DISSERTATION

# A SYSTEM FOR DETECTING FLUORESCENT TRACERS IN STREAMFLOW

Submitted by

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In partial fulfillment of the requirements

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WE HEREBY RECOMMEND THAT THE DISSERTATION PREPARED UNDER OUR SUPERVISION BY Harold Wolfgang Steppuhn

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ABSTRACT OF DISSERTATION

A SYSTEM FOR DETECTING FLUORESCENT TRACERS IN STREAMFLOW

A system is developed capable of continuously monitoring the relative concentration of a fluorescent tracer in streamflow. Stream-side instrumentation automatically registers stream-borne tracer concentrations as a function of time on a gelatin-coated film. The film is routed through a device which passes a continuous sample-aliquot diverted from the tracer-dosed stream over a small segment of the film. The "exposed" film is periodically gathered from stream sites and analyzed in a laboratory-based fluorometer.

Utility of the system is studied for the gaging of streamflow to produce a hydrograph, to measure stream discharge instantaneously, and to determine time-of-stream-travel.

Hydrographs resulting from 640 hours of gaging two Colorado mountain streams with the system are compared to those obtained from closely located sharp-crested weirs. The maximum instantaneous deviation between hydrographs reaches 10% and average absolute departure equals 1.8%, while algebraic departure averages +0.3%.

The practicality of using this system to obtain time-of-stream-travels is demonstrated for five Colorado mountain streams. A total of 62 traveling tracer-clouds are registered on gelatin-coated film, from which time-of-stream-travels are determined.

Processes involved in the system and factors affecting its precision are investigated. Theoretical and experimental evidence strongly indicates that the bulk of tracer uptake by gelatin follows processes that are physical rather than chemical in nature. Stream temperature changes and duration of film-tracer contact are the two most important factors affecting precision of the system. Neither major factor caused any unsolvable problem when field operations were standardized.

The system will have utility in operations where an expensive, temperature-sensitive fluorometer can not be stationed stream-side, and where the particular objectives of stream measurements do not justify the cost of conventional techniques, but where fair accuracy and continuous records of short to moderate duration are desired.

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# CHAPTER I

## INTRODUCTION

The use of fluorescent tracers in hydrology continues to multiply as the demand for basic hydrologic data increases. Fluorescent tracers have been used to detect the direction and speed of ground water flow, to investigate circulation in lakes and reservoirs, to sense the uptake of water by plants, to determine waste dispersion characteristics of rivers and harbors, to measure the time-of-travel through waterways, and to gage rates of streamflow. From these pursuits hydrologists have found certain fluorescent tracers to be very satisfactory with regard to stability, cost, toxicity and detectability.

Of the great number of fluorescent tracers available, only a few exhibit the combination of properties essential for water tracing. Five xanthene dyes have either been used extensively or are recommended as suitable tracers: fluorescein for ground water tracing; rhodamine B or Rhodamine BA[1/] for time-of-travel and dispersion studies; Rhodamine WT[1/] or Pontacyl Brilliant Pink B[1/] for stream gaging. Wilson (1967) characterized these dyes as (1) highly detectable, that is, their

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1/ Product of E.I. duPont de Nemours Co., Willmington, Delaware. (Trade names and company references are used for the benefit of the reader, and do not imply endorsement or preferential treatment by the Bureau of Reclamation, U. S. Dept. of Interior or Colorado State University)

fluorescence can be isolated and quantitatively measured, (2) water soluble, (3) harmless in low concentrations, (4) inexpensive, and (5) reasonably stable in natural waters.

Tracer techniques in hydrologic studies commonly consist of releasing dye into the water at one location and detecting its presence and strength at a second. In surface water studies two methods of dye detection are currently in use.

In one method a highly sensitive fluorometer is stationed stream-side or carried water-borne in a boat. A continuous sample of dozed water is passed through the instrument and quantitatively analyzed for dye presence. Fluorometer outputs are automatically recorded on a paper strip-chart or punch tape. This method is continuous, but not self-operative, for few hydrologists are willing to leave an expensive, temperature-sensitive instrument unattended in the field. Also, the entire utility of the fluorometer is spent at one sampling site.

