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FLOW MEASUREMENTS WITH FLUORESCENT TRACERS^a

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INTRODUCTION

Stream discharge measurements with chemical dilution techniques have been proposed in several forms since the beginning of this century (Groat⁴). Early techniques consisted of introducing a chemical, usually brine, at a known rate into flowing water and determining the resulting concentration of the chemical in the stream at a section far enough downstream to assure adequate mixing of the chemical with the water. A variation of this method, and the technique used in the present study, was described by Barbagelata⁵ in 1928. In that method, a known quantity of tracer was added, as a slug, to the stream to be measured. At a sampling station sufficiently far downstream for adequate lateral mixing, the tracer concentration-time curve was determined. The stream discharge was then calculated from the amount of tracer added and the area measured under the curve.

Later, Hull,⁶ in similar work using radioactive tracers, recognized that the tracer concentration-time curve did not have to be measured directly.

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⁴ Groat, Benjamin F., "Chemi-hydrometry and Precise Turbine Testing," Transactions, ASCE, Vol. 80, 1916, pp. 951-1305.

⁵ Barbagelata, Angelo, "Chemical-Electric Measurement of Water," Proceedings, ASCE, Vol. 54, 1928, pp. 789-802.

⁶ Hull, D. W., "The Total Count Technique: A New Principle in Flow Measurement," International Journal of Applied Radiation and Isotopes, Pergamon Press, Ltd., London, England, Vol. 4, pp. 1-15.

The area under this curve can be obtained, in the case of radioactive tracers, simply by inserting a Geiger counter in the stream some distance below the point of tracer injection. This counter then recorded the "total count" resulting from passage of the tracer wave. With a nonradioactive tracer, the area under the concentration-time curve can be obtained by continuously sampling from the stream during the passage of the tracer wave and mixing this continuous sample into a single container to obtain an "integrated sample." Only the tracer concentration of this integrated sample and the time length of the sampling period are needed to compute the stream discharge.

The salt brines used in early applications cannot be satisfactorily used in some waters with high natural amounts of similar salt. The necessarily large quantities of brine needed for accurate detection under ideal circumstances become prohibitive if large natural amounts of sodium chloride or similar salts are present in the stream.

The radioactive tracers, which have been used for both closed and open flows, 6,7 greatly improved the accuracy and ease of detection and reduced the quantity of material needed. However, these tracers have proven expensive from the material and equipment standpoint, and are severely limited by hazard, paperwork, and regulation.

Despite these problems, the dilution technique transcends most of the difficulties that beset other discharge measurement methods. It is applicable to any kind of conduit, open or closed. It does not involve the stream dimensions or the measurement of fluid levels or pressures. It does not require a pressure loss, a drop in hydraulic head or an impediment to the flow. It measures the flow directly by a simple theoretical formula which requires no empirical correction factors. These facts make the method especially attractive for gauging natural channels.

These dilution techniques were extended to exploit recent developments in fluorescence assay equipment and fluorescent dyes. These developments made possible the quantitative detection of fluorescent dyes in concentrations of a few parts per billion. Accurate quantitative detection can be obtained with commercially available equipment by comparing fluorescence of dilution samples with accurately prepared standards which are readily constructed for each stream flow measurement. Laboratory tests were conducted to evaluate the equipment, three of the more promising dyes, and the technique for field use.

APPLICABLE TECHNIQUES

Two general methods may conceivably be used in chemical dilution techniques, the "continuous-addition-of-tracer" method and the "slug-injection" method.

Continuous Addition of Tracer.—The continuous-addition-of-tracer method consists of uniformly and continuously injecting a tracer into the stream at a known rate. At a location sufficiently far downstream to assure good transverse mixing, samples are obtained to determine the quantity of stream flow

7 Schuster, Jack C., "Canal Discharge Measurements with Radioisotopes," *Journal of the Hydraulics Division, ASCE*, Vol. 91, No. HY2, Proc. Paper 4268, March, 1965, pp. 101-124.

that has mixed with the tracer. The degree of dilution of the tracer permits the stream flow rate to be calculated from the equation

$$q \cdot C = (Q + q) c \dots\dots\dots (1)$$

in which q = the rate of tracer addition to the stream at concentration C , Q = the stream flow rate, and c = the resulting concentration of the stream flow combined with the tracer.

Slug Addition of Tracer.—When a slug of tracer is added to a stream in an undefined manner, equal concentration across the stream at any section is theoretically never reached because of velocity distribution. However, as the wave progresses downstream, it becomes increasingly dispersed. At some station at distance x , the rate of change of the tracer concentration passing the sampling station becomes so small that the corresponding lateral gradient, assumed to be similar, results in negligible differences in the tracer wave at the center line of the stream and near the stream bank. For a tracer wave monitored at both the stream center line and the stream bank, there will be a translation of the wave front, peak, and end resulting from velocity distribution effects. These effects will cause the wave to appear at the center line first, but its passage will also be first, resulting in similar tracer wave patterns at both the center line and near the stream bank if adequate lateral mixing is occurring.

Several attempts are reported for determining adequate mixing length. 7,8 The results from the several approaches produce calculated required mixing lengths differing by as much as two magnitudes. Until further information is available, the tentative recommendation is to allow a mixing length equal to at least 100 stream top widths. Radioisotope measurements by Schuster⁷ indicated that 60 to 70 top widths were adequate. In field practice the use of several sampling stations in the cross section serve to clarify the particular situation. If the samples collected near the center line and near the bank agree, adequate lateral mixing was achieved.

The major effect of dispersion is to increasingly dilute the tracer as the tracer wave moves downstream. Thus, a short time after injection of the tracer, a typical time-concentration curve passing a sampling station would appear similar to that shown in Fig. 1(a). However, at a greater distance from the point of injection, the curve would be similar to that of Fig. 1(b). The significant relation here is that the area under curve 1a is equal to that under 1b. Thus, neglecting adsorptive losses of the tracer, the total quantity of tracer in the stream does not change; only the distribution changes.

Referring to Fig. 1, the tracer passing a sampling station in a channel with steady flow must equal the quantity, S , added at some upstream station. Thus,

$$S = \int_0^t Q c dt = Q \int_0^t c dt \dots\dots\dots (2)$$

in which Q = the stream discharge, t = the time from the beginning of sampling, and c = the concentration at time, t , at the point of sampling. The integral part may be evaluated from the area under the time-concentration

8 Hull, D. E., "Dispersion and Persistence of Tracer in River Flow Measurements," *International Journal of Applied Radiation and Isotopes*, Pergamon Press, Ltd., London, England, Vol. 13, 1962, pp. 63-73.

curve, but it is more practical to evaluate it by the integrated sample technique mentioned earlier. The integrated sample requires a constant sampling rate during the passage of the tracer wave. A single determination then evaluates the average concentration, \bar{c} , of the combined sample. Therefore, the discharge computation becomes simply

$$Q = \frac{S}{\bar{c} \Delta t} \dots \dots \dots (3)$$

in which Δt = the total time of the sampling period.

The slug of tracer furthermore does not have to be added instantaneously, since only adequate lateral or transverse mixing is required. The longitudinal shape of the wave is unimportant within rather wide limits.

The two methods described above, while similar, have certain distinct advantages. Both require transverse mixing, both require the determination of tracer concentration of a single sample, and both could possibly be manipulated to require similar quantities of tracer materials. The continuous addition method requires a constant and accurately known rate of tracer

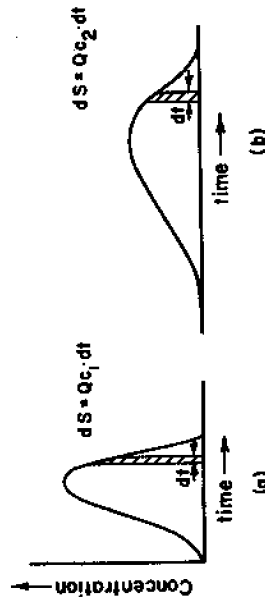


FIG. 1.—TYPICAL TIME-CONCENTRATION CURVES RESULTING FROM SLUG INJECTION OF TRACER MATERIAL

addition to the flowing stream. The slug method requires only the total quantity of tracer added. Usually the latter is far more easily achieved than determining precise injection rates. The slug method requires a steady rate of sampling during the entire passage of the tracer wave but this rate need not be known.

When the flow rate is changing rapidly or when the wave passage time is excessively long, as it may be in large rivers, the continuous injection system is to be preferred. For steady open channel flows of less than a few thousand cubic feet per second, the slug addition method is preferred.

SELECTION OF TRACER AND TRACER DETECTION EQUIPMENT

The dilution technique described here is potentially capable of accuracies to $\pm 1\%$. This high accuracy is the result of the high selectivity of recently available fluorescent tracing dyes, developments in fluorescence assay equipment which can quantitatively determine dye concentrations in dilutions on the order of 1 part per billion (ppb), and careful construction of accurate

comparison standards using water from the stream being measured in order to reduce background effects.

