriant Intensities. Fluorescein concentration 10ppb distilled water. Elutriant 32.5% NH_4OH, 43.0% 1-propanol, 24.5% distilled water.

E4. Conclusions

Although the many uncertainties associated with the studies resulted in their having little quantitative value, they did result in the design of efficient detectors which were utilized in a number of traces in the field (Thrailkill, et.al., 1982) when evaluated visually. Additional investigations (see Section G) with fluorescein have been designed using the background information acquired in these early studies, especially the importance of pH control.

The original objective of developing a technique to quantify the response of charcoal detectors to fluorescein has obviously not been attained, however. As shown in Table El, the fluorescein concentration of the elutriating solution does not come to equilibrium with the fluorescein adsorbed on the detector in any reasonable time. In retrospect, it is likely that this is caused by the fluorescein being adsorbed from the dye solution only on the outer surfaces of charcoal grains which themselves are on the outside of the detector, since the flow of dye solution through the detector is much slower than flow across its surfaces. The decline in concentration in the elutriant with time is due to fluorescein rapidly removed from these surfaces being readsorbed by charcoal within the detector and within the individual grains. It would probably require many days or even weeks for the elutriant to come to equilibrium with all of the charcoal in the detector, and at dye concentrations in the detector so low that precision would be significantly impaired.

A more promising technique would thus be to agitate the detector in the elutriant for a short (on the order of a few minutes) fixed time interval and then remove the detector to prevent readsorption. Alternatively, a small amount of elutriant could be passed, at a constant rate, through a column containing the detector.

Due to the widespread use of charcoal detectors in fluorescein water tracing, further studies of this kind should be performed.

E5. References

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F. DATA PROCESSING

J. Thrailkill, G.K. Nelson, and P.E. Byrd

F1. Introduction

Several data processing tasks were undertaken during the project to support the various project objectives. All utilized the University of Kentucky's IBM 370-65 and remote terminal facilities. No attempt will be made to include listings of data files or programs in this report.

F2. Field Data Management

Becuase of the number of individuals involved in the field studies conducted during the project and the importance of the data collected, a computer data file was begun in 1976. Programs were also written to reformat the data and to plot locations on map overlays.

F2a. Bluegrass Karst Data File

The basic data file consists of information recorded for each site visited during field investigations. The various data are recorded in fields of variable or fixed length identified by an * followed by a two-letter identifier (Table F1). Initially, data entry was by key punch and the file archived on punch cards, but conversion to terminal entry and storage on hard disk with tape backup was completed early in the project. This allowed convenient access to the data and facilitated supervision of the field work by the principal investigator. At the conclusion of the project the file contained more than 8000 card images.

Identifier	Date
*BD	BUG (detector) DATA. Time and date detector placed and removed, detector type, results of detector evaluation and dye type.
*BI	BUG (detector) IN. Time and data detector placed and detector type. Replaced by *BD.
*BO	BUG (detector) OUT. Time and date detector removed. Replaced by *BD.
*BR	BUG (detector) RESULTS. Time and date detector removed, results of detector evaluation and dye type. Replaced by *BD.
*CO	COMMENT. Any information regarding site.
*DI	DISCHARGE measurement or estimate with information on how obtained and precision.
*ED	ELEVATION DATA. Elevation (altitude) of site.
*FE	FLOW ESTIMATE. Replaced by *DI.
*FM	FLOW MEASUREMENT. Replaced by *DI.
*LC	LOCATION COMMENT. To refine location data.
*LL	LOCATION by LATITUDE and longitude. Replaced by *LT.
*LS	LOCATION by SEVEN and one-half minute quadrangle. Replaced by *LT.
*LT	LOCATION by TWO and one-half minute quadrangle. The standard location method used in the project. Explained in Section A2 of Thrailkill, et. al. (1982).
*NA	Site NAME(S), ADDITIONAL.
*NC	NAME of COUNTY.
*ND	NAME and DATE. Name of investigator and date site first visited.
*NQ	NAME of QUADRANGLE.
*OA	OWNERSHIP and ACCESS information.

*SA	SITE type, ADDITIONAL. Other information on site type (see *ST).
*SN	SITE NAME and source of name, if appropriate.
*SS	SITE identification number SAME as identification number listed.
*ST	SITE TYPE. Two letter code indicating nature of site. (e.g., SP, spring; WE, well; SI, sinkhole).
*TI	TRACER INTRODUCTION. Time and date of dye introduction, type and quantity of dye.
*WN	WORKING NAME. Site name contracted to 10 characters and spaces.
*WS	WATER SAMPLE. Time and date collected and other pertinent data.

Table Fl. Bluegrass Karst Data File field indentifiers.

F2b. Data Conversion

A FORTRAN program, PROG2, was written to search the Bluegrass Karst Data File for sites located within a specified area and produce output arranged by location and containing information on site identification number, site type, working name, and other data from fields in the data file (Table Fl).

F2c. Map Plotting

The output from PROG2 is used as input to a second FORTRAN program written to process project data. This program, PLOT2, produces a map of a 2.5 x 2.5 minute quadrangle on a pen plotter and shows the location of all sites within the quadrangle, which is drawn at a scale of 1:24,000 and may be overlaid on the topographic map. A sample map, where the site type is indicated by a symbol and the working name is used as a label, is shown in Fig. Fl. A variety of plotting and labeling options are available.

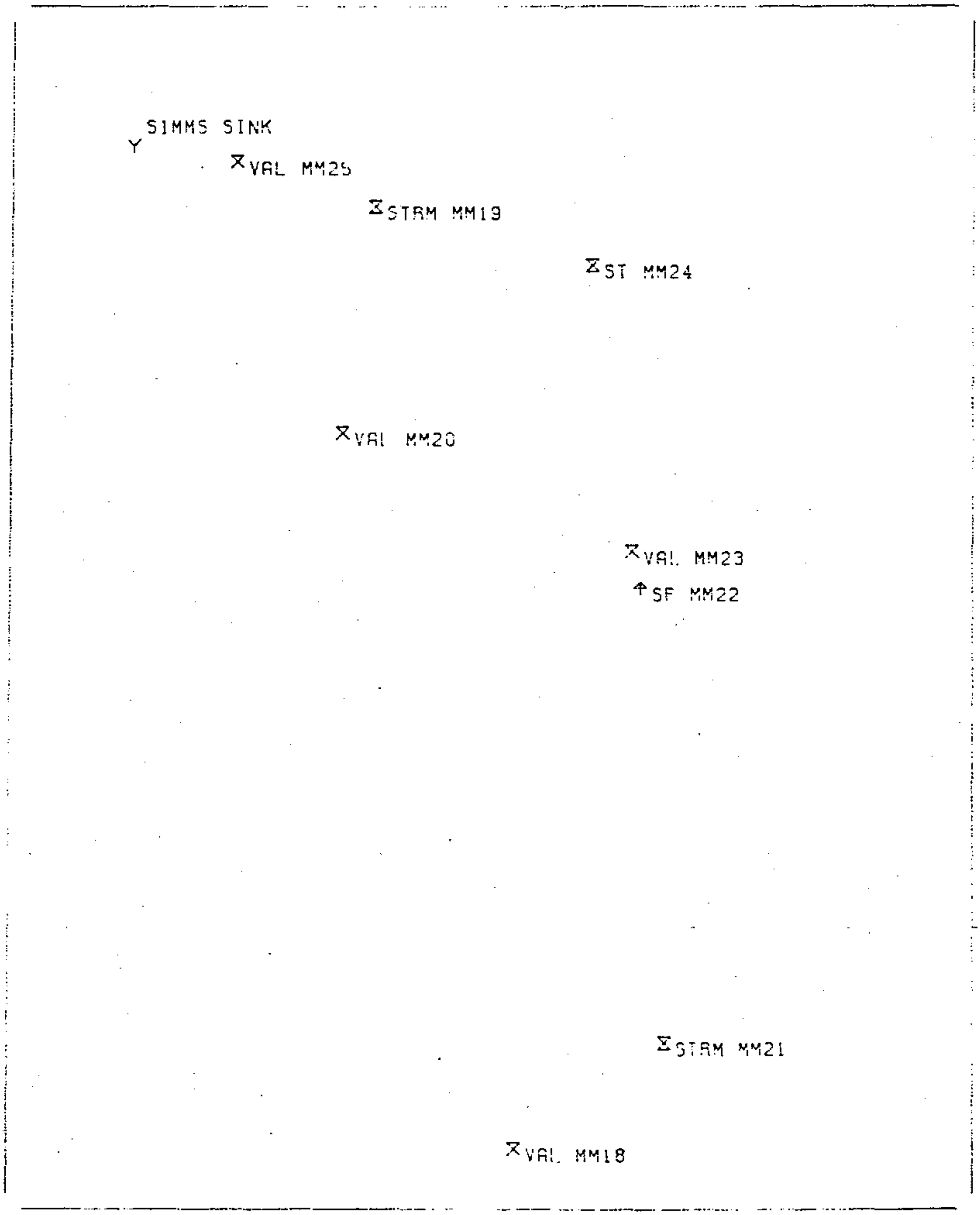

Figure F1. Sample map produced by PLOT 2.

MIDW SE

UK/I8KA/JT
02/07/80

F3. Fluorescent Intensity Mapping

During the investigation of the response of fabric detectors to optical brightener (Section C), a FORTRAN program FORMULAT GRID was written which accepts as input a matrix of spectrofluorometer intensities at excitation and emission wavelengths and produces log-transformed (optional) and reformatted output. This output was used as input into SURFACE II, a contouring package (Sampson, 1978), which creates an isopleth map of the data. Examples of such maps are shown in Fig. F2 for an undyed detector and in Fig. F3 for a detector exposed to 25 ppb optical brightener for 2 days. A comparison of the two figures shows the increase in fluorescence on the latter at an excitation wavelength of 335 nm (ordinate) and emission wavelength of 420 nm in Fig. F3 (see Section C for a discussion of optical brightener fluorescence). In both figures, the isopleths are in the log of the intensity, and the scattered high and low values probably represent errors in intensity determinations. The primary (diagonal high) and secondary (upper right) reflections from the fabric are clearly shown.

F4. References

Sampson, R.J., 1978. Surface II graphics system. Kansas Geological Survey, 240p.

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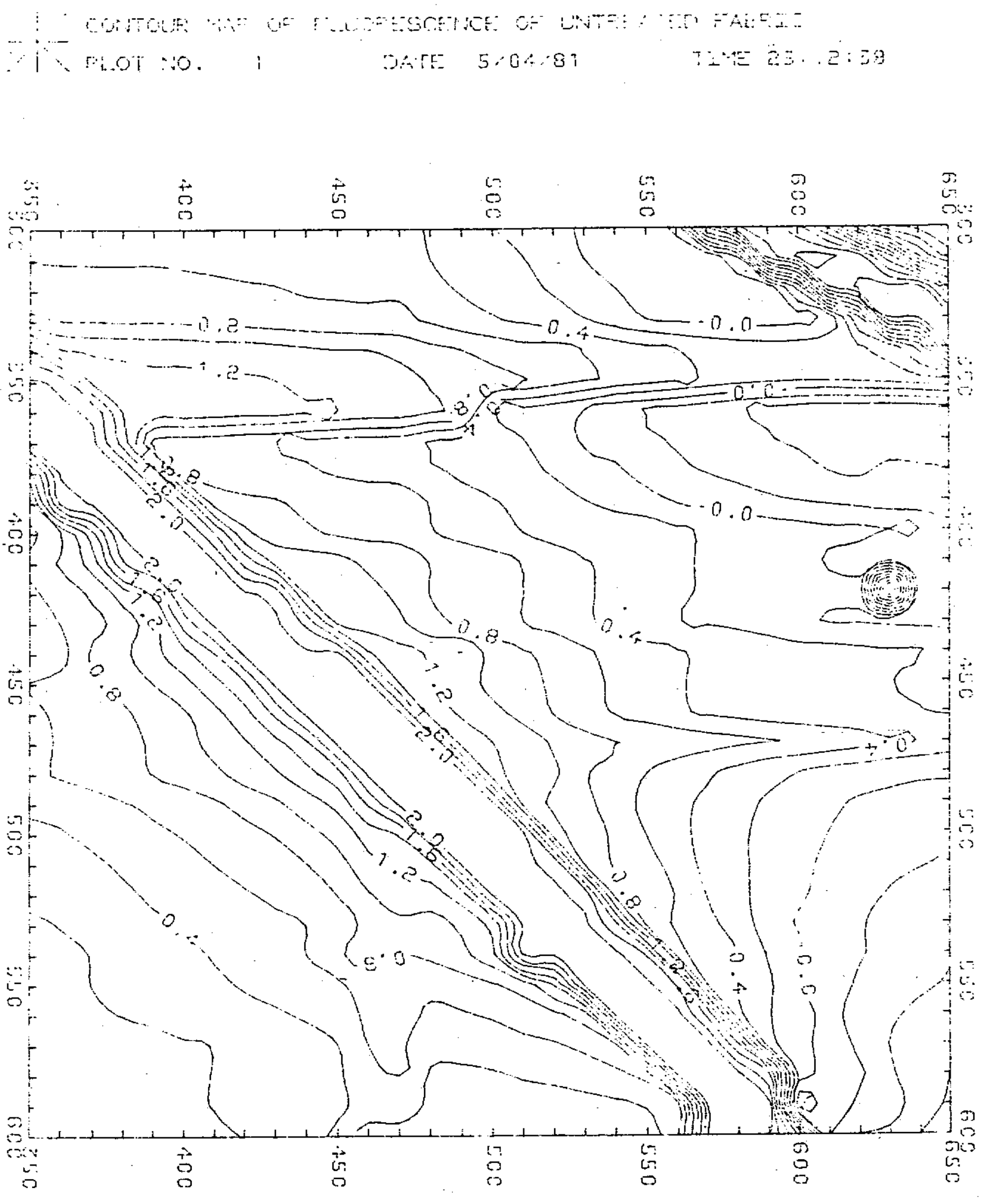


Figure F2. Fluorescence map of undyed fabric detector. See text for discussion.