The second method, or more precisely, group of methods, consists of obtaining liquid samples from the dosed water and either bringing the fluorometer to the samples or transporting the samples to the laboratory-based fluorometer. The latter transfer negates any need to calibrate the instrument for sample temperature variation (Dunn and Vaupel, 1965). Sampling by this method is neither continuous nor automatic. However, some researchers have developed automatic samplers, which integrate discretely apportioned liquid samples (Replogle, Myers and Brust, 1966; Goodell, Watt and Zorich, 1967). Fluorometric analysis

of the integrated sample yields an average value for the quantity of dye passing through the sampler during the time interval of operation. Integration methods do not supply any information concerning the time and distribution of tracer passage.

The ideal dye detection system probably varies with the information desired, the conditions during measurement, and the expense that can be tolerated. Never-the-less, several characteristics are universally desired in any system, namely: (1) that the system can accurately isolate and detect fluorescent dyes in low concentrations, (2) that it can automatically and continuously record the time-distribution of concentration changes in a dye-water solution passing the sampling point, (3) that it can sample a number of points within the water body investigated, (4) that it can operate inexpensively and reliably in all environments, (5) that it can readily be implemented, removed, and transported, and (6) that, if necessary, it can store tracer information prior to fluorometric analysis.

Seeking a technique to continuously gage streamflow with tracer-dyes, Zorich (1966) attempted to develop a suitable dye-dilution system. He reasoned that a successful system would require an intermediary operation between sampling in the field and fluorometric analysis in the laboratory. Attempting to perfect a stream-side apparatus for the intermediary operation, he passed strip-form filter paper under clockwork control across a small flow of the dye solution. The paper absorbed the solution, but the dye migrated along the moisture gradient

as the paper dried. He tried with modest success to limit migration with impermeable barriers applied at intervals along the strip, but he did show that a commercial fluorometer could be modified to accept and scan a continuous strip of dye-impregnated paper.

The study herein reported continued the research initiated by Zorich (1966). As in his study, the basic objective was to develop an inexpensive, field-operative system for detecting fluorescent tracers in streamflow. The system was intended to: (1) detect water-borne fluorescent dyes in low concentrations, (2) operate continuously and automatically at low cost, (3) possess sampling versatility, (4) consist of uncomplicated, portable field equipment, and (5) retain an informational storage capability prior to fluorometry.

The second objective of this study was to investigate application of the developed detection system for: (1) instantaneous measurement of stream discharge, (2) the production of a stream hydrograph, and (3) the direct measurement of stream travel time.

# CHAPTER II

## THE DETECTION SYSTEM

Two basic units, one on-site, the other laboratory located, constitute the tracer-detection system developed during this study. A portable stream-side unit automatically registers changes in stream-tracer concentration on a moving strip of gelatin-coated film under clockwork control. Depending on measurement objective, film strips are removed from the unit at intervals of up to ten days. They are brought to the laboratory and either stored temporarily or analyzed directly in a fluormetric unit. During analysis a sensitive null-balancing fluorometer measures continuously the intensity of fluorescent energy emitted by tracer molecules registered on these gelatin-coated film strips. The instrument generates a direct current, millivolt (or milliampere) signal, which permits the time-distributed fluorometric information to be readily recorded. Each laboratory-based fluorometric unit will service a number of stream-side units.

### Description and Operation, Stream-side

An automatic tracer detection system capable of operating at remote sites requires compact, reliable, portable equipment. Operation should be as simple as practical and as independent of electrical power

as possible. Stream-side equipment developed in the course of this study consists of three major components; (1) a stream sampler, (2) an electric power supply, and (3) a tracer registration device. The first two supply and serve the latter component; most parts of all three components are usually bank-mounted.

Stream sampling

The sampler was designed to provide a small, steady aliquot of the dosed stream to the registration device. (Figure 1) A screened intake vessel anchored to the stream bed allows gravitational flow through a hose to a stream-side, open-topped tank. Free overflow from this tank maintains a constant head on a hose leading to the tracer registration device.