At least two suitable instruments are manufactured for determining fluorescent tracer concentrations in the field or laboratory (the Turner Model 111 Fluorometer and the Beckman 77200 Ratio Fluorometer; a complete list of possible suitable instruments is available⁹). They operate satisfactorily with portable electric generators. Either a continuous flow cuvette for continuous sampling or a single test tube-shaped cuvette for measuring individual samples is available as well as devices to record all sample readings.

The Turner Model 111 Fluorometer, 115 volts, 60 cycles, was used in this study for quantitative detection of the fluorescent tracer. The fluorometer is basically a balanced optical bridge which measures the difference between the light being emitted by a fluorescing sample and that from a calibrated light source originating from the same bulb that is used to excite the sample to fluorescence. This dual use of the same bulb helps compensate for power fluctuations to the instrument. The optical system consists of a servomotor-driven light cam attached to a readout dial of 100 divisions, an exciting light source, a continuous flow cuvette, optical filters, a light interrupter, and a photomultiplier. Of these, the operator needs to be concerned with only the light source, the filters, and the cuvette type and size.

Several features require consideration when selecting the fluorescent tracer. Important among these are ease of quantitative detection at low concentrations, toxicity to animal and plant life, loss or deterioration in natural water systems, and cost of tracer and equipment.

Fluorescent materials possess different characteristics which enable only a few to be considered as water tracers. Tracers that fluoresce under ultraviolet light, for example, must compete with numerous mineral and organic compounds that also fluoresce under ultraviolet light. Thus, a suitable fluorescent tracer should preferably be excited in the visible light range and should not be naturally occurring, in order to be selectively and easily detected.

Feuerstein and Selleck¹⁰ evaluated three of the more promising of these fluorescent tracers suitable for use with water. These were the familiar sodium fluorescein; a chemically related dye, Rhodamine B; and still another related dye, Pontacyl Brilliant Pink B. A fourth related dye, Rhodamine WT, which was not available at the time of their report, was included in the studies reported herein. Fluorescein is more easily affected by light and bacterial action than the other dyes and is thus less suitable for water tracing techniques. The remaining three dyes are readily detected because of their fluorescence characteristics, have low photochemical decay coefficients for bright sunlight, are unaffected by pH values between 5 and 10, and have similar minimum detectable concentrations.¹⁰ While they are strongly excited by certain wave lengths of ultraviolet light, as are many materials, they also possess a relatively strong excitation or adsorption peak in the visible light range. They have maximum adsorption spectrums of 550 m μ , 556 m μ , and 560 m μ ,

⁹ Scherago, Earl J., "Guide to Scientific Instruments," Science, Washington, D. C., Vol. 150A, No. 3647A, Category No. 1745, November 23, 1965, p. 55.

¹⁰ Feuerstein, Donald L., and Selleck, Robert E., "Tracers for Dispersion Measurements in Surface Water," SERI Report No. 63-1, San. Engrg. Research Lab., Coll. of Engrg. and Sch. of Pub. Health, Univ. of Calif., Berkeley, Calif., February, 1963.

respectively, for Rhodamine B, Rhodamine WT, and Pontacyl Brilliant Pink B and corresponding fluorescence peaks of 570 m μ , 580 m μ , and 578 m μ . This adsorption spectrum range allows the molecule to be strongly excited to fluorescence by the green line of mercury (546 m μ).

The major difference between the behavior of the three dyes is found in their adsorption by suspended sediments. Rhodamine B is the most easily adsorbed of the three dyes. Wright and Collings¹¹ conducted adsorption tests of Rhodamine B dye on sand and some organic compounds by filtration through columns of the materials. While the sand retained very little of the dye regardless of concentration, certain organic substances tended to retain higher proportions at higher concentrations, representing tracer losses of 2% to 28%. Feuerstein and Selleck¹⁰ found measurable physical adsorption of Rhodamine B on suspended San Francisco Bay sediments but could not detect Pontacyl Pink B losses. Column filtration tests conducted during the preliminary phases of this study indicated that the quantity of Rhodamine B retained in a soil column was approximately 10 times the quantity of Pontacyl Pink B retained.

For the purposes of further checking the relative adsorption on suspended materials in stream waters, a comparison test was conducted for the three dyes. Two highly turbid solutions were prepared for each dye, one with 1 gram per liter of high-sodium bentonite clay and the other with 1 gram per liter of local canal sediments, both in tap water with 10-ppb dye concentrations. The sediment concentrations were high compared to those naturally occurring in streams, except perhaps in the bed load of a flash flood. This was intended to exaggerate the effects of adsorption.

Relative fluorescence indications were obtained immediately after the dry sediments were stirred into the solutions and were checked again after about 16 hr without further agitation. After 16 hr, in the canal sediment materials 41% of the Rhodamine B dye was no longer detectable while only 6% of the Rhodamine WT had been adsorbed. Pontacyl Pink B was not significantly different from Rhodamine WT, indicating a 5% loss. In a similar time, bentonite clay adsorbed 96% of the Rhodamine B, 65% of the Pontacyl Pink B, and 28% of the Rhodamine WT. The Rhodamine WT thus appears to be the most suitable of the fluorescent dyes.

TEMPERATURE DEPENDENCE

The fluorescence response of the three tracers is affected by the temperature of the sample at the time of reading. The higher the temperature, the lower the response. Feuerstein and Selleck¹⁰ determined that the temperature response for Pontacyl Pink B and Rhodamine B is described by the equation

$$F_r = F_s e^{n(T_r - T_s)} \dots \dots \dots (4)$$

In which F_r = the calculated fluorescence response of the sample at reference temperature, T_r ; F_s = the fluorescence response of the sample at the sample temperature, T_s ; and n = a temperature coefficient (having units of degree⁻¹).

¹¹ Wright, Robert R., and Collings, Michael R., "Application of Fluorescent Tracing Techniques to Hydraulic Studies," Journal, Amer. Waterworks Assn., New York, N. Y., Vol. 56, No. 6, June, 1964, pp. 748-750.

The values for n were found to be -0.029° C-1 and -0.027° C-1 for the Pontacyl Pink and Rhodamine B, respectively.

The temperature response curves were rechecked for the Rhodamine B and extended to include Rhodamine WT. For the Rhodamine B, $n = -0.027^\circ \text{C}^{-1}$ which agrees exactly with that reported by Feuerstein and Selleck.¹⁰ Rhodamine WT has a value of $n = -0.026^\circ \text{C}^{-1}$. Based on the agreement for Rhodamine B, the value for Pontacyl Pink B derived by Feuerstein and Selleck was accepted as adequate and was not rechecked.

INSTRUMENT ADJUSTMENTS AND ADAPTATIONS

Several methods are provided to change the sensitivity of the fluorometer over a very wide range. These include varying the light source intensity, the size of restricting light aperture, or the size of sample cuvette. High sensitivity is usually desired to reduce the amount of tracer material required.

The most intense routinely available light source suitable for the fluorescent tracers was obtained by filtering the green (546 m μ) line of mercury from a green lamp source (General Electric F4T5.G or equivalent) which has continuous emission from below 520 m μ to over 560 m μ . This lamp provides approximately a 10 to 20 times gain over other commonly used lamps.

Satisfactory filters used on the primary side of the sample (near the lamp) had color specifications, Corning 1-61, Wratten 61, and a second Corning 1-61, to provide a strong excitation peak at 546 m μ . Some light over a range from about 485 m μ to about 572 m μ was also transmitted. On the secondary side, to filter emission of the sample from the excitation light, "sharp-cut" filter, Corning 3-66, excluded all light below 560 m μ and a Corning 4-97, used in combination, excluded wavelengths above 640 m μ . These filters were essentially those recommended by the fluorometer manufacturer. A small percentage of the exciting light between 560 m μ and 572 m μ can be scattered by suspended materials in the sample, transmitted through the secondary filters, and picked up by the photomultiplier tube. This effect can be counteracted by constructing comparison standards from the stream water being measured.

Several sample containers, or cuvettes, are available. In general, it was found that individual test tube-shaped cuvettes were not uniform enough for accurate high-sensitivity comparisons. Readings varied by two or more dial divisions among cuvettes in supposedly high precision matched sets. Even using the same cuvette for all samples was not entirely satisfactory, since positioning of the cuvette caused variations in reading on the order of 1 to 2 dial divisions. The most consistent results were obtained using a continuous flow cuvette where the sample was continuously circulated through the fluorometer. This eliminated both the problem of cuvette differences and the effect of temperature change on the sample. The effects of temperature rise with time of residence in the fluorometer is serious enough with individual cuvettes to require special temperature stabilization equipment to cool the sample.