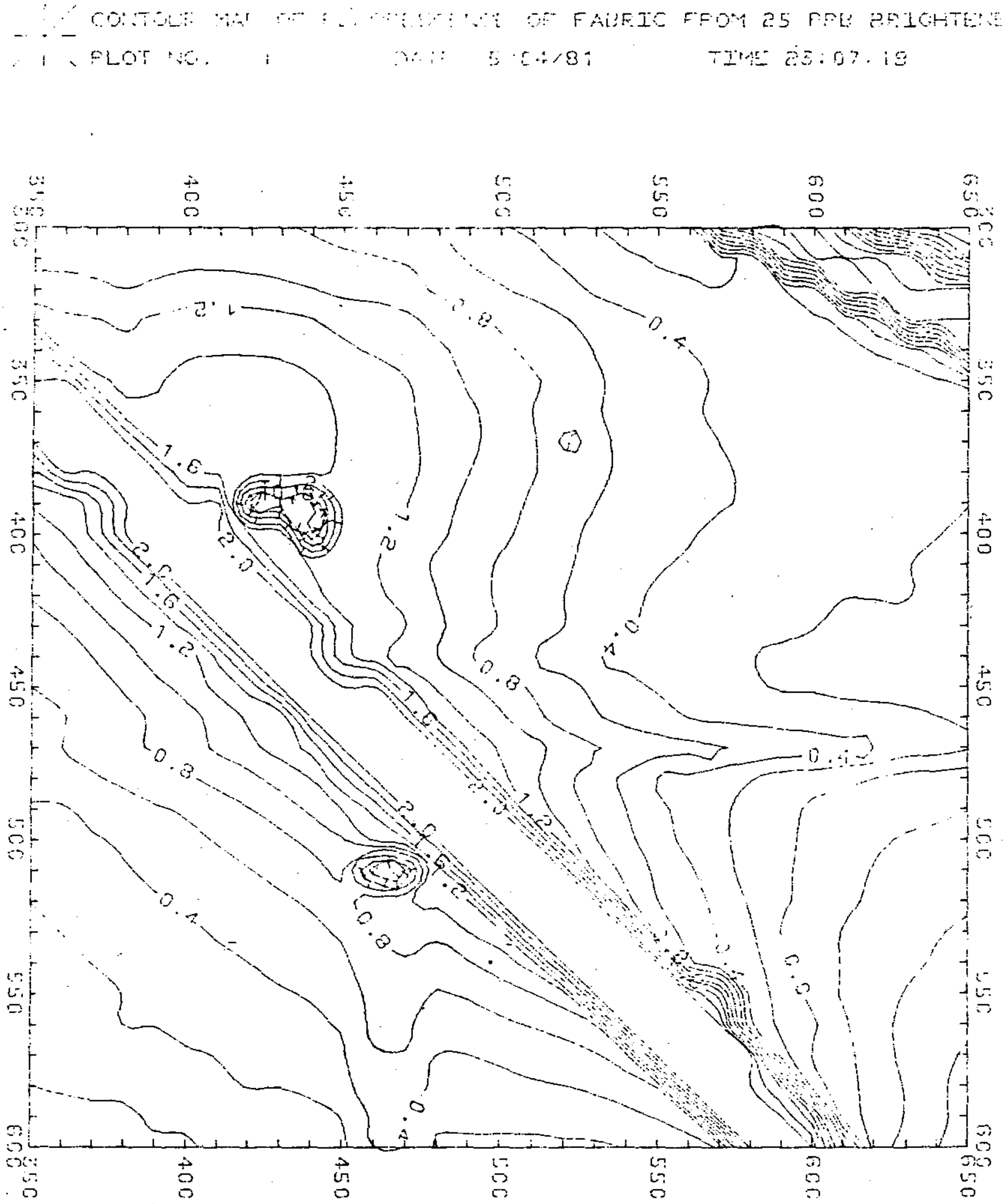


Figure F3. Fluorescence map of fabric detector dyed with optical brightener. See text for discussion.

G. QUANTITATIVE WATER TRACING IN TWO GROUNDWATER BASINS IN THE INNER BLUEGRASS KARST REGION, KENTUCKY

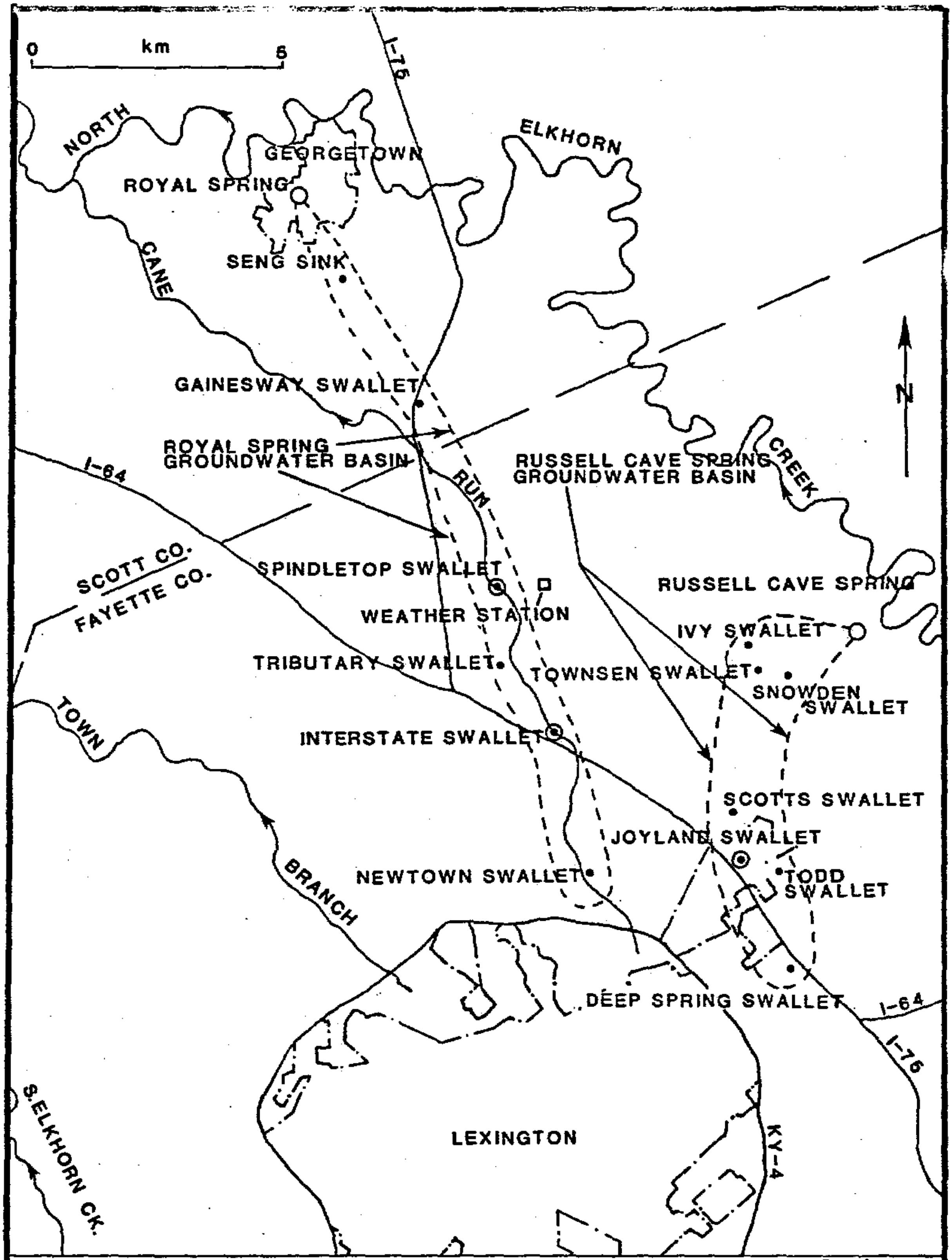
S.B. Sullivan and J. Thrailkill

G1. Introduction

The basins studied (Fig. G1) are in the Inner Bluegrass Karst Region, and information on the geology and hydrology of the area will be found in Thrailkill, et. al. (1982). In contrast to other water tracing in the area which had as its goal the delineation of groundwater basins, and utilized passive detectors to determine flow connections (Thrailkill, et. al., 1982), this study consisted of repeated traces conducted between swallets (sinking surface streams) and springs whose connection had been previously established. Water samples were collected using an automatic water sampler and dye concentrations determined in solution. Additional information on the study will be found in Sullivan (1983).

The results of the study were limited by several factors, of which two were predominant. Royal Spring was selected as the primary site to be investigated not only for its environmental significance (it serves as the primary water supply for the city of Georgetown), but because a gaging station was planned to be installed by the beginning of the study (the first on any spring in the region). Delays in its construction, and malfunction of its recorder after installation, resulted in its being unable to furnish any data for the study. Second, the most useful data generated during the study was from traces using both fluorescein and rhodamine (Rhodamine WT). The investigation was nearly complete before notification was received that Rhodamine WT had been approved by the Environmental Protection Agency for tracing into public water supplies.

Previous quantitative water tracing studies in karst are not abundant, being limited mainly to Brown, et. al. (1969), Brown and Ford (1971), Atkinson, et. al. (1973), and Smart (1980).



General Area of the Royal Spring and Russell Cave Spring Groundwater Basins in Northern Fayette and Southern Scott Counties,(From Thrailkill, et. al., 1982)

Figure G1. Location map.

G2. Methods

G2a. Discharge Determinations

Three techniques were used for spring discharge determinations. The first, individual current meter measurements, was used for Traces 1 and 2 at Royal Spring and Trace 3 at Russell Cave Spring. Velocity measurements were made at intervals of .30 or .61 m (depending on channel width) with a pygmy current meter (Teledyne Gurly 625) at .6 water depth. The Royal Spring measurements were made 115 m downstream from the spring in a natural channel below the impoundment. They were made at a time when water was not being withdrawn by the water service (which pumps a maximum of 175 l/s when in operation). At Russell Cave Spring, measurements were made approximately 100 m below the spring and 20 m downstream from the dam in a natural channel.

Discharge for Trace 4 at Russell Cave Spring utilized a rating curve (Fig. G.2) derived from current meter determinations and stage heights on a staff gage constructed of 2.5 cm pipe set in a concrete-filled plastic bowl. The upper portion of the pipe, which was marked in intervals with enamel paint, was tied to a tree.

As discussed in Section G1, anticipated discharge data from the newly installed gage at Royal Spring could not be obtained, and no discharge data is available for Traces 5 and 6. Periodic discharge during Trace 7 at Royal Spring were obtained from measurements of the depth of water flowing over a rectangular wier. The discharge was calculated using a rectangular wier formula (King and Brater, 1963).

The precision of the discharge measurements is difficult to evaluate, but believed to be on the order of 10- 20% (95% confidence interval) for the various techniques.

Precipitation records were collected at a weather station near the center of the area (Fig. G1) operated by the University of Kentucky.

G2b. Dye Tracing

Traces 1 through 5 were conducted with fluorescein, and traces 6 and 7 utilized both fluorescein and rhodamine (Rhodamine WT).

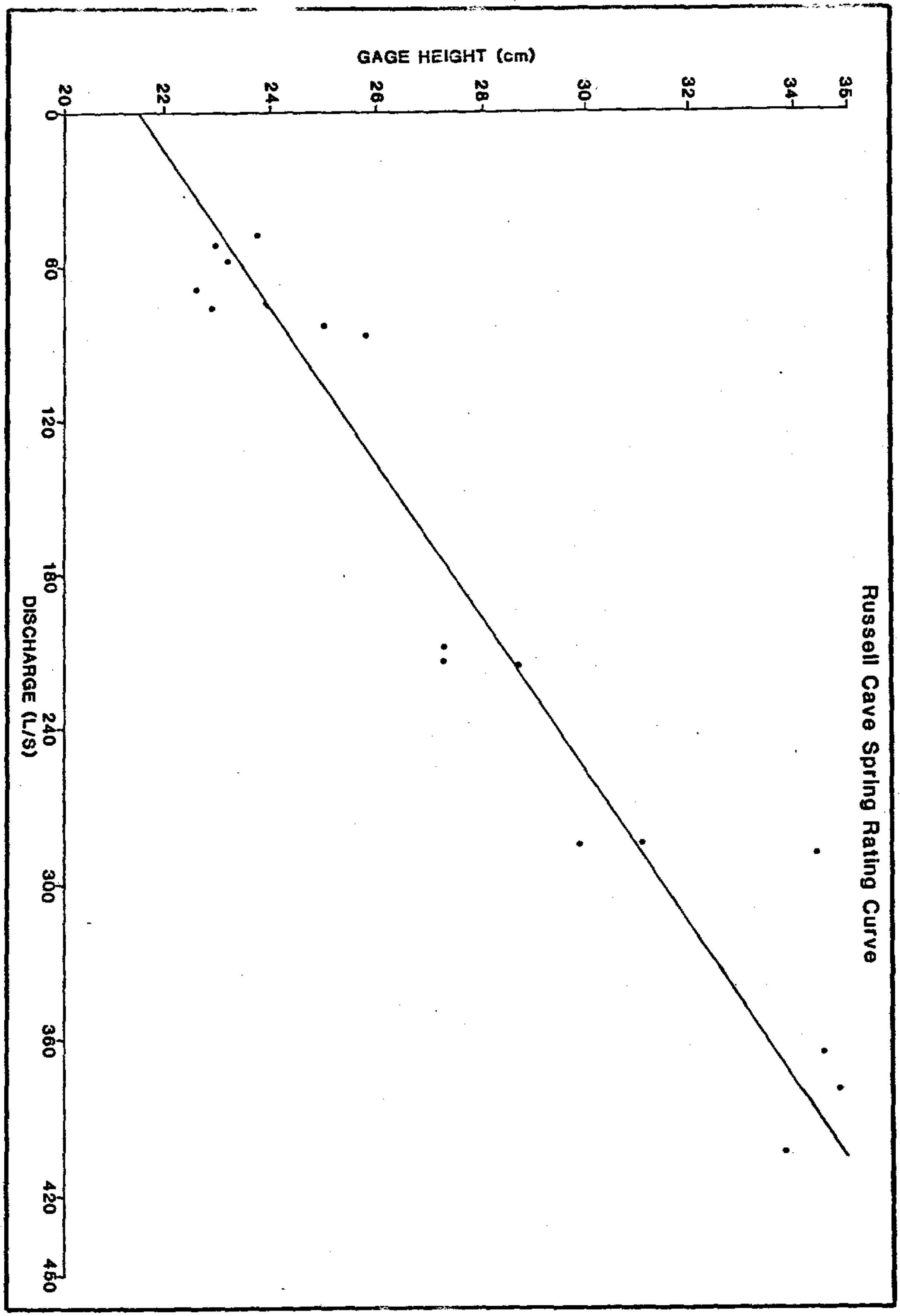


Figure G2. Russell Cave Spring discharge rating curve.