The intake vessel, or bucket, consists of a galvanized metal container about one foot in diameter and five inches deep (Figures 2 and 3). The open top of the container is covered with brass wire cloth of 80 mesh (openings approximately 177 microns square). In the stream the screen is kept clean by the passing current. Two parallel steel rods are welded to the vessel's bottom. These stabilize the vessel when it is submerged in the stream. Steel stakes are driven into the stream bed and further secure the intake vessel. Contents of the vessel drain continuously through an outlet to which a flexible 3/4-inch garden hose is attached.

Flow in the hose can be either gravitational or pump driven. Gravity systems rely on the natural fall of the stream channel which

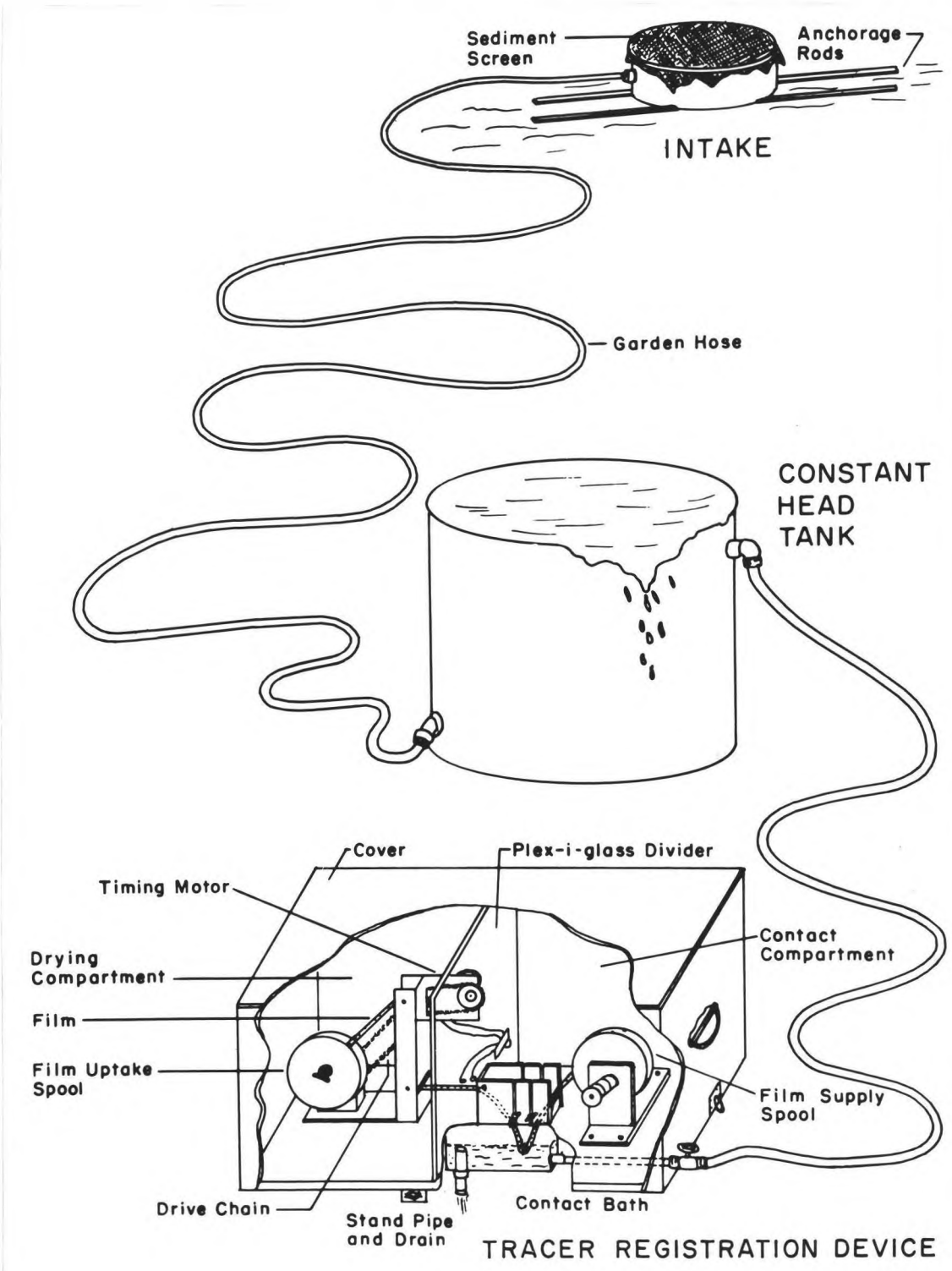


Figure 1. Stream-side unit of the detection system, shown with flow route of the stream aliquot.