Several continuous flow cuvette sizes are available. The 20-cc size provides a sensitivity gain of about 20 times that of the 5-cc size. However, since the practical lower concentration limit for remaining well above most background readings is on the order of 1 to 2 ppb, the 5-cc cuvette usually

provided sufficient sensitivity, required less sample to indicate a stable reading, and was more easily purged of bubbles.

Another instrument characteristic that should be checked, especially if the instrument is to be used in bright sunlight, is its bright-light sensitivity. Light is restricted from reaching sensitive areas in the fluorometer by a series of blackened overlapping light baffles designed to allow air circulation but restrict light entry. Extremely bright light such as full sunlight can be reflected through these baffles and cause a reading change. The severity of these light leaks is best checked with a photoflood lamp at close range. Most of the light leaks can be taped without detrimental effects on the ventilating system.

To reduce external light effects, a shielding box was constructed which also served as a carrying case for the fluorometer. A small supplemental ventilating blower was built into the box. The fluorometer has a tendency to change readings with changes in instrument temperature on the order of one dial division increase per degree centigrade increase. About 30 min were required for the temperature in the cuvette chamber to stabilize at approximately 10° C above ambient.

COMPARISON STANDARDS

Highest accuracy with the fluorometer was obtained by comparison of sample fluorescence with the fluorescence of an accurately known standard, both read under similar conditions, preferably during the same work period to assure that similar conditions did prevail. These accurately known standards were prepared with background water from the stream that was measured using dye from the same "mother" solution employed in the measurement. By using background water, dye adsorption on suspended materials is compensated if the sediment remains in a similar state of suspension in both sample and standard.

Standards prepared by volume techniques using class A volumetric flasks and pipets, requiring five to seven successive dilutions, frequently produced inconsistencies as high as 3% to 6% among supposedly identical standards. To improve accuracy and repeatability in the preparation of standards, weighed quantities were used whenever practical and procedures for reducing concentrations to a few parts per billion were limited to two or three successive dilutions.

One-part-per-billion standards were consistently and accurately constructed in the following manner:

A laboratory analytical balance was used to weigh 0.2500 ± 0.0002 grams of 20% Rhodamine WT solution from the same lot used in the stream flow measurement. This was then washed into 10,000 ± 1 grams of stream water to produce a 5-parts-per-million dilution ($\pm 0.1\%$ error). A calibrated 10-ml pipet, found to be repeatable to $\pm 0.03\%$, was used to transfer 10 ml of the 5-ppm dilution into 50,000 grams of the stream water (approximately 110.23 lb weighed on a 200-lb capacity platform scales) to obtain a 1-ppb solution. To determine the fluorescence, the solution was recirculated through the fluorometer and back into the 50,000-gram container (20-gal plastic garbage can) and a second 10 ml of 5-ppm solution added to obtain the 2-ppb fluorescence reading, etc.

Standards were constructed for a range of fluorescence readings covering those of the samples. Since the fluorometer responds linearly for dye concentrations below 10 ppb, only three points were needed to establish and check the fluorescence response curve. In these studies, the usual practice was to develop the least-squares linear-regression line using five or more points.

The accumulative addition of as many as ten of the pipet volumes to the 50,000-gram container caused a systematic error of only 0.2% in the standards. Thus, errors associated with the dye-dilution method of stream flow measurement are essentially those imposed by insufficient mixing, nonuniform sampling rates, and limitations in the accuracy of the fluorometer. The effects of fluctuations of the fluorometer dial, approximately 1/2 division or less, can be minimized by choosing an instrument sensitivity setting that causes the fluorescence readings of the samples to be near full scale on the dial.

STREAM SAMPLING

To assure uniform sampling rates for time periods frequently over an hour, the power supply must be reliable and the sampling line, control valves, and pump intake must resist clogging.

Small submersible pumps were used to obtain the integrated samples. The pumps each had a capacity of 175 gal per hr at 20 ft of head and a shut-off head of 26 ft. Only a small fraction of the pump capacity was required for sampling. Submersible pumps were chosen to keep the discharge line under pressure so that dissolved gases in the water would not be liberated and cause flow rate changes. Most small submersible pumps must be allowed to pump for several minutes to assure that all the air is washed out of the rotor housing. On these pumps, continuous streams of tiny bubbles issued from the pump outlet for several minutes after starting. This entrapped air could be quickly expelled by switching the pumps on and off a few times.

A tachometer attached to the power generator was continually monitored, and no changes in electrical load were permitted during a sampling period. After a 15-min warmup period under sampling load conditions the power generator was found to be quite stable and reliable.

The intakes to the sampling pumps were screened by wrapping plastic screen wire around a 1-ft section of 3/8 in. stainless steel pipe that was perforated with numerous drilled holes. The screened inlet area was purposely made several times larger than would be required to pass the small sampling flows, in order to minimize the effects of clogging. The ends of the pipe were also fitted with guide fins that kept the sampling-pipe inlet in the wake of the pump. This helped keep floating weeds and other debris from covering the inlet screen.

Control of the sample quantity was necessary to eliminate excessively large sample containers for obtaining the integrated sample. This was accomplished by either increasing the length of tubing to decrease the sampling rate or by splitting the sample with tubing tees in the outlet line and wasting the flow from one leg of the tee. By properly selecting the tubing lengths from the tee to the sample container and from the tee to waste, small changes in elevation of the waste line outlet would change the flow rate to the sampling container from zero to full-line flow. Control of the flow rate with tubing clamps or valves

was unsatisfactory. The resulting constrictions trapped fine, fibrous particles which caused the sampling rate to change with time.

For convenience and improved sampling time accuracy, a noncontaminating switch valve was fashioned to switch the flow from the pumps into either the sample container or to waste. It was simply two clamping bars operating alternately to "gang clamp" all the sampling tubes on one leg of tee connections and simultaneously release the tubing on the other leg. Thus, the sampling could be quickly started or stopped to facilitate accurate time measurement.

LABORATORY FLUME MEASUREMENTS

A study was conducted to check the accuracy and precision of tracer-determined discharge measurements in a laboratory flume where the flow rate could be controlled and accurately measured. The basic test channel was a straight rectangular flume 1 ft wide and 1.2 ft deep. Flow was supplied directly from a centrifugal pump to a headbox and stilling basin of about 6 cu ft, fitted with a sluice gate.

The first series of tests involved measuring flow into the flume with a volumetrically calibrated 3-in diameter elbow meter accurate to $\pm 1.0\%$. Maximum flow was about 0.75 cfs, and the flume was 36 ft long. Flume length was about one-third of the length recommended to obtain adequate mixing. Four sampling pumps were randomly scattered in the last 8 ft of the flume. The upstream sampling pump discharge was directed through the fluorometer to detect the start and end of the tracer wave. Samples were collected separately from each pump while the wave was passing and were later analyzed for dye concentration. Three ranges of channel flow were chosen and three tracer drops made for each range. The absolute discharge could not be exactly repeated because of power fluctuation to the channel supply pump.

The fluorescent tracer (50 ml, taken from an initial 8 liter supply that was diluted to 2 gm per liter of Pontacyl Pink B) was first introduced into the channel near the upstream end. Visual observation of the poor lateral mixing was confirmed by the wide variation in discharge calculated from the four samples taken during each run. To test the precision and accuracy of the equipment, artificial lateral mixing had to be induced. The tracer was then introduced into the channel headbox with some, but not sufficient, improvement. Finally, injection was made on the suction side of the pump. The tracer passed through the pump rotor, then through about 25 ft of 3-in. pipe with five elbows, and finally through a diffuser outlet into the headbox. The improved mixing resulted in discharge determinations for seven runs which differed from the true discharge, as determined from the elbow meter, by -1.7% to + 1.8% with an average error of + 0.2%. The maximum standard deviation, calculated from four samples for each test, ranged from $\pm 0.3\%$ to $\pm 2.0\%$, with an average of $\pm 1.3\%$. Some of the apparent error between the tracer-determined discharge and the elbow meter discharge can be attributed to the elbow flow meter. The standard deviations among samples for individual runs indicated that adequate mixing was not achieved.