Information on both dyes will be found in Section B. Because neither dye had previously been used for quantitative tracing in the region, the shape of the dye hydrograph to be expected was not known. Although recent sewer tests using fluorescein by others in the city of Georgetown had produced strong visual coloration of Royal Springs, it was planned to keep the peak concentration of fluorescein below the visibility limit of about 100 ppb. This concentration slightly exceeded (123 ppb) on Trace 5 due to the smaller than expected dispersion in this first trace from a more distant swallet. The maximum concentration of Rhodamine WT produced at Royal Spring was 57 ppb, which is less than approved limits (Section B). Fluorescein was introduced in powdered form for Traces 1 through 5 and in solution with rhodamine and water for Traces 6 and 7.

Water samples were collected with an automatic water sampler (ISCO Model 1680) powered by a line current at Royal Springs and by a nickel-cadmim battery pack at Russell Cave Spring. The pumping mechanism of the sampler reverses both prior to and following sample collection to clear the 6 m sampling tube.

The fluorescent intensities were determined in a spectrofluorometer using equipment and techniques described in Section B. Fluorescein was evaluated at an excitation wavelength of 484 nm and emission wavelength of 507 nm; rhodamine at 558 and 582 nm, respectively. A major depression of fluorescein intensities in distilled water, as discussed in Section E, was found. Much steeper working curves were obtained with buffered distilled water, which was nearly the same as a working curve for solutions made up with a sample of water from Russell Cave Spring (Fig. G3). Working curves used to evaluate the field samples from Traces 4 through 7 were determined from standards buffered to a pH of 7.8 (considered to be average for the spring waters) and concentrations from Traces 1, 2, and 3 were corrected. Solutions were buffered by the addition of $NaHCO_3$ to distilled water which had previously been acidified with HCl .

Before conducting traces using both fluorescein and rhodamine simultaneously, it was necessary to determine if either dye interfered in the determination of the other. Emission spectra of high concentration

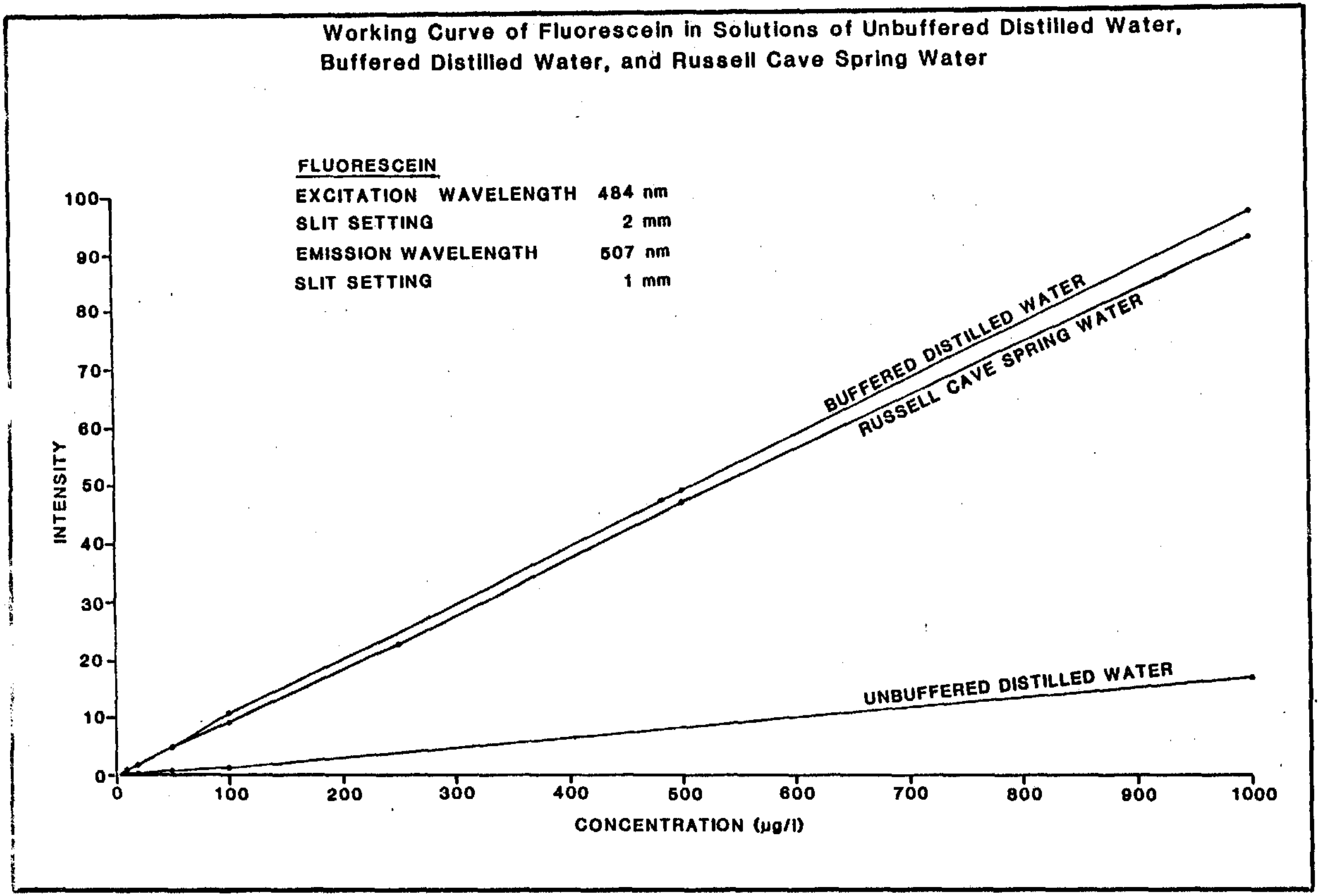


Figure G3. Fluorescein working curves.

mixtures of the two dyes compared with the spectra of the single dye are shown for fluorescein (Fig. G4) and Rhodamine (Fig. G5). It is apparent that the enhancement of the intensity of one dye by another is very slight at the emission wavelengths used (507 nm for fluorescein and 583 nm for rhodamine), and could probably be reduced even more by a slight shift in the emission wavelengths. Working curves for each dye in the presence of the other are shown in Figs. G6 and G7.

G3. Results

Dye hydrographs, discharge measurements, recorded precipitation, and other pertinent data are shown on Figs. G8 through F14. Additional data for each trace is given in Table G1.

Spring Resurgence	RS	RS	RC	RC	RS	RS	RS	RC	RC
Trace	1	2	3	4	5	6F	6R	7F	7R
Dye	FL	FL	FL	FL	FL	FL	RH	FL	RH
Intro. Time	1440	1325	1200	1235	1545	1025		1345	
Intro. Date (1981)	Spindeltop 16 Feb	13 Mar	13 Apr	27 May	Interstak 31 Jul	11 Aug		28 Oct	
Time to Centroid (hr)	32.08	23.46	75.26	17.42	NA	NA	NA	78.03	79.21
Surf. Temp. (C) Max/min	19/-3	17/-6	27/2	29/11	33/15	29/13		24/6	

Table G1. Trace Data.

G4. Discussion

The results of the dye tracing experiments in the Royal Spring and Russell Cave Spring groundwater flow furnish information on the nature of subsurface flow in the major conduit of these basins that was not previously available.

G4a. Dye Recovery

Total volume of dye emerging at the spring may be determined from

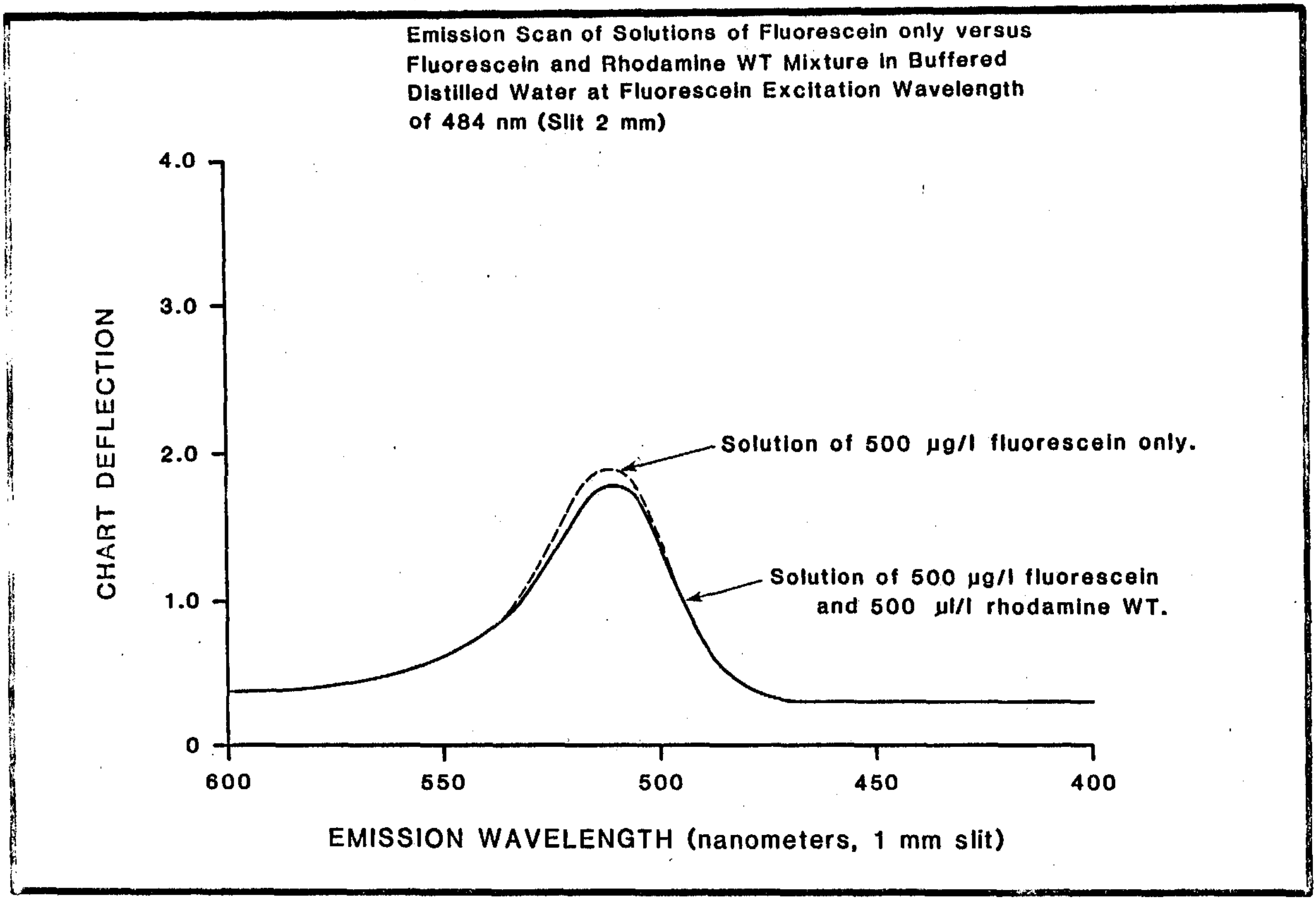
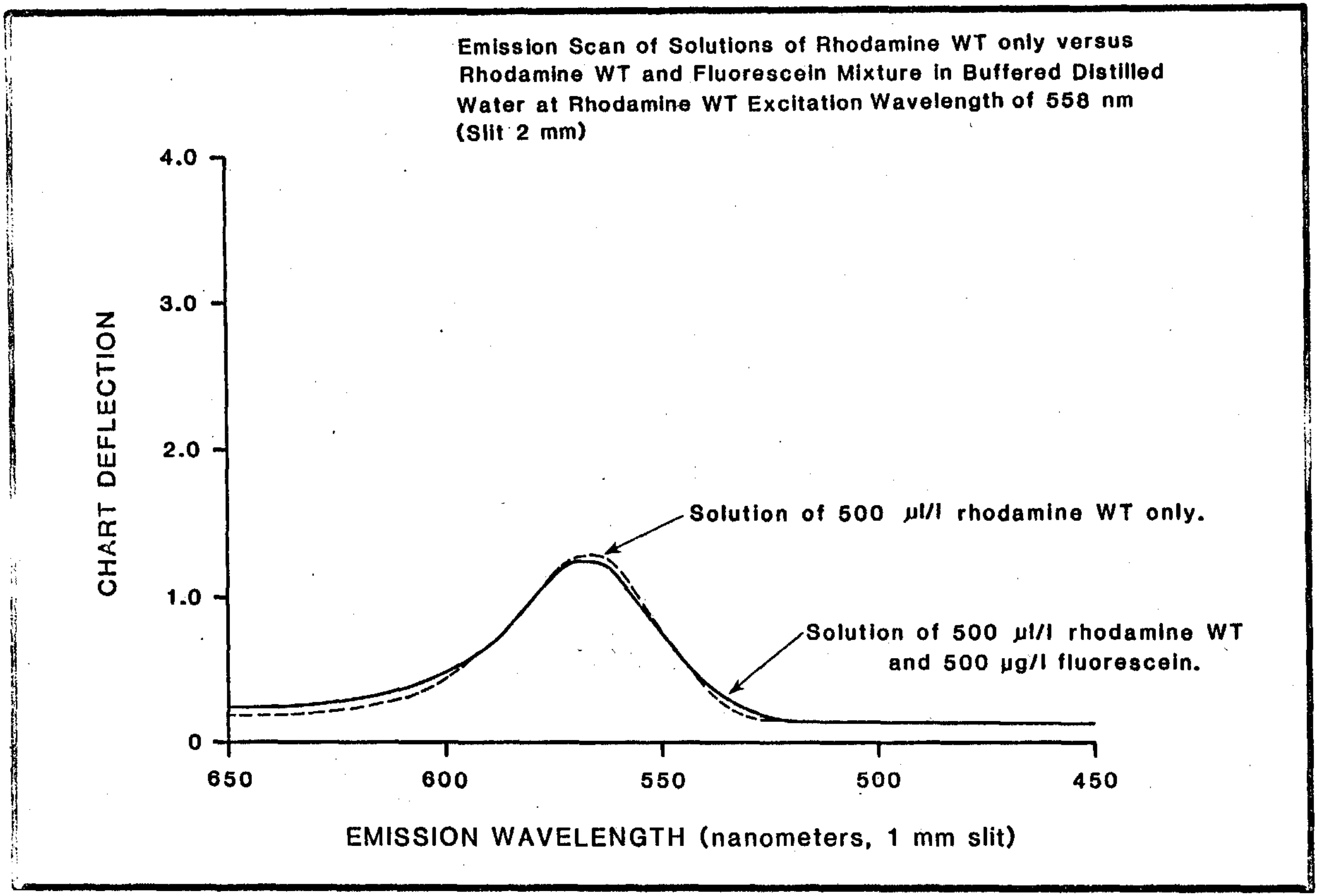


Figure G4. Fluorescein emission spectra.