Figure 2. Intake vessel, showing screen covering.

Figure 3. Intake vessel placed in stream.

controls the hose length. A minimum flow of three liters per minute can be obtained on most mountain streams with hose lengths of 300 feet.

The lower end of the hose fastens directly to the constant-head tank. As its name implies, and Figure 1 shows, free overflow from this tank maintains an invarient hydraulic head causing a small flow from this tank to the tracer registration device. The stream aliquot is here reduced to about 1.5-2.5 liters per minute and is carried between units by an 8-foot, valve-controlled conduit.

The tank also promotes settlement of any suspended sediment before the sample passes through the registration device. The larger the tank, the greater the settling potential, but a larger tank also causes tracer concentrations to be distributed over longer periods of time. Tank capacity is therefore dependent on measurement objective; time-of-travel measurements require a smaller vessel (Figure 4), while stream gaging allows a larger tank to promote settling (Figure 5).

Power supply

The tracer registration device demands a small, but constant supply of electrical power. The supply can be furnished from any battery pack capable of providing continuously for a week or longer 22 milliamperes at from 19 to 30 volts.

In this study, three four-cell, zinc-carbon storage batteries ("Hotshots"), two 12-volt and one 6-volt, were wired in series to form an adequate battery pack (Figures 6 and 7). At a continuous drain of 22 milliamps and a 20-volt cutoff, the rated service life of these

Figure 4. Constant-head tank, 1.4-liter capacity.

Figure 5. Constant-head tank, 28-liter capacity.

Figure 6. Battery pack, lid open.

Figure 7. Battery pack, lid closed.

batteries is 1000 hours or about six weeks. In the outdoor environment characteristic of this study, service life was shortened to about 950 hours.

Tracer registration

The tracer registration device sketched in Figure 1 and photographed in Figure 8, performs the central stream-side task of continuously recording the relative tracer concentrations in the stream aliquot. Flow from the constant-head tank supplies a reservoir of about 155 cc capacity located within the registration device. Liquid levels in the reservoir are maintained constant by a standpipe drain through which the flow returns to the stream. Standpipes of varing heights serve to adjust the volume of storage in the reservoir, while a plastic ball-valve allows manual regulation of flow rates through the reservoir.

Immersed in the impounded flow to a pre-set and constant depth is a loop of gelatin-coated film[1/] . The film, which is perforated for sprocket gear drive, is drawn through the tranquil flow of the stream aliquot in the reservoir by a five-watt timing motor[2/] . From the reservoir the film passes through a drying chamber activated by a desiccant and then into storage on a motor-driven spool.

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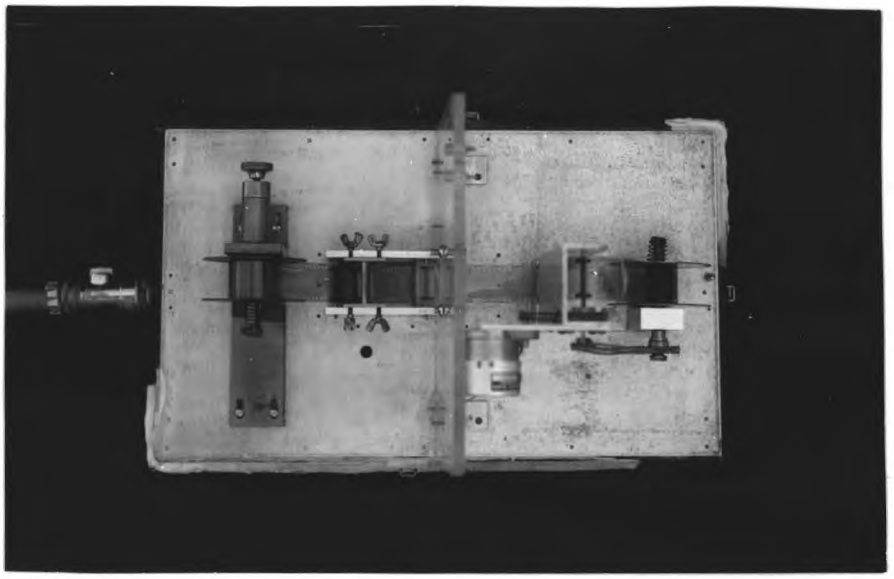
1/ Dry Bimat Transfer Film, Type SO-111-A (double-coated) and Type 2436-A (single coated); Products of Eastman Kodak Company, Rochester, New York.