Following the first series of measurements a gravimetric system was installed which could measure flow rates to better than $\pm 0.5\%$. The same supply pump was used, but the connecting pipe was changed to 15 ft of 6-in.

pipe and the maximum flow rate was increased to 1.0 cfs. New space limitations caused the flume length to be reduced to 28 ft, or about one-fourth the recommended length. The dye was injected as before through the pump rotor, but it was visibly evident that mixing was not adequate. This was confirmed by high differences between the four samples. Finally, inducing a strong hydraulic jump with the sluice gate from the headbox and then running the flow through a slatted baffle produced better lateral mixing and improved discharge measurements. Table 1 lists the pertinent data. The standard deviation was reduced to an average of approximately $\pm 0.9\%$ for all runs with a maximum of + 1.3%. The discharge computed from the four samples in each series varied a maximum of 1.4% from the actual discharge, averaging

TABLE 1.—LABORATORY DISCHARGE MEASUREMENTS USING FLUORESCENT DYE AS THE TRACER WITH WEIGHED DISCHARGE COMPARISONS

| Series (1) | V_e in feet (2)a | \bar{V} in feet per second (3)b | R (4)c | S, in grams (5)d | Δt , in minutes (6)e | \bar{c} in $\mu\text{g/L}$ (7)f | σ_c in percent (8)g | Q_s in cubic feet per second (9)h | Q_w in cubic feet per second (10)i | ΔQ in percent (11)j |
|------------|--------------------|-----------------------------------|---------|------------------|------------------------------|-----------------------------------|----------------------------|-------------------------------------|--------------------------------------|-----------------------------|
| 1 | 0.84 | 1.16 | 305,000 | 0.100 | 3.00 | 20.40 | ± 1.4 | 0.962 | 0.973 | - 1.0 |
| 2 | 0.84 | 1.16 | 305,000 | 0.100 | 3.00 | 20.41 | ± 0.8 | 0.962 | 0.976 | - 1.4 |
| 3 | 0.87 | 0.68 | 162,000 | 0.100 | 3.00 | 43.23 | ± 0.7 | 0.454 | 0.454 | 0.0 |
| 4 | 0.87 | 0.68 | 162,000 | 0.100 | 3.00 | 43.51 | ± 0.4 | 0.451 | 0.452 | - 0.2 |
| 5 | 0.60 | 0.62 | 370,000 | 0.100 | 6.00 | 26.27 | ± 1.2 | 0.375 | 0.373 | + 0.5 |
| 6 | 0.60 | 0.62 | 370,000 | 0.100 | 6.00 | 26.28 | ± 0.4 | 0.374 | 0.369 | + 1.3 |
| 7 | 0.68 | 0.90 | 640,000 | 0.100 | 6.00 | 15.97 | ± 0.3 | 0.618 | 0.614 | + 0.3 |
| 8 | 0.68 | 0.90 | 640,000 | 0.100 | 6.00 | 15.97 | ± 1.9 | 0.618 | 0.613 | + 0.5 |
| 9 | 0.75 | 1.08 | 890,000 | 0.100 | 5.00 | 14.65 | ± 1.8 | 0.806 | 0.818 | - 0.5 |
| 10 | 0.75 | 1.08 | 890,000 | 0.100 | 5.00 | 14.41 | ± 0.2 | 0.820 | 0.809 | + 1.3 |

a Flow depth in laboratory channel near sampling stations.

b Average velocity in flume near sampling stations.

c Reynolds number based on hydraulic radius = VR/ν .

d Amount of dry weight tracer used.

e Sampling time length.

f Average concentration derived from four collected samples, $\mu\text{g/L} = \text{ppb}$.

g Standard deviation computed for four samples from each series.

h Discharge determined by tracer dilution technique.

i Discharge determined gravimetrically by weight-time relation.

j $100 (Q_s - Q_w)/Q_w$.

only + 0.1% from the actual discharge for all runs (determined gravimetrically to better than $\pm 0.5\%$). Differences among runs can be attributed to mixing inadequacies, slight changes in channel flow (noted to be on the order of 0.5% because of power fluctuations to the recirculating pump), and to limitations in the fluorometer readout.

Several runs were made while releasing the tracer unevenly over periods up to approximately one minute. As expected, the injection rate had no significant influence on the computed discharge.

From the laboratory measurements, it was concluded that accurate stream flow measurements could be obtained if the effects of tracer losses through adsorption on banks, and inadequate lateral mixing were reduced to negligible amounts.

Preparation for stream flow measurements includes estimating the required quantity of tracing dye to be injected. The quantity to drop can be estimated from the relation

$$S = Q \bar{c} \Delta t \dots\dots\dots (5)$$

In which S = the amount of tracer injected, \bar{c} = the average concentration in the integrated sample, and t = the sampling interval which must be equal to or greater than the tracer-wave passage time. Greater time lengths than necessary do not change the value of Q , but do lower the value of \bar{c} . Therefore, the detection accuracy may be slightly reduced. An estimate of Δt can be obtained from rough estimates of the time of travel from the drop station. The upper limit would be Δt = total time of travel between injection and sampling station. Stream eddies and channel pickets will infrequently be sufficient to cause the time of passage to exceed this estimate.

For example, assume that a desirable value of τ is chosen to be 10 ppb based on 100% dry weight dye, and Q in the stream is estimated to be near 1,000 cfs. In a 10,000-ft reach of channel with an approximate velocity of 5 fps, Δt can be estimated to be about 2,000 sec. Therefore, the amount of tracer required would be

$$S = 1,000 \text{ cfs (62.4 lb per cu ft)} \left(\frac{10 \text{ parts}}{10^9 \text{ parts}} \right) (2,000 \text{ sec}) = 1.25 \text{ lb}$$

FIELD TESTS

Preliminary field tests, which consisted of a limited number of discharge measurements using Rhodamine B, were conducted on two canals, the Arizona

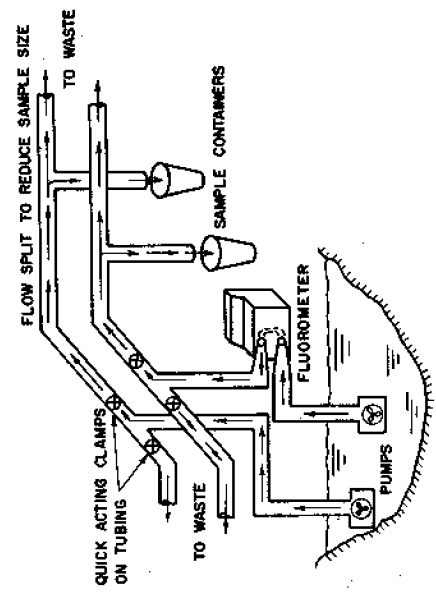


FIG. 2.—SCHEMATIC ARRANGEMENT OF FIELD SAMPLING SYSTEM

Canal and the South Canal located east of Scottsdale, Ariz. The dye was added near the stream center line about 1 mile upstream from the sampling stations. The schematic arrangement of the field sampling system using two pumps is shown in Fig. 2. The pump near the stream center line, was connected through the fluorometer to sense the arrival of the tracer wave front. The timing interval was then begun and the pump discharge switched into the sample containers. The samples were continuously collected until the fluorometer indicated that the end of the tracer wave had passed. Sampling was continued about 10% to 20% longer to assure that the dilute "tail" of the wave was adequately sampled. The valve was then switched to waste and the sampling time interval, Δt , recorded.

The integrated sample collected in each container was thoroughly mixed and about 2 liters retained for fluorometer analysis to determine tracer concentration. Enough of each sample was obtained to allow discharge to waste

TABLE 2.—FIELD DISCHARGE MEASUREMENTS WITH RHODAMINE B

| Drop No. | Canal | Mixing length, in miles | Tracer added, in grams | Integrated sample, in parts per billion | Sampling time, in minutes | Travel time, in minutes | | Calculated discharge, in cubic feet per second |
|----------|-------|-------------------------|------------------------|---|---------------------------|-------------------------|------|--|
| | | | | | | Front | Peak | |
| 1 | Ariz. | 1.0 | 940.8 | 24.8 | 35.00 | 33.00 | 39.0 | 630 |
| | | | | 26.4 | | | | 599 |
| 2 | South | 1.2 | 470.4 | 15.9 | 17.07 | 18.0 | 22.0 | 1020 |
| | | | | 15.7 | | | | 1033 |
| 3 | South | 1.2 | 470.4 | 15.8 | 17.15 | 19.0 | 22.5 | 1022 |
| | | | | 15.8 | | | | 1022 |
| 4 | South | 1.2 | 470.4 | 16.0 | 17.30 | 19.5 | 23.5 | 1001 |
| | | | | 16.3 | | | | 982 |
| 5 | South | 2.9 | 1411.2 | 26.4 | 30.65 | 62.5 | 65.0 | 1026 |
| | | | | 26.1 | | | | 1038 |

a First value is from canal center and the second 5 ft from canal bank.

during measurement and thus avoid inter-sample contamination. The fluorescence readings and sample temperatures were recorded for each sample. As mentioned earlier, it is desirable to have the readout dial on the fluorometer operating near full scale for optimum accuracy. Neutral density filters and a range of exciting-light-intensity apertures allows considerable latitude in obtaining this condition. Of course, all filters and light apertures used on the sample must also be used with the standards to eliminate transfer errors between filters and light intensity ranges.

Lateral dispersion in the Arizona Canal was not adequate at the 1-mile sampling point, as indicated by the 5% difference in concentration between the sample taken near the stream centerline and one taken about 5 ft from the bank. In the South Canal, mixing was adequate at 1.2 miles as indicated by the good agreement between the two samples. The pertinent data for these two canals are given in Table 2. While the mixing lengths were comparable for the two canals, the flow conditions were somewhat different. The Arizona

Canal flowed with an average velocity of 1.3 fps, while the South Canal flowed at an average velocity of approximately 2.5 fps.