Emission Scan of Solutions of Rhodamine WT only versus Rhodamine WT and Fluorescein Mixture in Buffered Distilled Water at Rhodamine WT Excitation Wavelength of 558 nm (Slit 2 mm)

Figure G5. Rhodamine emission spectra.

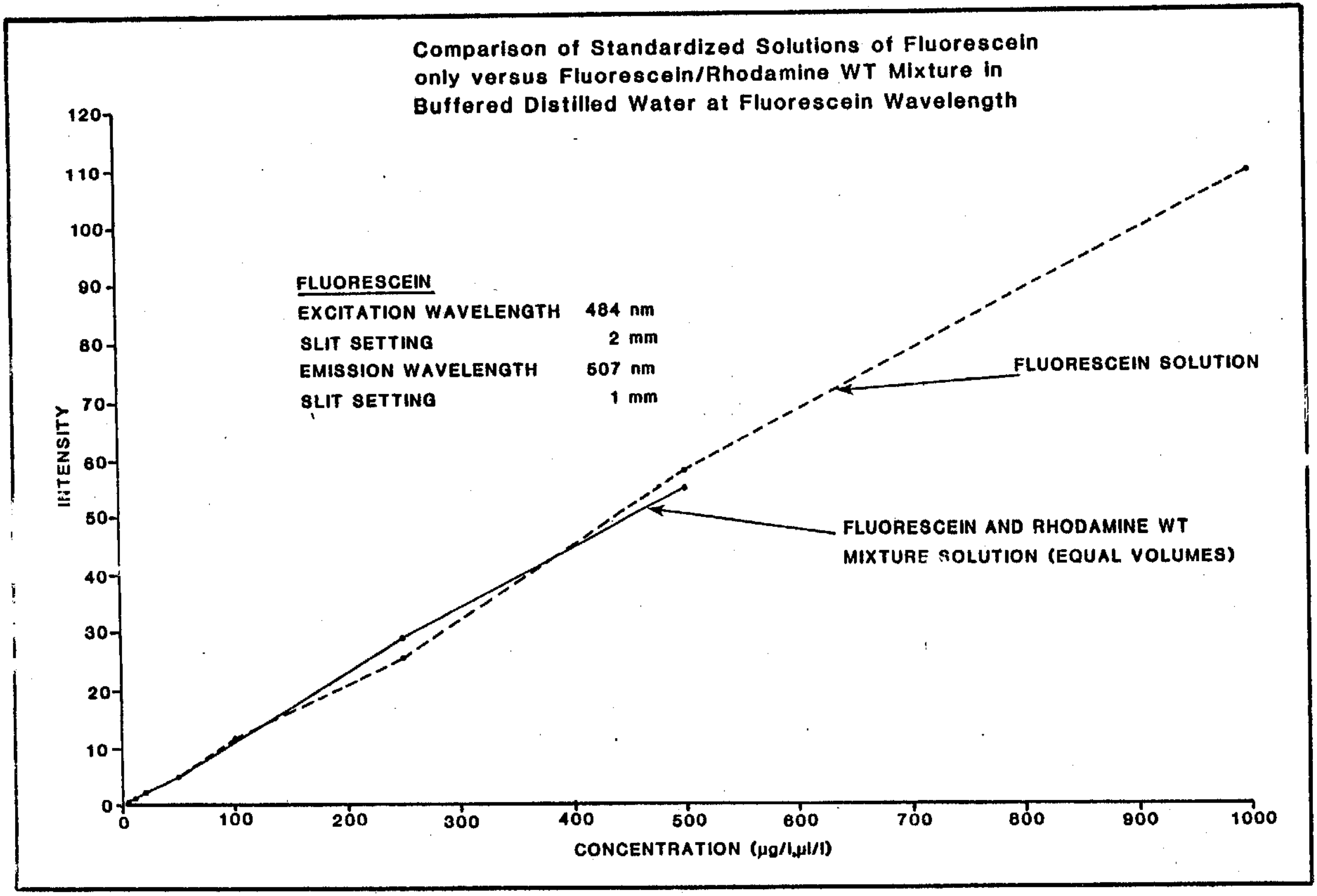


Figure G6. Fluorescein working curve in presence of rhodamine.

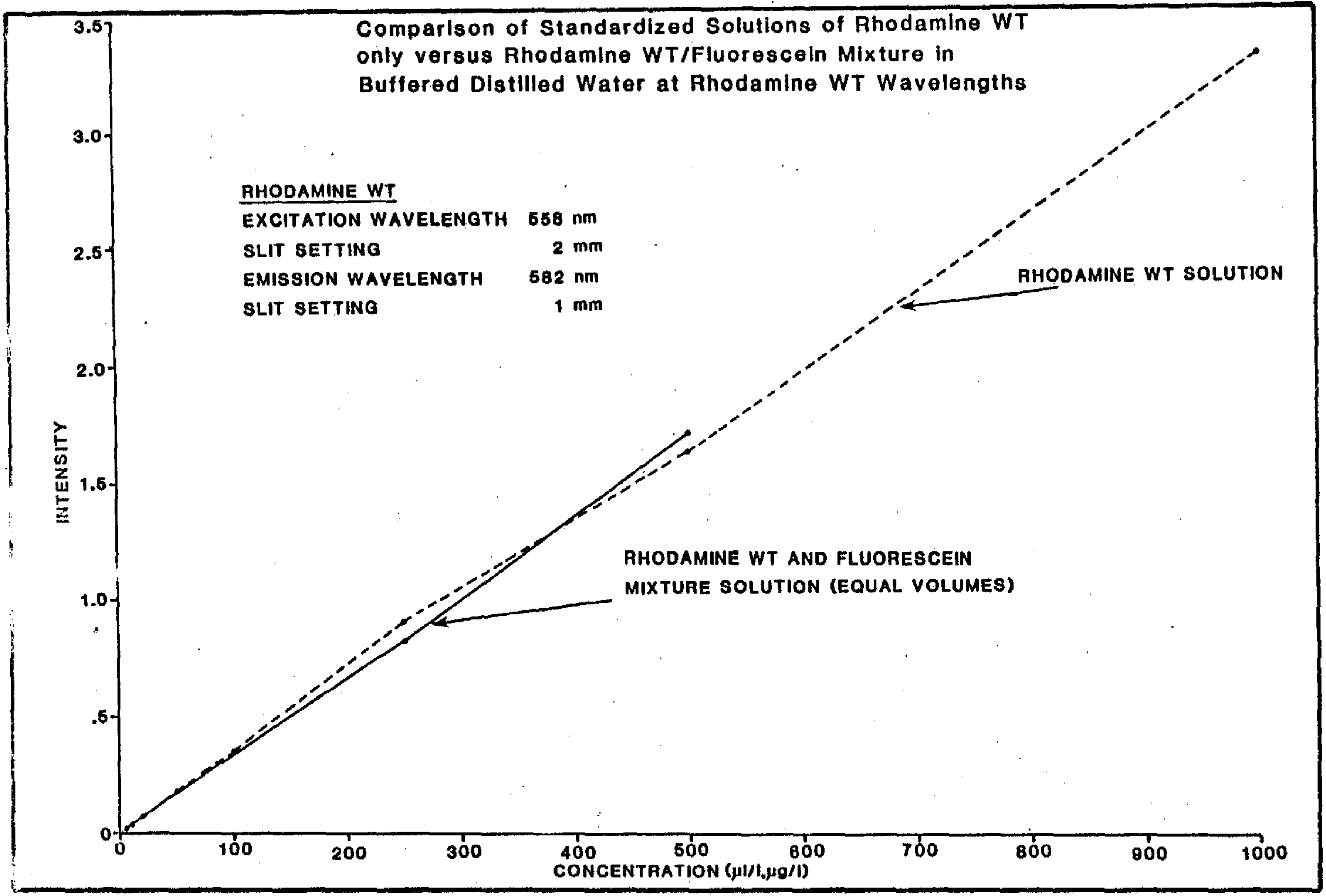


Figure G7. Rhodamine working curve in presence of fluorescein.

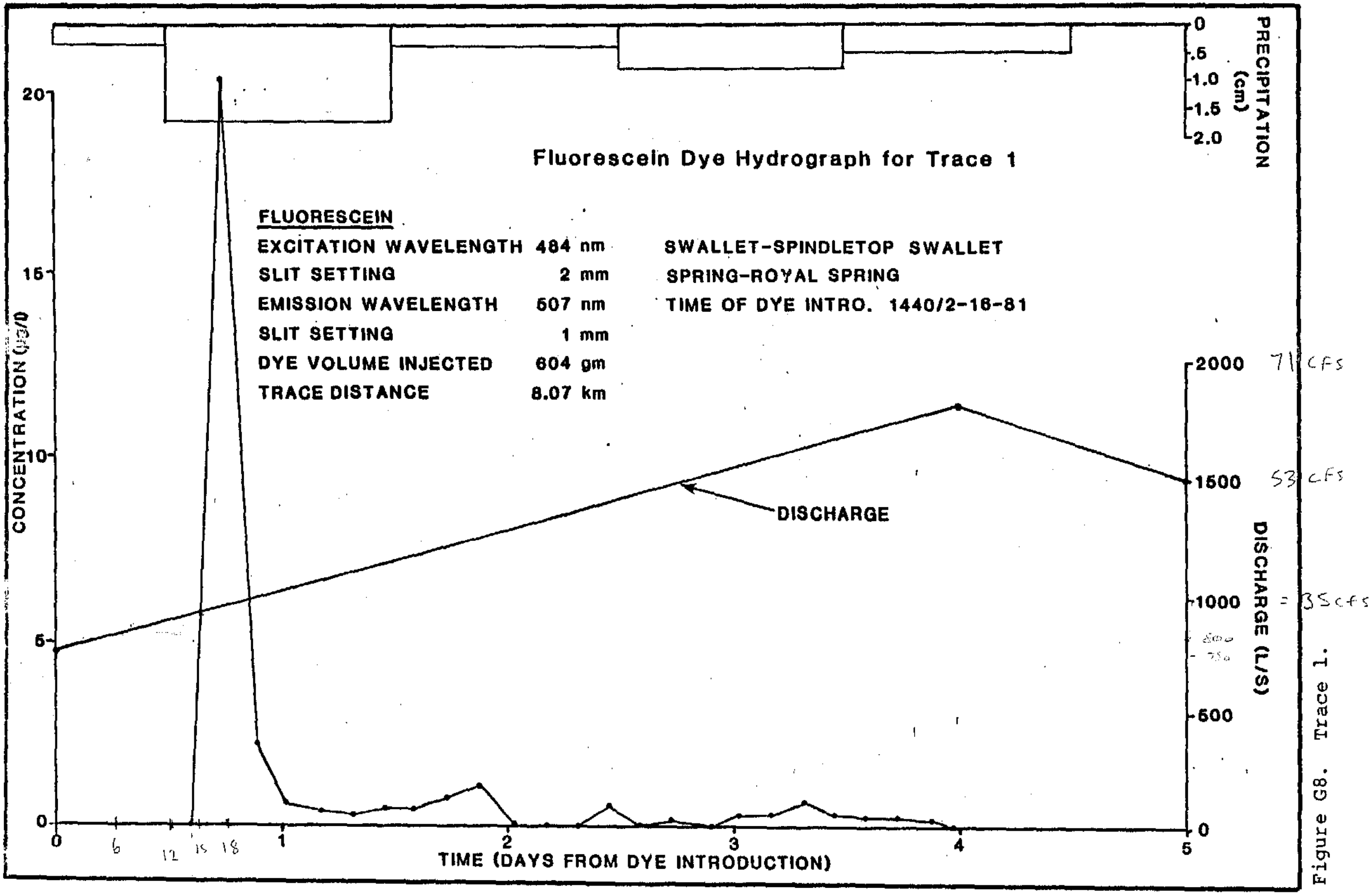


Figure G8. Trace 1.