2/ Timing Motor; Manufactured by A. W. Hayden Company, Waterbury, Connecticut.



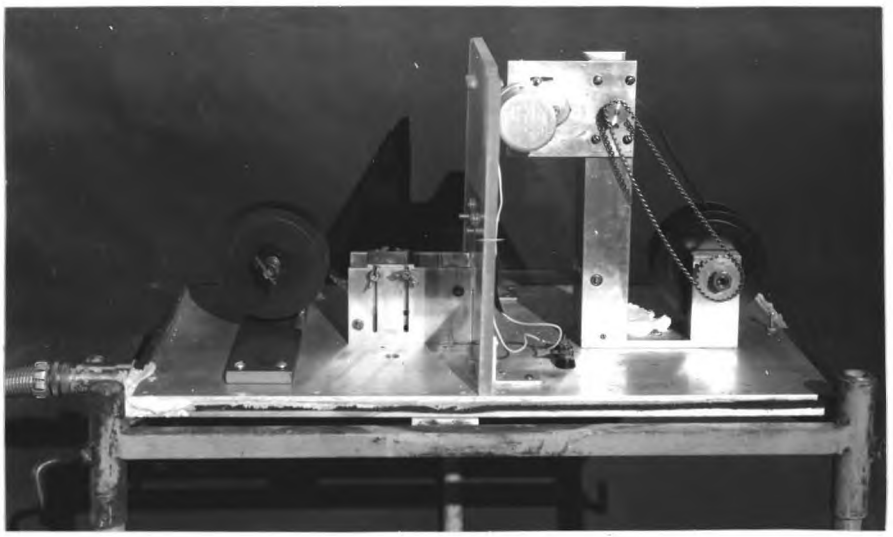


Figure 8. Tracer registration device, top and side views.

The gelatin-coated film used is a commercially available product consisting of a polyethylene terephthalate support film coated with a hydrophilic gelatin layer. The 4-mil (101.6-micron) support film carries either a single gelatin coating of 0.8-mil (20.3-micron) thickness or a double coating of 0.8 mils on one side and 0.1 mils (2.5-microns) on the other. Both films are available in 35mm widths and 100-foot lengths and are supplied on standard, Number 10 spools, 9.3 cm in diameter and 3.7 cm wide.

Installation of "fresh" film into the tracer registration device is simple. A Number 10 spool containing fresh film is centered on a rotating axle whose torque drag can be adjusted. Sufficient drag is applied to eliminate any slack in the subsequent film train. The lead end of the fresh film is threaded around six directional sprockets which engage the perforations along the film's edges. One sprocket is adjustable vertically and serves to immerse a loop of film into the reservoir to any desired depth. The last of the six sprockets is rotated by the timing motor and drives the film train.

The motor, which is powered by the battery pack, can be geared to deliver different speeds to the film-drive sprocket. Optimum film speed varies with measurement objective, 4.5 inches per hour for stream-gaging and 9.0, 11.25, or 27.0 inches per hour for time-of-travel studies. At a film speed of 4.5 inches per hour a full spool of film contains a supply sufficient for ten days of operation.