The problem of inadequate mixing may be solved by multiple sampling procedures. Even with imperfect mixing, the average of several samples simultaneously collected from a single stream cross section should approximate the true discharge more closely as the number of samples collected is increased. The relatively low cost of the small submersible pumps permits the additional samples to be obtained economically.

No precise comparison of the discharges calculated from the tracer technique and the absolute flow rate was possible. Estimates of the release rates into the canals were obtained from Salt River Project Irrigation personnel. The tracer measurement was 8.4% lower than the estimate for the Arizona Canal and 8.5% higher than the estimate for the South Canal. The accuracy of the estimated release rates is not known.

These preliminary field tests indicate that the tracer loss levels are small in natural streams. Measurements were made on the South Canal (drops number 2 to 5, Table 2) using Rhodamine B. The integrated sample was collected at both 1.2 and 2.9 miles below the injection station. The discharge at the 1.2-mile station, calculated from the average of drops number 2, 3, and 4, was 1,013 cfs, while that at the 2.9-mile station, calculated from a single run only (drop number 5) was 1,032 cfs.

The difference is less than 2%. Approximately 1% of the difference might have been caused by error in measuring dye concentration. Bank and center line measurements on runs 2, 3, and 5 show differences caused by imperfect mixing which slightly exceeded 1%. Depending on the direction of instrument and mixing errors, error caused by dye loss of Rhodamine B could have ranged from 0 to 4%. Laboratory tests indicate that only 10% to 20% as much Rhodamine WT would be adsorbed. These field measurements led to the belief that any loss of Rhodamine B to the channel boundaries was small and that loss of Rhodamine WT would be insignificant. Additional investigation of this question is in progress.

CONCLUSIONS

1. Fluorescent tracer concentrations of less than 10 ppb can be quantitatively detected in most natural stream waters with errors less than $\pm 1\%$. This permits stream gaging with a potential accuracy of this same order provided the tracer is not adsorbed on the stream boundaries and adequate mixing of tracer with stream flow is obtained.
2. Flow measurement with fluorescent dyes, using integrated sample dilution technique, requires no special handling of materials, presents no health hazard through the water supply being measured, and is convenient to apply to natural streams, since it eliminates the requirement for detailed channel data.
3. Loss of Rhodamine WT to the stream boundaries does not appear to be a significant problem.
4. Accurate flow measurements with fluorescent dye dilution methods require the use of precision procedures including preparation of comparison standards by weighing techniques, the use of continuous flow sample cuvettes,

the application of accurate temperature correction coefficients, and proper sampling techniques.

APPENDIX.—NOTATION

The following symbols are used in this paper:

| | | |
|------------|---|---|
| C | = | concentration of tracer being injected into stream; |
| c | = | concentration of tracer in stream after mixing with streamflow; |
| \bar{c} | = | average concentration of tracer; |
| E | = | subscript used to denote flow measurement made with an elbow meter; |
| F_r | = | fluorescence reading at reference temperature; |
| F_s | = | fluorescence reading at sample temperature; |
| n | = | temperature coefficient (having units of 1 per temperature degrees); |
| q | = | tracer injection rate; |
| Q | = | streamflow rate; |
| R | = | hydraulic radius; |
| R | = | Reynolds number, based on hydraulic radius; |
| r | = | subscript referring to a property of a reference; |
| S | = | quantity of tracer; |
| s | = | subscript referring to a property of a sample; |
| T | = | temperature; |
| t | = | time; |
| w | = | subscript used to denote flow measurement made by weighing the discharge. |
| y | = | channel depth; |
| σ_c | = | standard deviation; and |
| ν | = | kinematic viscosity. |

level of the natural stream may vary, and the accuracy of the one continuous sample is reduced.

In a natural stream, the continuous addition method will probably be found to be more accurate than the slug addition method. This is because a continuous addition over a period of several hours allows an equilibrium to be established between the high-velocity parts of the main stream, the low velocity parts, and the side pockets. Downstream from a slug injection, concentrations at the sides lag those at the center; in the head part, concentrations at the side are lower than those in the center, but in the tail section the side concentrations are higher than the center. In the continuous injection method, each point sample is actually an integrated sample of slug additions over all previous time, so that differences between the sides and the center are evened out. Thus, the distance downstream for adequate lateral mixing will be less for the continuous than for the slug injection.

With respect to the so-called "adequate mixing length," the writer¹³ has suggested, on theoretical grounds, that the distance required for cross-section mixing of a slug injection in a natural stream is given by

$$L = k \frac{l^2 U}{r U^*} \dots \dots \dots (6)$$

in which L = the distance downstream from the injection point, l = a distance related to the width of the stream (approximately one-half the width), r = the hydraulic radius, U = the mean velocity, U^* = the shear velocity, and k is a constant empirically determined to be approximately 2. In terms of widths, this formula predicts a requirement of between approximately 20 widths for a rough stream with small width-to-depth ratio and more than 200 widths for a smooth stream with a large width-to-depth ratio. In the Green-Duwamish study, significant lateral variations were found at a station 150 widths downstream from a slug injection. It seems unlikely that any adequate criterion for mixing length will be found which is based on numbers of widths alone.

FLOW MEASUREMENTS WITH FLUORESCENT TRACERS^a

Discussion by Hugo B. Fischer

HUGO B. FISCHER,¹² A. M. ASCE.—The authors should be congratulated for their careful and detailed description of dyetracer techniques. Past studies have sometimes neglected the importance of temperature corrections, preparation of accurate comparison standards, and attention to the details of the instruments. It is refreshing to read of a dye study in which accuracy has been emphasized and achieved.

The writer agrees that by careful attention to detail the concentration of tracer in natural water can be measured within an accuracy of 1%, except at low concentrations (less than 1 ppb). It does not follow, however, that the discharge of natural streams can be measured to this accuracy. The dispersion characteristics of a natural stream are significantly different from those of a laboratory channel or a manmade canal. One difference is the existence of pockets of low-velocity water along the sides of almost all natural streams, whose exchange with the faster parts of the main stream is slow. During passage of a tracer cloud, some of the tracer will be caught in each of these pockets to be returned to the main stream over a prolonged period. Because of this, the time-concentration curve for a natural stream will exhibit a long, slowly-decaying tail, which may contribute 5% to 10% of the total tracer passing the measuring station, but whose concentration will be difficult to measure accurately.

As an example, the authors report a maximum measuring time of 35 min at stations as much as three miles downstream from the injection point in a manmade canal. In a natural stream, in contrast, the writer was able to detect tracer concentration in excess of background during a period of over 3 hr at a station only two miles below the injection point (a report of this study, made in the Green-Duwamish River, Washington, is being prepared for publication by the U. S. Geological Survey, and is currently available in part¹³). When measurements are continued over such a long period, the background

^aSeptember, 1966, by John A. Replogle, Lloyd E. Myers, and Kenneth J. Brust (Proc. Paper 4896).

¹² Asst. Prof. of Civ. Engrg., Univ. of California, Berkeley, Calif.

¹³ Fischer, H. B., "Longitudinal Dispersion in Laboratory and Natural Streams," thesis presented to the California Institute of Technology at Pasadena, Calif., in 1966, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

FLOW MEASUREMENTS WITH FLUORESCENT TRACERS^a

Discussions by Martin A. Mason, Cloyd H. Scott,
and James K. Culbertson, and R. V. Worstell

MARTIN A. MASON,¹⁴ F. ASCE.—The need for a simple and inexpensive, yet accurate, means of measuring the flow of water has intrigued many engineers and scientists throughout recorded history. The use of pollutants of some sort has a special appeal because of the apparent ease of procedures and relative absence of disturbance of the flow.

The writer found himself attracted to these possibilities in connection with research on the Allen salt-velocity method¹⁵ conducted in 1937, and recorded the results¹⁶ in 1940. A substantial part of the studies concerned what is believed to be the first recorded use of fluorescent materials for the measurement of water flow.

Studies were made of methods of injection of the pollutant, of various fluorescent dyes (including sodium fluorescein and Rhodamine B used by the authors), of methods of detecting the fluorescent pollutant, some elementary considerations of the diffusion of the injected material into a "cloud," and of the movement of the injected material in relation to the water movement. The writer would certainly not suggest that this early research was definitive. It was, in fact, but a small part of study of flow measurement by injected pollutants carried on in the 1920's and 1930's. It is disappointing that the authors' research did not uncover this earlier material and the contributions there made.

The authors mention the problem of mixing as a major problem in the use of pollutants for flow measurement. The same question was examined in the writer's paper,¹⁶ and had been noted much earlier by Allen and others. All available evidence shows that accuracy of pollutant methods is affected significantly by the mixing discipline of the flow.