flows @ 26 cfs

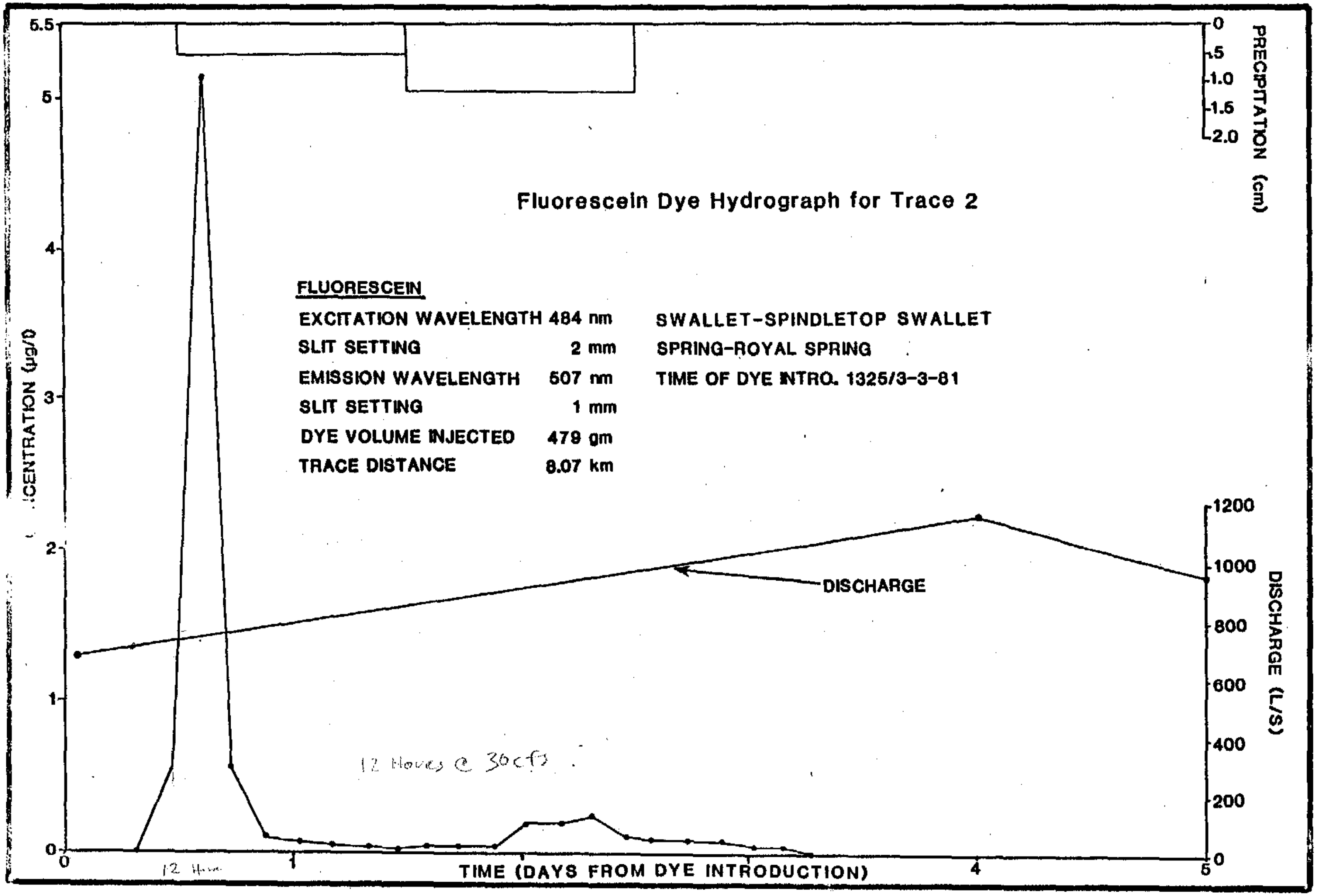


Figure G9. Trace 2.

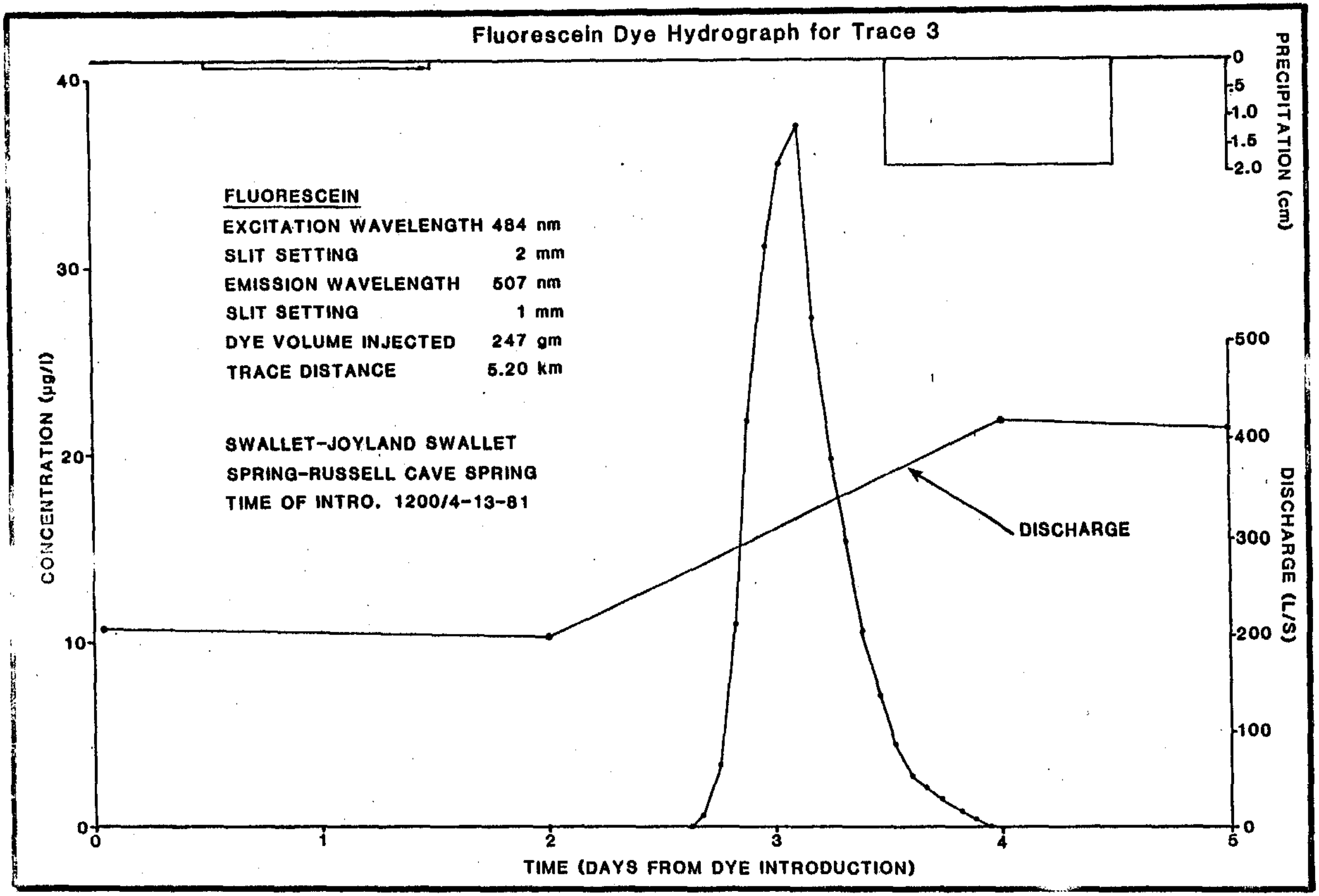


Figure G10. Trace 3.

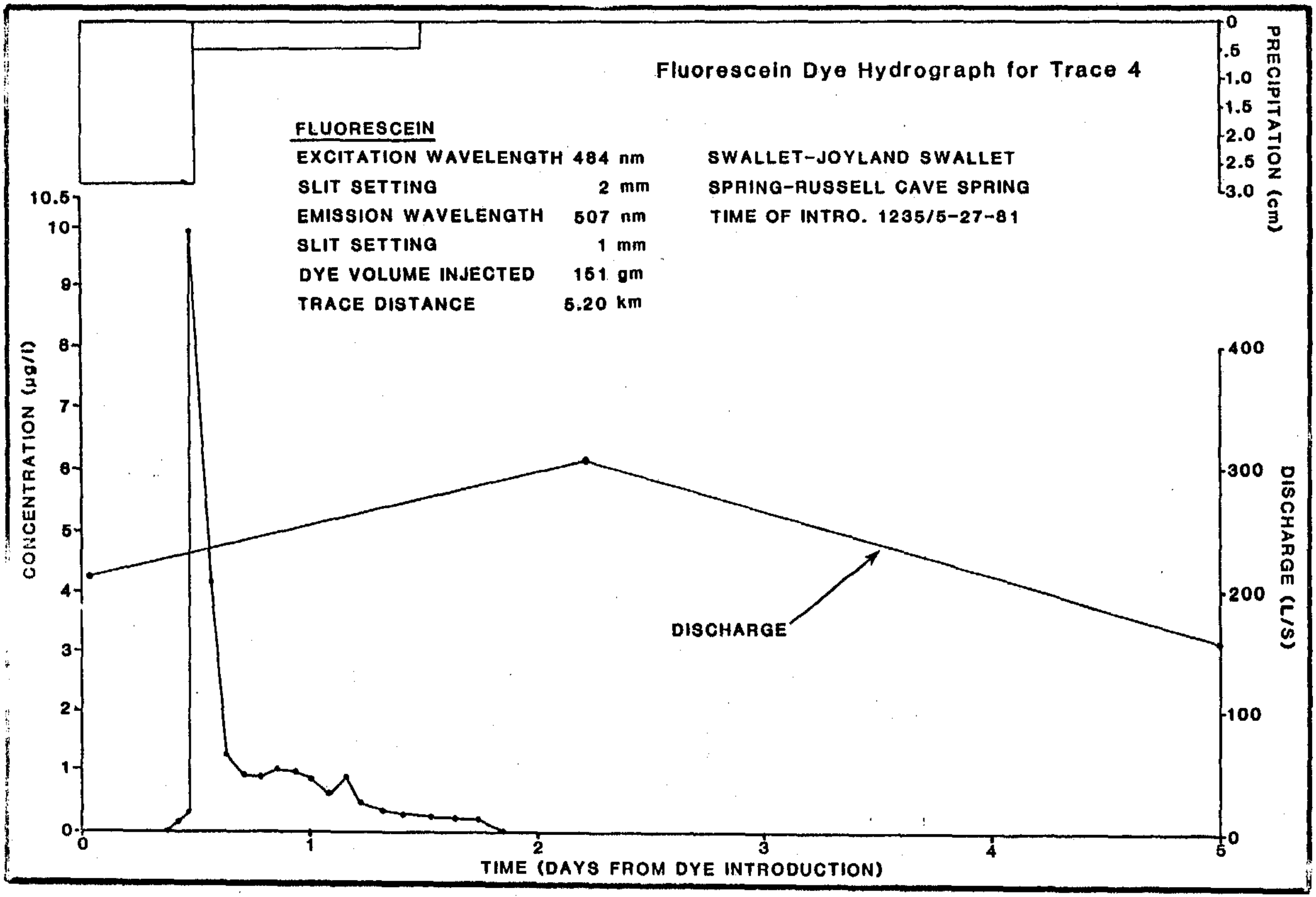


Figure G11. Trace 4.

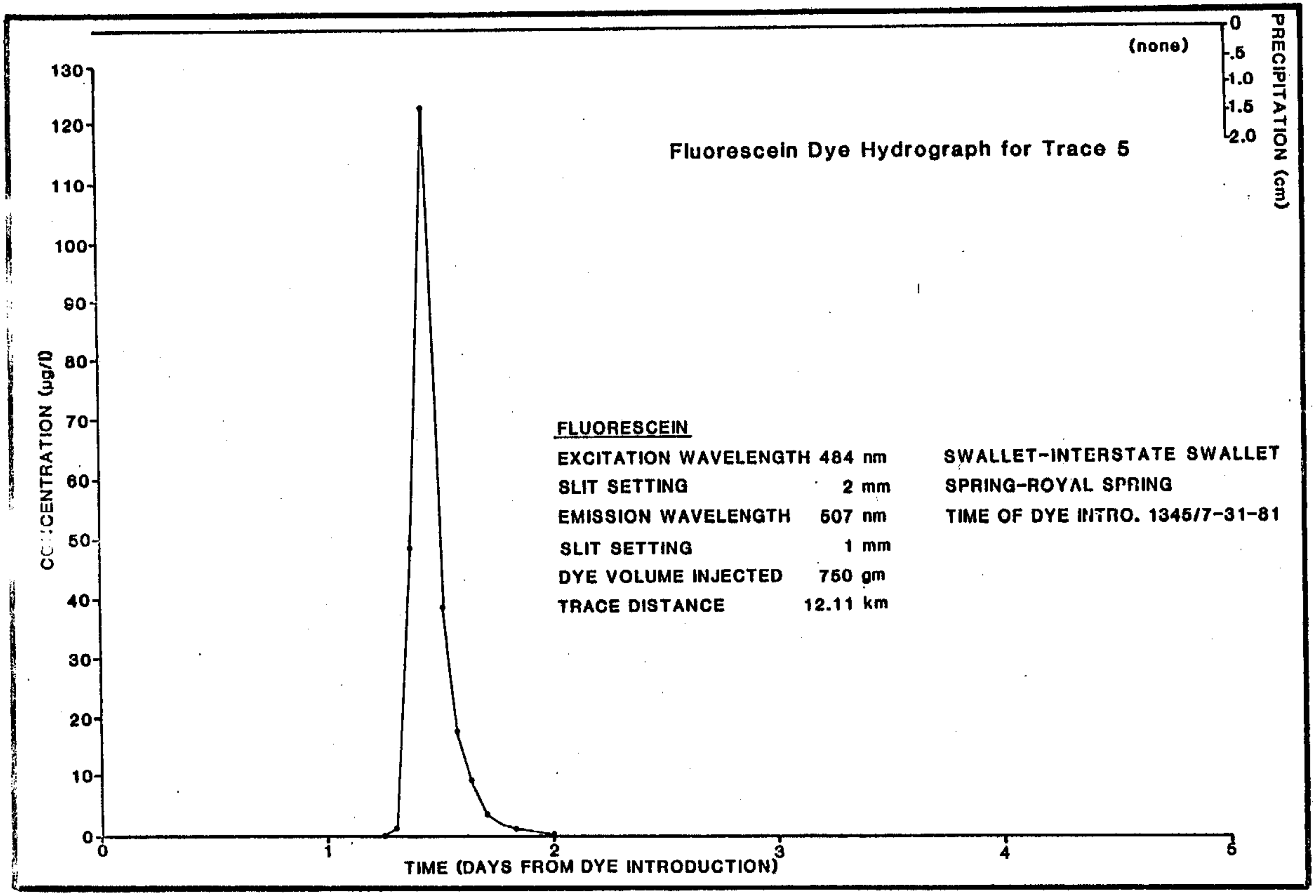
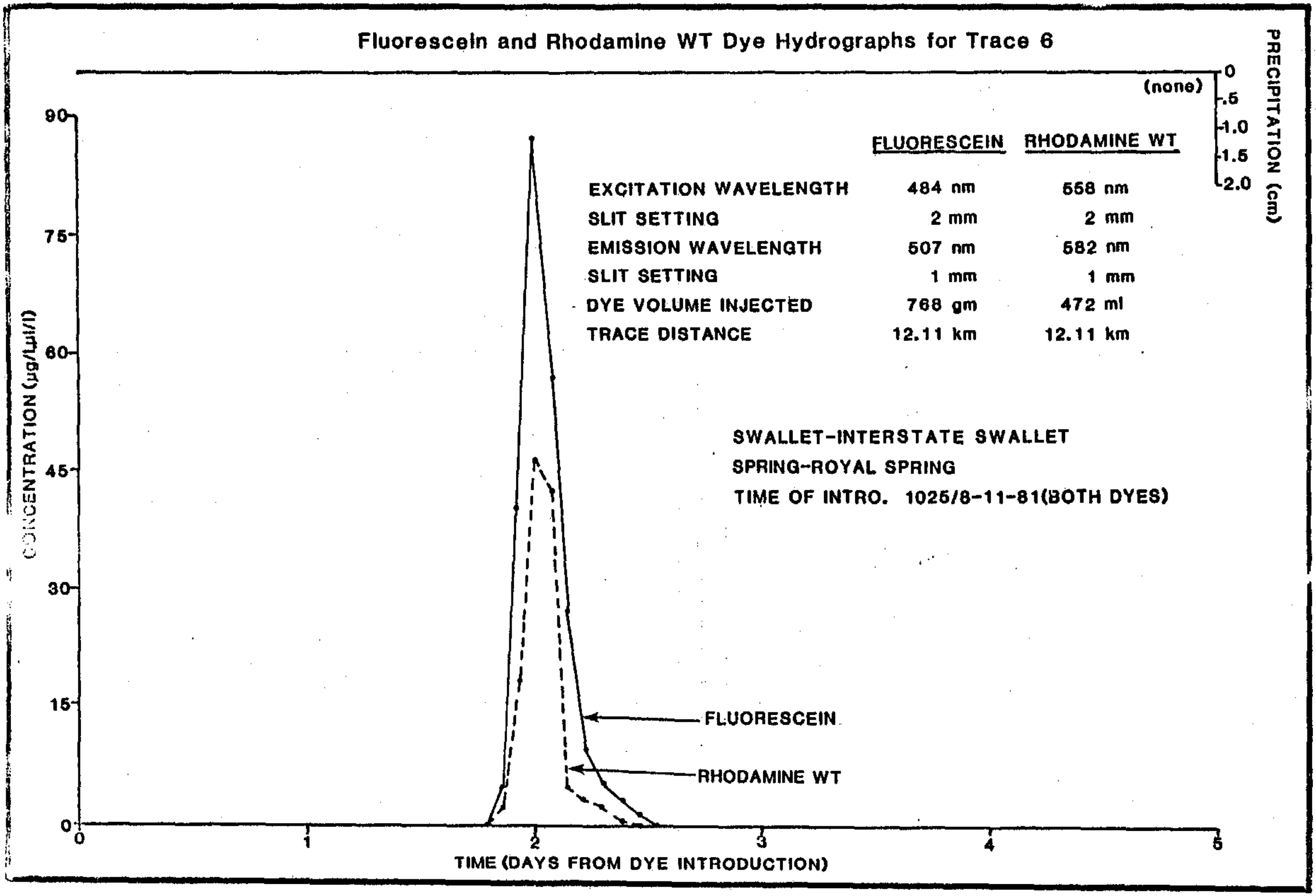


Figure G12. Trace 5.

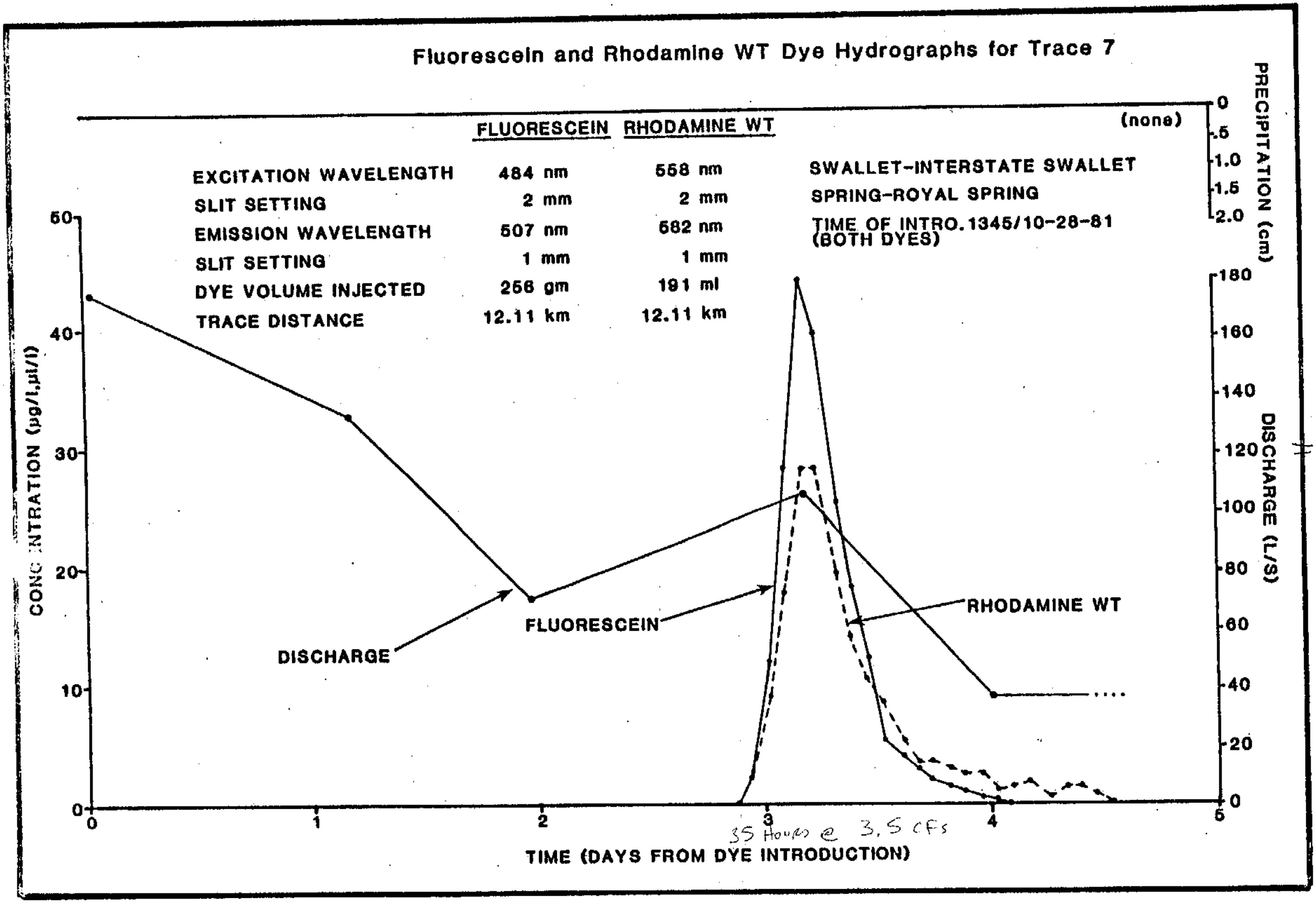


Fluorescein and Rhodamine WT Dye Hydrographs for Trace 6

	FLUORESCEIN	RHODAMINE WT
EXCITATION WAVELENGTH	484 nm	558 nm
SLIT SETTING	2 mm	2 mm
EMISSION WAVELENGTH	507 nm	582 nm
SLIT SETTING	1 mm	1 mm
DYE VOLUME INJECTED	768 gm	472 ml
TRACE DISTANCE	12.11 km	12.11 km

SWALLET-INTERSTATE SWALLET
SPRING-ROYAL SPRING
TIME OF INTRO. 1025/8-11-81(BOTH DYES)

Figure G13. Trace 6.



	FLUORESCEIN	RHODAMINE WT
EXCITATION WAVELENGTH	484 nm	558 nm
SLIT SETTING	2 mm	2 mm
EMISSION WAVELENGTH	507 nm	582 nm
SLIT SETTING	1 mm	1 mm
DYE VOLUME INJECTED	256 gm	191 ml
TRACE DISTANCE	12.11 km	12.11 km

= 4.23 cfs

35 Hours @ 3.5 cfs

Figure G14. Trace 7.

the dye and discharge hydrographs and, when ratioed to the volume introduced, yields the total dye recovery. Calculated dye recoveries (fluorescein) in Traces 1 through 3 at Royal Spring ranged from 16% to 155%. This was probably due mainly to inaccuracies in the working curve for fluorescein used for these traces. Working curves for these three traces were derived by correcting the original unbuffered working curves by a constant factor, since the original samples had already been discarded when the importance of pH control was determined (see Section G2b).

The fluorescein recovery during Trace 4 at Russell Cave Spring was 27%, and no discharges were available for Traces 6 and 7 (see Section G2a). Trace 7 yielded recoveries of 49% for fluorescein and 50% for rhodamine. Although the uncertainties associated with the various measurements (especially discharge, see Section G2a) would seem to limit the precision of recovery calculations, the close correspondence of the fluorescein and rhodamine values for Trace 7 suggest that a substantial fraction of the dye, and hence the water in the system, does not emerge at the spring. This flow probably enters the stream downstream from the spring, inasmuch as field studies in the area have not shown the flow diverted into other springs outside a basin (Thrailkill, et. al., 1982).

Russel Cave

The close correspondence of the recovery values for the two dyes in Trace 7 suggests also that neither dye is being adsorbed or decomposing significantly, since their characteristics are known to be quite different (Smart and Laidlaw, 1977). Further, there is little evidence of significant retardation of one dye relative to the other, as shown by the coincidence of the dye hydrographs on Fig. G13 and G14.

G4b. Conduit Flow Characteristics

Flow velocity (V) was calculated from the time interval between dye introduction and the dye hydrograph centroid (time at which one-half the recovered dye volume has emerged), and the straight-line distance between the dye introduction point and the spring. Mean discharge (D) for the period is in transit may be determined (or at least estimated) from the discharge measurement, and ratioing D/V yields the average cross sectional area of the conduit. Using any reasonable assumption of conduit shape, the value of the Reynold's Number is so high that it is certain that the flow mode in the conduit is turbulent, unlike the laminar (Darcy) flow of granular aquifers. In addition, the cross sectional area calculated varies with discharge, indicating the flow is in an open channel with a free surface. These relationships will be further discussed below.

G4c. Velocity - Discharge Relationships

Water from Royal Spring serves as the primary water supply for the city of Georgetown, and Russell Cave Springs drains to North Elkhorn Creek upstream from Georgetown, and the creek serves as Georgetown's secondary water supply. The groundwater basins of the two springs underlie interstate highways, major rail lines, and industrial areas of Lexington (Fig. G1). One of the primary goals of the project, therefore, was to provide the operators of the municipal water supply with information on flow velocities as a function of discharge so that the travel time and duration of a pollution spill in the groundwater basin could be determined.

This relationship was found to be complex due to conduit and system geometry, as discussed below. A plot of flow velocity (V) versus mean discharge (D) for the various elements of the dye hydrograph of the traces run is shown for Royal Spring (Fig. G15) and Russell Cave Spring (Fig. G16). An envelope was fitted to the data in each diagram and the values obtained was used to construct Table G4 in the Conclusions (Section G6). The general relationship at Royal Spring is believed to be that velocity initially increases with discharge until the stream in the conduit overflows, increasing the cross-sectional area and causing a decrease in velocity (Fig. G15).

The same relationship may also hold at Russell Cave Spring (Fig. G16), but is obscured by uncertainties in discharge measurements (i.e., the discharges during Trace 3 are probably higher than those during Trace 4).