One aspect of all pollutant methods of measurement that deserves more discussion is the matter of what might be called the natural pollution of water courses. It should be recognized that the large number of complex pollutants now found commonly in water courses may render pollutant methods of measurement largely ineffective. It seems to the writer highly probable that the widespread pollution of water by chemical, human, and industrial wastes

^aSeptember, 1966, by John A. Replogle, Lloyd E. Myers, and Kenneth J. Brust (Proc. Paper 4895).

¹⁴Dean, Sch. of Engrg. and Applied Science, The George Washington Univ., Washington, D. C.

¹⁵Allen, C. M., and Taylor, M. E., "The Salt Velocity Method of Water Measurement," Transactions, American Society of Mechanical Engineers, Vol. 14, 1923.

¹⁶Mason, Martin A., "Contribution to a Study of the Allen Salt Velocity Method of Water Measurement," Journal, Boston Society of Civil Engineers, Vol. XXVII, No. 3, July, 1940.

may well so complicate the possible uses of tracer methods of measurement as to make them practically useless. One can make a reasonably good case for the belief that large numbers of water measurement problems today involve more nearly "soups" of complex chemical nature than the relatively clean waters of two generations ago. Perhaps the authors would discuss this aspect of the matter in their closure.

CLOYD H. SCOTT,¹⁷ A. M. ASCE, AND JAMES K. CULBERTSON,¹⁸ M. ASCE.—The dye-dilution method of measuring discharge described by the authors is a practical tool for use by researchers and hydrographers. This has been brought about by the development of stable fluorescent dyes and fluorimeters for detection of the dyes. However, the dye-dilution method is not likely to replace the current meter in situations where a reliable current meter measurement can be obtained because of the relatively greater time and work involved in obtaining a dye-dilution measurement. The technique will become valuable for measuring discharges accurately where the current meter method is difficult or impossible to apply such as in flow in steep, rocky mountain streams, under ice, or through diversion tunnels.

Of the two methods for making discharge measurements by the dye-dilution technique, the authors have chosen the "slug-injection" method as being easier to apply than the "continuous-addition-of-tracer" or "constant-injection" method. This choice was made mainly because of the relative ease of determining a total quantity of tracer to be injected as a slug compared to achieving a precise constant injection rate. However, precise constant injection rates are possible with equipment that is commercially available or that can be fabricated.

The writers were recently (June, 1966) involved in the collection of field data for a study of lateral and longitudinal dispersion of dye in the Albuquerque Main Canal under the technical supervision of Hugo B. Fischer. Although the measurement of discharge by the dye-dilution technique was not the main purpose of the study, the results can be used to illustrate some of the problems involved in measurement of discharge with dye. A constant injection of dye was used to study lateral dispersion and a slug injection of dye was used to study longitudinal dispersion.

The injection tank used was a constant-head Mariotte tank with a capacity of approximately 60 l, equipped with a calibrated tube for reading volume of dye. This tank is much larger than would ordinarily be required for measuring discharge but, for this dispersion study, the injection rate had to be maintained for several hours.

The injection rate was checked at the beginning and at the end of each run by catching the dye in a graduate cylinder for approximately 1 min with time measured by a stopwatch. The injection rate during each run was checked by reading the volume change in the tank from the calibrated tube at approximately 15-min intervals with time measured to the nearest 5 sec by a watch with a sweep second hand. Readings from the calibrated tube at 15-min intervals served to indicate any large changes in the flow rate during the injection period.

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¹⁸Research Hydr. Engr., Water Resources Div., Geol. Survey, U. S. Dept. of the Interior, Albuquerque, N. Mex.

Three runs, each of about 3 hr duration, were made with the tank injecting Rhodamine WT 20% dye diluted to a concentration of approximately 8×10^6 parts per billion (ppb). For the three runs, the injection rates as determined with the graduate cylinder and stopwatch were 5.02, 4.71, and 4.86 ml per sec and as determined by the average of readings of volume change in the tank were 5.02, 4.70, and 4.85 ml per sec, respectively. During one run, a large reduction in flow rate was noted but this was quickly remedied by running a wire through the orifice. The reduction in flow rate was thought to be caused by formation of air bubbles in the orifice. F. A. Kilpatrick¹⁹ had noted that air bubbles might form in the orifice and had suggested the addition of a couple of drops of laboratory grade liquid detergent to the dye solution to eliminate the problem. It was found that one drop of detergent in 7 l to 10 l of dye solution eliminated the formation of bubbles in the orifice and did not cause objectionable foaming of the dye solution. For two runs the flow rates as indicated by tank volume change readings had maximum variations of +0.4% to -1.8% and from +1.5% to -1.4% from the average rate. This indicates that injection rates may be maintained within 2%.

The problem of mixing length is very real for either the slug-injection or the constant-injection methods. This problem is best solved by preliminary work at the site to determine an adequate mixing length. The authors recommended allowing at least 100 top widths for mixing length, but this may not be adequate. For instance, in the Albuquerque Main Canal, about 130 top widths of length were required for nearly complete mixing when the dye was injected at the center of the channel. The problem of mixing length can be avoided if the samples obtained for fluorometric analysis at several points in the cross section are proportional to discharge in the subsection which the sample represents. This can be seen by considering Eq. 3 which is rearranged to give

$$S = Q \bar{c} \Delta t \dots \dots \dots (7)$$

and letting $S = s_1 + s_2 + s_3 \dots + s_n$ $\dots \dots \dots (8a)$

and $s_n = \bar{c}_n q_n \Delta t \dots \dots \dots (8b)$

in which s_n = the portion of dye passing the n th subsection, \bar{c}_n = the concentration of dye, and q_n = discharge in the n th subsection. Then,

$$S = s_1 + s_2 + s_3 + \dots + s_n = (\bar{c}_1 q_1 + \bar{c}_2 q_2 + \bar{c}_3 q_3 + \dots + \bar{c}_n q_n) \Delta t \dots (9)$$

and the total volume of dye injected, which is required for computing the correct discharge by the slug-injection method, can be accounted for at a downstream section, provided there are no losses of dye at the boundary. It can be shown by a similar procedure that the concentration in Eq. 1 must be discharge weighted if lateral mixing is not complete. Estimates of the portion of total discharge in each subsection can be made in the field but, if these are more than "eyeball" estimates, the usefulness of measuring discharge by the dye dilution method is, in part, negated.

If samples could be obtained that were discharge weighted mechanically, there would be no need for estimating the discharge in the subsections. Samples for analysis of suspended-sediment concentration are obtained with samplers which collect the water-sediment mixture at approximately stream

velocity. The samples are obtained by the equal-transit-rate (ETR) method²⁰ in which a sample of water-sediment mixture is taken at each of several equally spaced verticals in the cross section at the same transit rate in each vertical; the resulting sample is discharge weighted.

Kilpatrick¹⁹ used the ETR sampling method to obtain discharge-weighted dye concentrations in conjunction with the constant-injection method and found that discharge computed by the dye-dilution method compared well with discharge measured by current meter. The ETR sampling method was also used during Albuquerque Main Canal dispersion study. During the particular run that the ETR samples were obtained for analysis of discharge-weighted dye concentration, the dye was injected at a constant rate from a Mariotte tank about 2 ft from the left bank. ETR samples were obtained at cross sections 4,000 ft and 6,500 ft below the injection point where the mixing was computed as 68% and 81%, respectively based on surface samples obtained at 2-ft intervals. The discharges computed by the constant-injection method from the discharge-weighted dye concentrations and an average injection rate of 4.85 ml per sec were 263 cfs and 258 cfs, respectively, at the sections 4,000 ft and 6,500 ft below the injection point. The discharge as determined as the average of eight current meter measurements at eight cross sections was 262 cfs, with maximum deviations from the mean of +2.3% and -3.1%. It should be noted that these results were based on a single set of ETR samples obtained at each cross section. Had several sets of ETRs been taken at each cross section and the results averaged, the final result might have been improved. The ETR method of sampling works quite well for obtaining a discharge-weighted dye concentration with the constant-injection method where lateral mixing is not complete, but would be very difficult or impossible to apply to the slug-injection method because of the rapid change of concentration with time.

The authors discussed loss of fluorescence in the presence of sediments, indicating that rather large losses are possible, but that losses to sediments can be compensated for by making standards from the stream water. Unfortunately, the authors had only estimates of discharge at the time their field tests were made and therefore an absolute check on losses of dye is not possible. However, the agreement between run 5 and the average of runs 2, 3, and 4 does indicate that total recovery of dye was achieved.