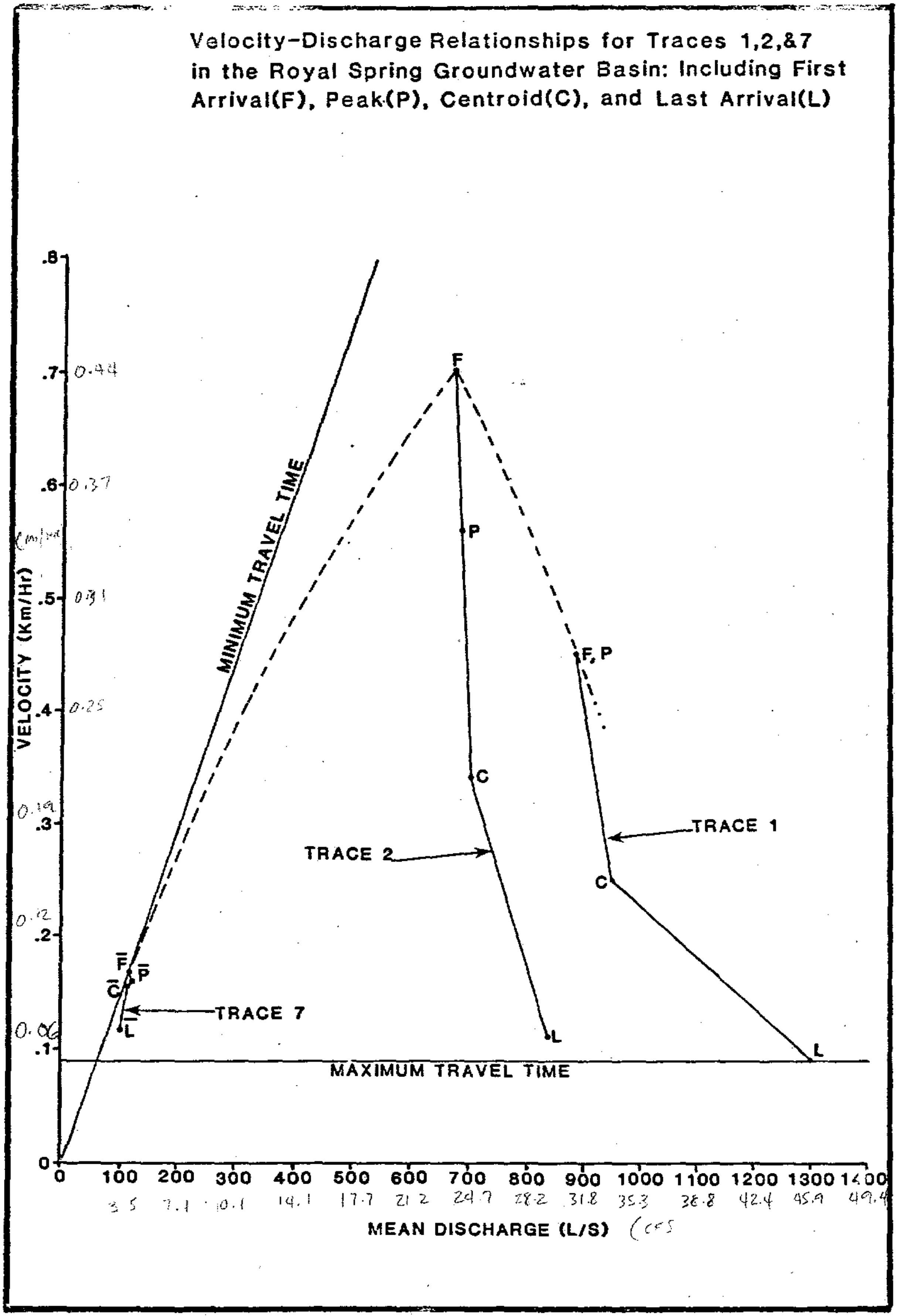


Figure G15. Velocity- discharge relationships for Royal Spring.

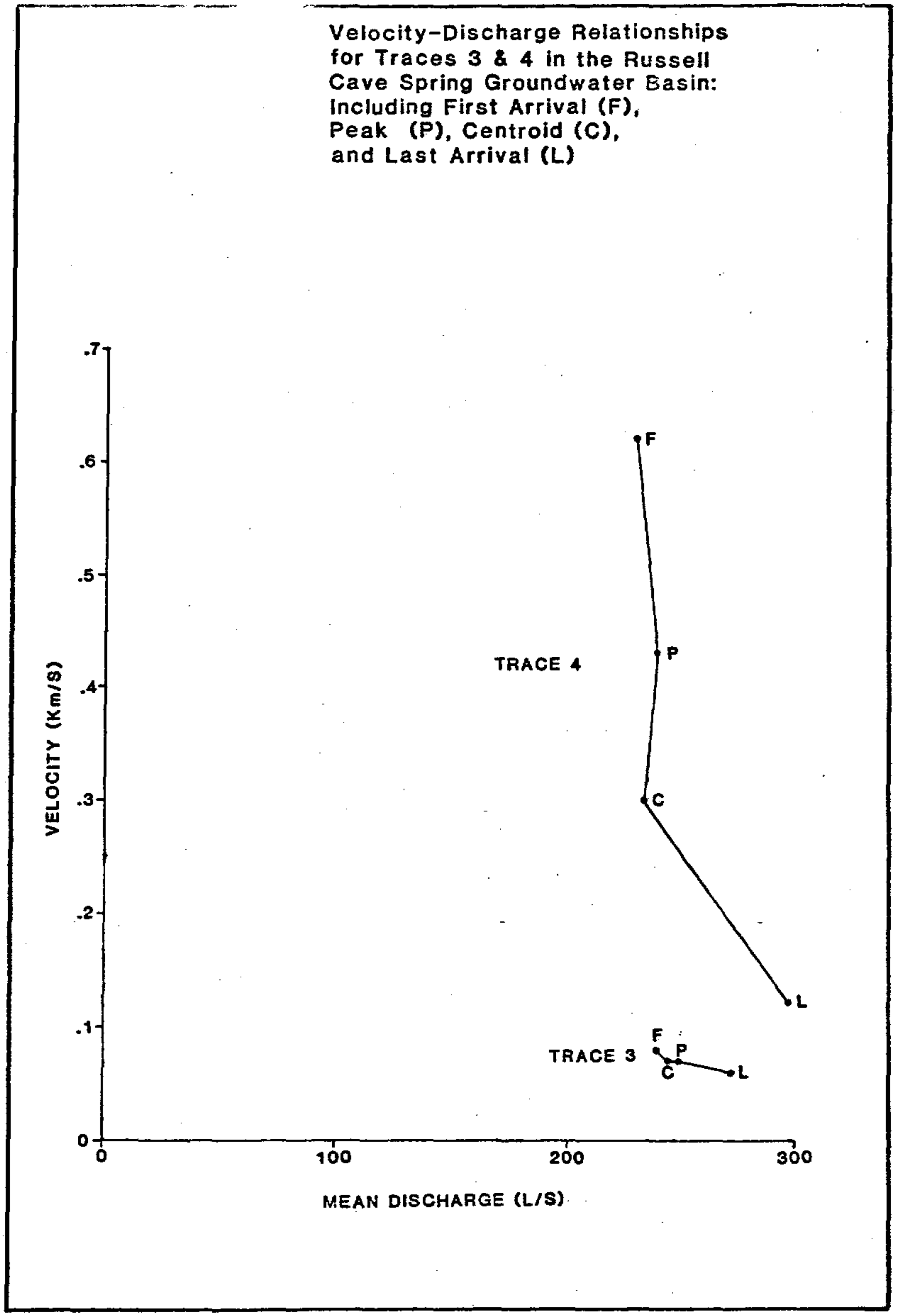


Figure G16. Velocity- discharge relationships for Russell Cave Spring.

G4d. Conduit Geometry

As discussed earlier there was no simple relationship between V, the velocity of the dye hydrograph centroid assuming a straight-line path between the swallet and the spring, and D, the mean spring discharge while the dye was in transit. Although V was higher for the trace (1) at high discharge than for the trace (7R) at lower discharges, it was even higher for the one (2) at intermediate discharges, as shown in Table G2.

Trace	$\bar{D}$(m 3/s	V(m/s)
1	.95	.069
2	.70	.094
7R	.11	.042

Table G2. Mean discharge and flow velocity for three Royal Spring groundwater basin traces.

Inasmuch as the flow is turbulent and with a free surface (G4c), it is evident that the usual equations of groundwater flow based on Darcy's Law do not apply. Instead, the best conceptual model would seem to be a channel in which flow similar to a surface stream occurs. The assumption is made that such a channel may adequately be considered to be rectangular. In such flow, the conveyance, K (defined below) replaces the hydraulic conductivity (K_D) of Darcy flow.

The basic equations are:

$Rh = AP^{-1} = wd(w+2jd)^{-1}$ (hydraulic radius of J rectangular channels)

$D = VA = Vwd$ (mass equation for rectangular channels)

$V = h^{-1}\ Rh^{.67}\ S^{.5} = KS^{.5}$ (energy equation)

$V = LT^{-1}$ (velocity defining equation)

$S = HL^{-1}$ (slope defining equation)

Where Rh is hydraulic radius, A is the cross-sectional area, P is the wetted perimeter, W the total width of J channels, J the number of channels (here assumed to be one), d the channel depth, D the discharge, V the velocity (straight line), n the Manning coefficient, S the slope of the energy line, L the (straight line) distance, T the time to centroid, and H the head difference. Later in the discussion values of L (and hence V and/or S) which are greater than the straight line distance will be employed.

Manipulation of these equations results in a quadratic equation for the depth d:

$$d = (1 - (1-42c)^{.5})(2a)^{-1}, \text{ where}$$
$$a = (2Jn^{1.5}H^{-.75}L^{3.25}T^{-1.5}D^{-1}, \text{ and}$$
$$c = (n^{1.5}H^{-.75}L^{2.25}T^{-1.5})$$

Thus the depth of flow can be calculated using measured values of T and D and estimated values of n,H, and L.

Observations made in accessible conduits in other groundwater basins in the region indicate a (Manning) roughness coefficient of .060 is appropriate. Flow in all major conduits is believed to be equilibrium flow (Thrailkill, et. al., 1982) similar to that in surface streams. If the headloss gradient is similar to that of Cane Run (a surface stream which overlies portions of the basin), the headloss (H) is approximately the same as the elevation difference between Royal Spring and the swallets into which the dye slugs were introduced. A smaller headloss at lower discharges is likely, however, and is evidenced by the observed water level in one of the swallets being at least 3 m below the land surface during such conditions.

The Royal Spring groundwater basin is quite linear (Fig. G1), and the length (L) of the principal conduit may be little greater than the straight-line distance between the swallet and the spring. At low discharges, however, observations in other conduits suggests the flow may follow a more tortuous path, thus increasing its length.

The results of these calculations are presented in Table G3 (see below for a discussion of the 7R* and 7R** entries).

The most striking feature is the very small value calculated for depth of flow (5 cm maximum) and, to a lesser degree, the large value for width. Although there are other indications (Thrailkill, et. al., 1982) that the Inner Bluegrass Karst Aquifer is quite thin, it is likely that the calculated values are too small, probably because of uncertainties in discharge and simplifying assumptions that had to be made to evaluate the limited number of experiments conducted.

	Measured		Estimated		
Experiment	T(hrs)	D(m^3/s)	n(s/$m^{1/3}$)	H(m)	L(m)
1	33	.95	.060	14	8100
2	24	.70	.060	14	8100
7R	80	.11	.060	20	12000
7R*	80	.11	.060	20	13000
7R**	80	.11	.060	17	12000

	Calculated					
Experiment	d(m)	w(m)	A(m^2)	V(m/s)	Vm(m^3)	K(m^3/s)
1	.031	440	14	.069	110000	4.0
2	.050	150	7.5	.094	60000	4.4
7R	.015	180	2.7	.042	33000	1.4
7R*	.019	130	2.5	.046	3300	1.6
7R**	.017	160	2.7	.042	3300	1.6

Table G3. Results of flow calculations. Vm is volume of conduit (L · A), other abbreviations defined in text.

The calculated depth and width values do suggest the reason velocity does not appear to increase monatonically with discharge, however. At discharges up to .7 m^3/s, flow appears to be in a channel of nearly constant width, which is over-topped at higher discharges resulting in a substantial increase in average width but a decrease in average depth. Because it is reasonable (although not absolutely required by the conduit geometry) that average width would increase monatonically with discharge, calculations for experiment 7R were repeated after increasing the length (7R*) and decreasing the headloss (7R**) and indicates relatively minor adjustments in these factors (especially length) based on observations discussed earlier cause a substantial decrease in the calculated width for experiment 7R.

G5d. System Geometry

A number of workers have utilized dye recovery values, discharge, and analysis of the shape of the dye hydrograph to deduce information on the system geometry (Brown and Ford, 1971; Atkinson, et. al., 1973; Bogli, 1980). For example, incomplete dye recovery indicates downstream bifurcation of the conduit(s) with some flow bypassing the sampled spring (as discussed in G4a), and bimodality of the dye hydrograph would result from a splitting and rejoining of the conduit, with the water following the longer (or slower) path being delayed.

Furthermore, given adequate data, information on the conduit geometry of various portions of the system should be obtainable from the dye hydrograph and comparison of the results of traces introduced into different swallets in the basin, since the conveyance of a series of reached is the geometric mean of the conveyance of each individual reach, and the conveyance of parallel reaches is directly related to the square root of the length and the discharge of each reach.

An examination of the dye hydrographs of the Traces (Figs G8 through G14) shows that traces 1 and 2 in the Royal Spring Basin and possibly trace 4 in the Russell Cave Spring Basin are bi- or multimodal. An examination of the precipitation and discharge record suggests, however, that these later peaks are probably due to release of water stored during high discharge or the temporary damming of dyed water by an inflow from the surface between the dye introduction point and the spring.

G6. Conclusions

Estimated earliest travel times for a contaminant introduced into a swallet in the Royal Spring groundwater basin are shown in Table G4, as well as the latest time the contaminant would be expected to be present in the spring (assuming no retardation). These times are based on the envelope shown on Fig. G15. The data did not permit a similar tabulation for Russell Cave Spring.