An example will serve to illustrate that a large loss of dye, either apparent or real, can result for the slug injection method. For the longitudinal dispersion study in the Albuquerque Main Canal, 100 ml of Rhodamine WT was mixed with approximately 900 ml of stream water and the solution was injected from a boat by pouring the solution as uniformly as possible as the boat was moved across and downstream. The resulting slug appeared as a line across the channel intervals at cross sections 5,000 ft, 9,000 ft, and 12,200 ft downstream of the injection point. Standards for calibration of the fluorometer were made from stream water at the same time the experiment was carried out and, therefore, losses to sediment or effects of chemical quality of water on fluorescence should have been largely compensated. The concentration of suspended sediment at the time of the study was about 1 g per l of which 70% was

²⁰"Methods Used in Measurement and Analysis of Sediment Loads in Streams: Determination of Fluvial Sediment Discharge," Report No. 14, U. S. Inter-Agency Committee on Water Resources, U. S. Government Printing Office, Washington, D. C., 1963, p. 41.

¹⁹Kilpatrick, F. A., personal communications, May, 1966.

in the clay and silt size range. Contrary to the statement by the authors that a concentration of 1 g per l is high for a natural stream, many streams in the southwest and central plains experience much higher concentrations; concentrations in excess of 400 g per l have been recorded.²¹

The concentration-time distributions for the slug-injection test were well defined and, from these, the areas under the curves were determined by planimeter which is equivalent to the product of the mean concentration and time used by the authors. The percentage recovery of dye at the various cross sections was computed from the known quantity of dye injected, the water discharge (by current meter), and the unweighted mean concentration at each section. The recoveries were computed at 93%, 90%, and 87% at cross sections 5,000 ft, 9,000 ft, and 12,200 ft downstream of the injection point, respectively.

It should be noted that the dye was apparently not injected uniformly across the channel because the peak and mean concentration at the center of the 5,000-ft cross section was higher than at the other two points in the cross section. At the 12,200-ft cross section, the peak concentrations at the quarter points were equal but the means still differed slightly. The concentration peaks occurred at the same time at the 5,000-ft section but the peak at the center preceded the peaks at the sides by about 3 min at the 12,200-ft section even though the leading and trailing edges of the dye were so close together that no difference in time of arrival could be distinguished among them.

It is thought that the computed loss of dye is more apparent than real and resulted because not enough points in the cross section were sampled to give a correct average concentration of dye. However, if the loss of dye was real, then the usefulness of the slug-injection method may be limited as a tool for measuring water discharge. Certainly, more investigation of real losses of dye on sediments and apparent losses of dye by sampling procedure in the field is needed.

The procedure outlined by the authors for making standard solutions for calibration of the fluorometer is rather time consuming if carried out for each measurement. From Eqs. 1 and 3, it is seen that the computed discharge depends, in part, on the ratio of the concentration of the dye injected to the concentration of the dye in the stream. Because the computed discharge depends on the ratio of dye concentrations, or more specifically, the ratio of relative fluorescence, it is necessary to determine only the correct relative fluorescence of the samples from the stream and the dye that is injected. This can be done as follows. At the time the discharge measurement is made, a small measured quantity of the dye to be injected is diluted in a measured volume of the stream water to a concentration that can be conveniently run on the fluorometer. The sample obtained from the stream and the diluted injection dye are then run on the fluorometer and, if readings for both can be obtained at the same light intensity setting of the fluorometer, the correct ratio of concentrations is obtained as the ratio of the instrument dial readings multiplied by the dilution factor, provided the relation of dial readings to concentration is linear. The dilution factor is computed from the known quantities of dye and water used in diluting the sample of injection dye for fluorometric analysis. Of course, it may not always be possible to read the relative fluorescence at the same light intensity setting and then it is necessary to

²¹Beverage, Joseph P., and Culbertson, James K., "Hyperconcentrations of Suspended Sediment," *Journal of the Hydraulics Division*, ASCE, Vol. 90, No. HY6, Proc. Paper 4136, Nov. 1964, pp. 117-128.

have the fluorometer calibrated. The only purpose of the calibration is to provide the correct relative concentration and therefore the only stringent requirement of the calibration is that it yield the same concentration for a given sample at different light intensity settings.

The standard solutions for calibration can be made with any water although distilled water is preferred. Tap water containing chlorine should not be used because chlorine is known to quench fluorescence of rhodamine dyes. The calibration standards, if properly stored, are usable for several months. The main advantage in this procedure is that a complete set of standards do not have to be made for each discharge measurement. Also, the computed discharge is no longer dependent on the manufacturers' stated concentration of the dye which, by the authors' procedure, could introduce an unknown, but probably small, error in the computed discharge.

The authors devised a system for recirculating a sample through a continuous flow cuvette to overcome the problems of nonuniform individual cuvettes and effects of temperature rise on samples run in individual cuvettes. The system does offer distinct advantages with respect to these problems, but if a number of unknown samples are to be run, adequate flushing of the system to prevent intersample contamination could become time consuming. The problems of temperature rise and readings from cuvettes were also encountered by the writers but it was found with some experience that the problems could be overcome. The samples were run in individual 5-ml cuvettes from a matched set, and during some practice sessions made to perfect techniques for operating the fluorometer, it was found that temperature rises of the samples of 2° C or 3° C were not uncommon. Such a temperature rise would, of course, require a correction but, because as many as 200 samples were to be collected during a single run, it was desirable to avoid temperature corrections and this was accomplished by the following procedure: The samples and standard solutions, stored in 25-ml glass vials, were temperature stabilized in a water bath at room temperature. When the cuvette was placed in the cuvette chamber of the fluorometer, the dial reading would rise to a maximum value and then fluctuate about a mean for a few seconds before beginning to slowly decrease. The slow decrease was due to temperature rise of the sample. The reading taken for the sample was the mean maximum value. Because the sample was in the cuvette chamber only a matter of seconds, temperature rises were less than 0.5° C as indicated by measurements.

The door of the cuvette chamber was left open between samples to allow cooling of the chamber. No drift of the instrument was detectable because of a change in chamber temperature as indicated by the zero reading with a blank cuvette. However, 1 hr or more warmup time of the components was allowed before instrument zero was set. Based on experience, several hours warmup time of components should be allowed. Instrument drift experienced by the authors may have been caused by warmup of components rather than warmup of the cuvette chamber.

Dial readings of one or two divisions for the individual cuvettes with the largest light opening of the instrument were also found during the practice sessions. Although the cuvettes appeared to be clean, it was found that a complete scrubbing of the cuvettes with a soft brush in a laboratory grade detergent followed by a rinse in demineralized water eliminated the problem completely and zero readings with cuvettes filled with demineralized water could be obtained. Also, it was found that a rinse in demineralized water be-

tween samples was all that was necessary to prevent inter-sample contamination. Once a cuvette had been allowed to dry, a scrubbing in detergent was usually necessary even though the cuvette had been rinsed before drying.

The dye-dilution method is practical for measuring water discharge under conditions where the conventional current meter method would be difficult or impossible to apply. Perhaps the authors should not overlook the constant-injection method as a practical field method because of the apparent difficulty in maintaining constant injection rates. The constant-injection method may be easier to apply than the slug-injection method in terms of time and equipment required in the field. This is particularly true if the ETR method of sampling is used to obtain a discharge-weighted dye concentration.

ROBERT V. WORSTELL,²²—The authors used fluorescent dye techniques to measure water flows in open channels. Using careful laboratory techniques and cross-checking of downstream sampling, field measurements were achieved that were repeatable within 2% or less when comparing midstream and near-the-bank measurements. However, with a similar procedure, it has been impossible to get satisfactory duplication of flow measurements in an earth canal of smaller capacity in southern Idaho.

The channel characteristics are as follows: Top width, 25 to 30 ft; average maximum depth, 5-1/2 ft; shape, approximately a circular bottom; average cross-sectional area ranges between 70 sq ft and 100 sq ft; average cross-sectional velocity ranges between 1.0 fps and 1.85 fps. The channel alignment is carried around the contour of the slope, usually with gentle curves. The soil is silt loam texture and the canal has been in service for more than 10 yr. Some moss and algae were present while these flow measurements were made. The water, which is pumped from the Snake River, is of good quality with respect to salinity, but may contain some treated industrial effluents from food processing plants.

Slugs of a 20% solution of Rhodamine WT fluorescent dye were weighed to an accuracy of about 0.01% on a Mettler balance. This dye was poured into the canal at midstream at a point immediately above a drop structure so that turbulence below the structure would mix the dye and water across the width of the channel. The dye was carefully washed out of the container as rapidly as possible.

The minimum desirable mixing distance was determined to be one mile or more from the point of dye injection. This distance corresponded to length requirements recommended by the authors and by Schuster.⁷ The dyed water was observed to meander down the channel in an uneven distribution for a distance of nearly 1/2-mile from the point of dye injection.

The downstream sample was collected with a submersible pump suspended at midstream about 1 ft below the surface. The pump was purged of air bubbles by switching on and off several times.

The fluorometer was carefully sealed to eliminate stray light effects and was allowed to warm up for at least 20 min before measuring the fluorescence of the integrated sample. Temperature differences were compensated for. The 20-cc flow-through cuvette was used with a lower power lamp than that used by the authors, because bubbles were not found to be a problem. The larger cuvette and the lower power light source gave about the same sensitivity

²²Research Agric. Engr., Northwest Branch, Soil and Water Conservation Research Div., Agric. Research Service, U. S. Dept. of Agric., Kimberly, Idaho.

as the combination used by the authors.

Calibration standards were carefully prepared by weighing and diluting the dye to concentrations of 1 to 10,000. Carefully weighed amounts of this solu-

TABLE 3.—COMPARISON OF FLOW RATES BETWEEN IRRIGATION DISTRICT MEASUREMENTS AND REPEATED FLUOROMETER MEASUREMENTS IN IRRIGATION CANALS

| Test No. (1) | District flow rate, in cubic feet per second | Fluorometer flow rate, in cubic feet per second | Difference compared to district flow rate, in percentage | Difference between mean of fluorometer flow rates, in \pm percentage |
|--------------|--|---|--|--|
| 1 | 78 | 64 | -18 | 8.5 |
| | 78 | 76 | -3 | |
| 2 | 79 | 95 | +20 | 2.6 |
| | 79 | 100 | +27 | |
| 3 | 82 | 59 | -28 | 0.8 |
| | 82 | 60 | -27 | |
| | 82 | 68 | -17 | 2.9 |
| | 82 | 72 | -12 | |
| 4 | 95 | 67 | -29 | 0.7 |
| | 95 | 68 | -28 | |
| | 95 | 66 | -30 | 1.5 |
| | 95 | 68 | -28 | |
| 5 | 98 | 102 | +4 | 8.4 |
| | 98 | 120 | +23 | |
| 6 | 96 | 110 | +15 | 7.3 |
| | 96 | 95 | -1 | |
| 7 | 33 | 27 ^b | -18 | 13.5 |
| | 33 | 36 ^b | +8 | |
| 8 | — | 49 ^b | — | 8.0 |
| | — | 42 ^b | — | |
| 9 | 98 | 98.5 | 0 | — |
| 10 | 148 | 140 | -6 | — |
| 11 | 173 | 164 | -5 | — |
| 12 | 99 | 95 | -4 | — |
| 13 | 101 | 116 | +15 | — |
| 14 | 101 | 84 | -16 | — |
| 15 | 92 | 63 | -32 | — |
| 16 | 85 | 73 | -14 | — |

^a \pm 8%.

^b Measurements of a canal lateral.

tion were then used to dilute a 40,000-g sample of the canal water to concentrations ranging between 0 and 10 ppb. These data were plotted and found to be linear within \pm 1% for any one day's calibration. The total error of concentration measurement of the integrated sample using this simplified method amounts

to $\pm 2.3\%$ maximum if readings are made in the upper one half of the range of the fluorometer dial.

This procedure was used on the above canal system and duplicate runs were made (within about 2 hr of each other) 11 times for comparison with each other and 26 times for comparison with the flow determinations used by the irrigation district. The district measurements are obtained from a large flow meter with an assumed accuracy of $\pm 5\%$ as compared periodically to stream gage measurements. Between this flow meter and the reach of canal to be tested, there are also constant diversions (24-hr periods) of 15% to 20% of the canal water. These diversions are measured with weirs with a probable accuracy of $\pm 10\%$. This gives a 24-hr constant flow rate known to approximately $\pm 8\%$ accuracy in the reach of canal being tested by the fluorometric method.

TABLE 4.—COMPARISON BETWEEN FLOW RATES AS DETERMINED BY REPEATED FLUOROMETRIC MEASUREMENTS ON REYNOLDS CREEK CHANNEL

| Test No. | Flow rate by weir measurement ^a , in cubic feet per second | Fluorometer flow rate, in cubic feet per second | Difference between mean fluorometer rate, in \pm percentage |
|----------|---|---|---|
| 1 | 25 | 21.30 | 0.70 |
| | 25 | 21.60 | |
| 2 | 28 | 24.40 | 4.90 |
| | 28 | 26.90 | |
| 3 | 28 | 28.50 | 3.80 |
| | 28 | 26.40 | |
| 4 | 25 | 21.25 | -3.33 |
| | 25 | 22.45 | +2.15 |
| | 25 | 22.23 | +1.14 |
| 5 | 25 | 23.95 | 2.04 |
| | 25 | 24.95 | |
| 6 | 30 | 28.00 | -1.70 |
| | 30 | 29.21 | +2.57 |
| | 30 | 28.23 | -0.88 |

^a $\pm 10\%$.

Table 3 shows the results of a comparison of the fluorometric flow measurements with the irrigation company flow readings. These measurements varied from -32% to 27% of the irrigation district values. Table 3 also shows that fluorometric readings for identical flows vary to $\pm 13.5\%$. In ten comparisons between identical flows, only three fell within a potential computed accuracy range of $\pm 2.3\%$. Two other comparisons fell close to this accuracy, but not within it. One-half of these comparative readings indicate that the fluorometric technique does not always have great precision or repeatability under these flow conditions.

Table 4 shows a similar comparison between duplicate flow measurements that were taken on a small mountain stream of clear, snowmelt water flowing in a fairly steep, rocky channel. Mixing distances were short because of the turbulence and the smaller dimensions of the channel. In these comparisons, six out of ten of the comparisons fell within the accuracy of $\pm 2.3\%$. The

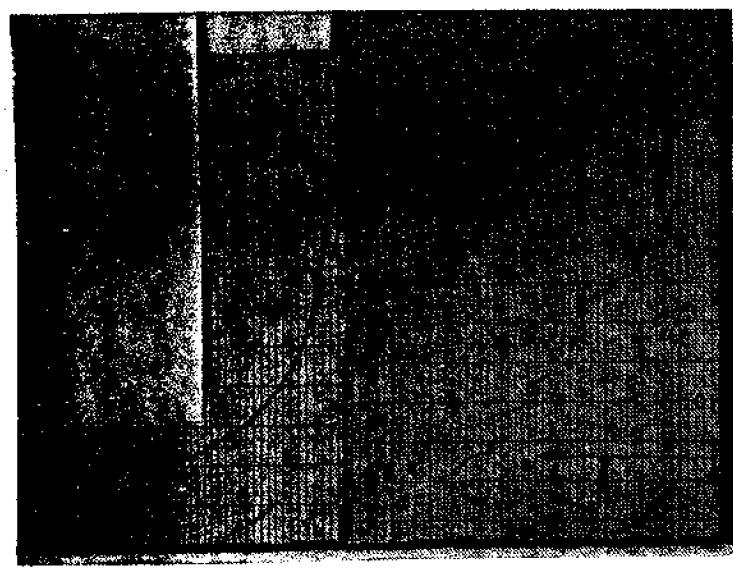


FIG. 3.—ENDS OF TWO FLUOROMETER RECORDS

TABLE 5.—DATA FOR FIG. 3

| Location | Upper trace | Lower trace |
|--|-------------|-------------|
| Amount of dye used, in grams | 8 | 12 |
| Flow rate measured, in cubic feet per second | 24 | 42 |
| Travel velocity, in feet per second | 2.5 | 1.2 |
| Dye concentration in integrated sample, in parts per billion | 23 | 9.2 |
| Repeatability, in percentage | ± 2 | ± 8 |

other four readings fell within 5% of each other. In this instance, the flow was increasing slowly while the "duplicate" runs were being made so some of the fluorometer measurements may be somewhat more accurate than indicated in Table 3.

Possibly as a result of the turbulence that was visible in the rocky channel, the trace of the fluorescence of the water at the downstream point showed much less variation in amplitude than did the trace of the fluorescence of the canal water as is shown in Fig. 3.

In Fig. 3, the horizontal scale is 0.375 min per division and the vertical scale is 0.46 ppb of fluorescent dye per large division. All data pertinent to the figure is given in Table 5.

The lower trace is from the end of the recorder chart for a test run in a 10-ft-wide canal lateral. The upper trace is from the end of a test run in the channel on the mountain watershed. In both cases, the fluorometer sensitivity setting was the same. It can be seen that the fluorometer readings fluctuated several percent of full scale in the canal measurement. The computed flow rate associated with the lower trace on Fig. 3 was about 15% lower than that of a run taken about 30 min earlier under supposedly identical conditions. The flow rate associated with the upper trace of Fig. 3 was about 4% lower than one taken 30 min later under supposedly identical conditions.

The fluorometer technique for measuring channel flow rate seems to be affected by some undefined variables which prevent repetitive measurements of the same flow. In certain types of flow, the meandering action of the main stream of flow in a channel may continue to give varying concentrations of dye across the channel width no matter how long the mixing length of flow after the dye is injected. There may be other variables which are not readily apparent.

It may be concluded that the measurement of open-channel flows by fluorometric methods needs further study before it can be used as a precise method for research. Unknown variables can cause differences in measurement of as much as 25% between two supposedly identical tests.