	SWALLET	DISTANCE	300 L/S (10.6 CFS)	600 L/S (21.2 CFS)	900 L/S (31.8 CFS)	1200 L/S (42.4 CFS)	1500 L/S (53.0 CFS)
B2	Seng Sink	2.08(1.29)	4.6	2.3	1.5	1.2	.9
			23.1	23.1	23.1	23.1	23.1
B7	Gainesway	3.98(2.47)	8.8	4.4	2.9	2.2	1.8
	Swallet		44.2	44.2	44.2	44.2	44.2
B8	Spindletop	8.07(5.00)	17.8	8.9	5.9	4.6	3.6
(KCER)	Swallet		89.7	89.7	89.7	89.7	89.7
D80	Tributary	10.49(6.52)	23.3	11.7	7.8	5.8	4.7
(Bruner)	Swallet		116.5	116.5	116.5	116.5	116.5
D9	Interstate	12.11(7.53)	26.9	13.5	9.0	6.7	5.4
Cane Run	Swallet		134.6	134.6	134.6	134.6	134.6
D48	Newtown	15.03(9.34)	33.4	16.7	11.1	8.35	6.68
Cane Run Sink	Swallet		167.0	167.0	167.0	167.0	167.0

Table G4. Estimated earliest and latest travel times for contaminent transport to Royal Spring. See Fig. G1 for swallet locations. Times are in hours.

Despite difficulties encountered, especially with pH control of standard solutions and discharge measurements, the findings of the study indicated the feasibility of the method of investigation and provided insight into the nature of the Royal Spring groundwater basin and, by extension, the karst aquifer of the region.

Both fluorescein and rhodamine (Rhodamine WT) may be instrumentally determined by spectrofluorometry in the presence of the other with little or no interference. Neither dye appears to be adsorbed or retarded underground.

A substantial fraction of the flow in the basin probably bypasses Royal Spring and emerges elsewhere. Flow in the conduit feeding the spring is turbulent and in a channel with a free surface and calculations suggest that the depth of flow is quite shallow and wide in a conduit whose gradient under at least low flow conditions is similar to that of a surface stream.

The results of the study must be considered preliminary, but are sufficiently encouraging that additional research is planned utilizing dye-dilution techniques to determine discharge.

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H. FRACTURE TRACES IN THE INNER BLUEGRASS KARST REGION, KENTUCKY

C.J. Taylor and J. Thrailkill

H1. Introduction

Fracture traces are considered by many to be a highly useful guide to the occurrence and flow of groundwater in limestone areas (Lattman and Parizek, 1964). They had been studied in the Inner Bluegrass Karst Region in only one 7.5 minute quadrangle (Hine, 1970), and some investigation of these features as part of the project seemed appropriate.

H2. Methods

Twenty five of the 316 two-and-a-half minute quadrangles (1:24000) that cover the Inner Bluegrass Karst Region were randomly (using a random number table) selected for examination (Fig. H1). Each of the quadrangles was examined for indications of fracture traces reflected in the topographic contours (3.0 or 6.1 m interval) or other features shown on the map. Considerable pains were taken to reduce the subjectivity of this evaluation to a minimum. The investigator (CJT) was unaware of the geology or subsurface hydrology of the quadrangles being examined, and reference was continually made to a series of type examples. Most of the fracture traces were defined by three or more nearby sinkholes in line, but in some cases a combination of sinkholes and other features (e.g., stream segments and the trends of small valleys) were used.

For each fracture trace, its indicated length, width, relief, sinkhole density, orientation, and linearity were recorded. Width refers to the maximum width of the features (usually sinkholes) along the trace. Relief is the elevation difference of the highest and lowest points. Sinkhole density is the fraction of the length which is within depression contours. Linearity is similar to width but is the width of the band of sinkhole centers along the trace, rather than that of the depression contours.

Following the recording of the above data for all fracture traces

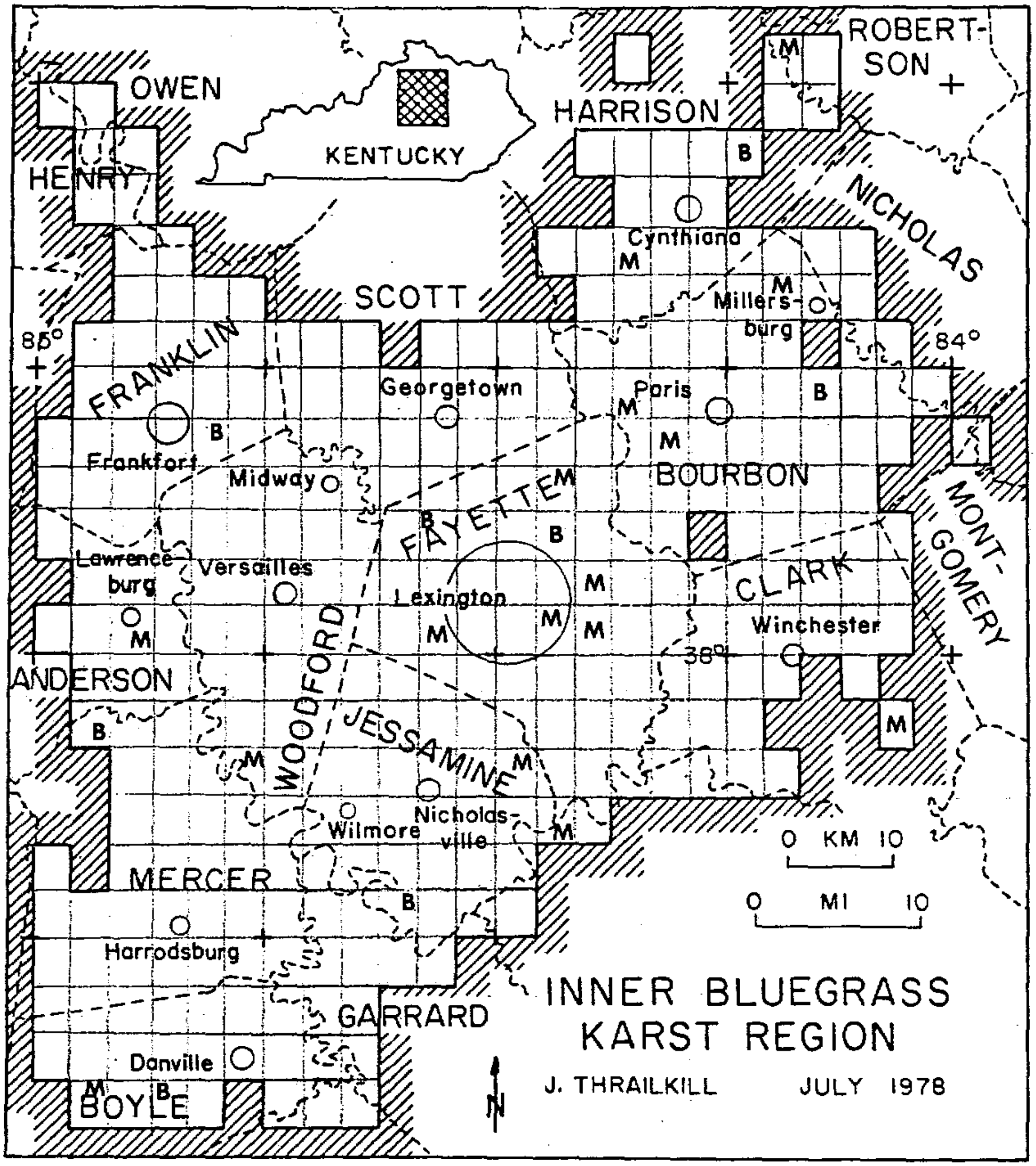

Figure H1. Map of Inner Bluegrass Karst Region. M indicates 2.5 minute quadrangles examined using topographic maps and B those examined both on maps and aerial photographs.

on all quadrangles, the large scale (1:24000) geologic maps were examined, and the stratigraphic unit in which the fracture trace was located and its relationships to any mapped faults was recorded.

The third phase of the study was the stereoscopic examination of aerial photographs. For this phase, a random sample of 8 quadrangles was selected (again using a table of random numbers) from the original sample of 25. Three of the quadrangles had not shown fracture traces in the first phase of the study (which was known to the investigator) and five had contained one or more. The third phase was conducted several months after the first two, and there was little or no recollection by the investigator of the location or measured parameters of fracture traces identified. The topographic maps were not consulted during the third phase.

Fracture traces were identified on the aerial photographs mainly on the basis of sinkhole alignment (as on the topographic map), but soil tone was also used extensively. Only length and orientation could be recorded with confidence, the other parameters were too difficult to quantify on the photographs.

The techniques of Lattman (1958) were found to be highly useful. The final task undertaken was to determine if any water tracing had been done in the vicinity of the identified fracture traces and if so, the relationship between the fracture trace and the water trace. Prior to this, the investigator was not informed of the location or results of water traces in the region.

H3. Results

Table H1 lists the quadrangles examined, and the number of fracture traces identified in each. Each 2.5 minute quadrangle is one-ninth of a 7.5 minute 1:24000 quadrangle, and is designated by the 7.5 minute quadrangle name followed by a two-letter code (CC, center; NW, northwest, NC, north-center, etc.) to indicate its position. The figure in parentheses following the number of aerial photograph fracture traces is the number which were identified both on the map and the photographs.

2.5 Minute Quadrangle	Topographic Fracture Traces	Aerial Photograph Fracture Traces
1. Frankfort East - CC	6	7(3)
2. Junction City - NW	1	2(1)
3. Lexington West - NC	6	7(4)
4. Little Hickman - SW	3	6(2)
5. Lexington East - NC	6	8(5)
6. McBrayer - CC	0	0
7. Shady Nook - WC	0	0
8. Paris East - NE	0	0
9. Millersburg - CC	2	-
10. Paris West - NW	7	-
11. Paris West - CC	2	-
12. Centerville - SC	5	-
13. Lexington East - SC	1	-
14. Lexington East - SE	1	-
15. Coletown - SW	10	-
16. Valley View - NC	3	-
17. Georgetown - NW	13	-
18. Lexington West - SC	9	-
19. Lawrenceburg - SE	1	-
20. Claysville - SE	0	-
21. Hedges - CC	0	-
22. Shawhan - NW	0	-
23. Lexington East - EC	0	-
24. Salvisa - SE	0	-
25. Parksville - NC	0	-

Table H. Quadrangle name and number of fracture traces identified. Aerial photographs examined for 1 through 8 only.

A total of 76 fracture traces were identified on topographic maps on 16 of the 25 quadrangles, and as many as 13 were identified on a single quadrangle. A total of 22 were identified on quadrangles 1 - 8 on the map, and 30 on the aerial photographs, but none were identified on aerial photographs of the 3 quadrangles where none had been identified on the map (Table H1).

Of the 76 "map" fracture traces, 9 trended west to northwest, 33 northwest to north, 14 north to northeast, and 20 northeast to east. Mean values of the parameters measured for the 76 fracture traces were: length, 706 meters; width, 137 meters; relief, 4.9 meters, sinkhole density, 53 % ; and linearity, 58 meters.

In the five quadrangles (Table H1, 1-5) on which fracture traces were identified both by map and aerial photograph examination, the mean length of those identified on the map was 803 but 1760 meters for those identified on the photographs. Of the 14 fracture traces identified both on the map and the photographs, the mean length on the map was 800 meters and 1860 meters on the photographs. Directional trends were the same for those identified both on the map and photographs, but the trend of the fracture traces identified only on the map was quite different than the trend of those identified on the aerial photographs (Table H2).

	WEST TO NORTHWEST	NORTHWEST TO NORTH	NORTH TO NORTHEAST	NORTHEAST TO EAST
IDENTIFIED ONLY ON MAP	1	3	0	3
IDENTIFIED ONLY ON PHOTOGRAPH	2	2	8	3

Table H2. Orientations of fracture traces.

Of the 76 fracture traces on the maps, 65 were in the Tanglewood and Grier Members of the Lexington Limestone or in the Tyrone Formation, which are relatively pure limestones, while the remaining 11 were in the more argillaceous Brannon and Millersburg Members of the Lexington or the Clays Ferry Formation. Six of the 76 features identified as fracture traces followed mapped faults, while in another 7 a fault had been mapped nearby.

Thirteen of the 76 fracture traces on the maps had been the site of dye introductions, and in somewhat more than half the cases the dye trace followed the fracture traces while in the remaining cases it diverged from it.

H4. Discussion and Conclusions

Based on the sample of 2.5 minute quadrangles examined (25) and the total number in the Inner Bluegrass Karst Region (316), the 76 fracture traces identified on the map suggest that there are about 960 such fracture traces in the region. In the smaller sample of 8 quadrangles examined on aerial photographs, 36% more fracture traces were identified than on the maps of the same area, but there was only partial overlap (i.e., some identified on the map were not identified on the photographs), and no attempt will be made to predict the total number of fracture traces which could be identified by both techniques due to the small sample.

Some investigations of the distributions of fracture trace parameters were conducted but will not be discussed here, since the significance of most is still in doubt. It seems clear, however, that fracture traces where visible on photographs (not all were, as noted above) are much longer than those on maps. The average length of the same fracture trace was more than twice as long on the photographs as on the maps.

The significance of the difference in orientation between features identified only on the map and those identified only on the photographs is not clear. It may be that sun angle was a major factor.

Similarly, the apparent abundance of fracture traces in the purer limestones is difficult to interpret. Much of it is due to the manner in which the Inner Bluegrass Karst Region was defined (Thrailkill, et. al., 1982) as the area in which at least one sinkhole is visible on topographic maps. The region is surrounded by the argillaceous Clays Ferry Formation, in which sinkholes are largely confined to the lower 25 meters or so. Since the fracture traces are mainly defined by alligned sinkholes, few would be expected in the Clays Ferry, and most of the quadrangles in the sample which had no fracture traces have extensive areas underlain by this unit. The other two argillaceous units (Brannon and Millersburg Members) are relatively thin, and the proportion of fracture traces located in their outcrop areas (12%) may be about the same as the proportion of their area to that of the region.

The small number of fracture traces which follow mapped faults was rather suprising, but in areas of poor outcrop it is by no means certain that all of the faults have been mapped. It is likely that many of the fracture traces are single pervasive and extensive joints, however, as discussed in Thrailkill, et.al. (1982)

Finally, the relationship of groundwater flow to fracture traces tends to bear out the conclusions reached in Thrailkill, et. al. (1982), that such features are likely to be followed by flow conduits provided they are favorably oriented relative to the regional flow pattern.

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