During contact with the stream aliquot in the reservoir, the gelatin layer imbibes enough liquid to swell it to many times its original bulk. The swollen gelatin is flexible, soft and easily torn. To facilitate drying, the film is routed through a drying chamber. Here the gelatin layer is dried to about 15% moisture (by weight) by the deliquescent action of a super-saturated aqueous solution of the hexahydrate of magnesium chloride ($MgCl_2 \cdot 6H_2O$). About 500 grams of the desiccant is sufficient under most conditions to dry the film within 1.5 hours when exposed in a drying compartment containing 900 $inch^3$ of free air space (Figure 9). A small battery-powered fan blowing over the film increased drying efficiency by three-fold during time-of-travel trials conducted during this study. Richardson and Malthus (1955) wrote that $MgCl_2$ in a saturated aqueous solution maintained an ambient relative humidity of 32.4% at 25°C.

As the film is advanced, immersed, and dried, it is wound on a rotating storage spool previously described. This uptake spool is mounted on an axle rotated at an angular speed sufficient to eliminate slack in the film as it is stored. A set of gears linked by a chain and powered by the timing motor maintains the desired rotational speed. A slip-clutch assembly prevents excessive film stress and breakage as the circumference of the film core, and thus the film speed, increases due to successive film windings.

Figure 9. Tracer registration device in service complete with magnesium chloride desiccant.

Servicing the instrument

The frequency and degree of attention required by the stream-side units depend on measurement objective. Normally, time-of-stream-travel measurements involve more servicing than do stream discharge measurements, because of faster film speeds typical of the former. Stream gaging operations can be adequately serviced under a weekly schedule.

If the instruments are found to be functioning smoothly, servicing of the on-site operation is reasonably expedient. The chronological sequence of servicing involves:

(1) checking the instruments to insure that they are functioning properly; in stream gaging operations this should include inspection of the injection system supplying the stream with dye tracer;

(2) putting a detectable mark (time mark) on the film and noting the time;

(3) measuring the approximate flow rate of the stream aliquot through the tracer registration device to detect any variance in flow since the last servicing;

(4) checking the supply of desiccant in the drying compartment and draining any excess liquid from the super-saturated solution;

(5) removing the exposed film stored on the uptake spool, taking care to include the time mark of (2);

(6) installing fresh film;

(7) when stream gaging, obtaining an instantaneous discharge measure of streamflow; this will normally be obtained using dye-dilution techniques described by Watt (1965) and Siverts (1967); and

(8) putting a detectable mark (time mark) on the freshly installed film and noting the time.

Time marks placed on the gelatin-coated film become the basis for calibration of tracer concentration as a function of time. At any given instant the tracer concentration that is being registered on the film occurred minutes earlier at the sampling section (intake vessel) in the stream. The time lag between tracer events at the sampling section and the registration device varies with site and stream sampling equipment.

Film time is correlated with stream events by suddenly changing the tracer concentration in the stream at the intake vessel and recording the time the change occurred. Tracer concentrations can be altered suddenly either by adding a small quantity of tracer to the stream just over the intake vessel or by shunting for three minutes or so the continuous injection of tracer into the stream during stream gaging. In subsequent analysis of the film, the stream event can be identified and used to correlate the film record according to "stream-time".

## Description and Operation, Laboratory

Gelatin-coated film gathered from the stream-side detection device is ready for immediate fluorometric analysis or it can be stored for later scanning. Although storage at room temperatures is not excessively detrimental to the film and its tracer information, a cool environment extends its storage life.

The laboratory where the film is analyzed may be housed in permanent or in "field" quarters. The laboratory requires a water tap, a 110-volt A.C. source, and a room whose temperature remains relatively constant. Equipment basic to the laboratory include a film rewinder, a fluorometer, a recorder, and appropriate software.

### Film rewinding

Figure 10 shows the manually-operated film rewinder[1/] used in this research. Because the final storage spool in the tracer registration device automatically winds the exposed film so that the most recent stream-tracer events are near the periphery of the film core, film rewinding is necessary to order the events chronologically. As an orientational aid, lead ends of film strips handled in this study were cut with a diagonal slant, while strip tails were sliced perpendicularly.

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1/ Neumade Film Rewinder; Supplied by Eastman Kodak Company, Rochester, New York.

Figure 10. Film rewinder.

Fluorometry

The fluorometer performs the major task of converting tracer quantities registered in the gelatin-coated film into an intelligible time-distribution of relative tracer concentrations monitored in the stream. The fluorometer[1/] used in this study was a null-balancing type featuring a servo-mechanism. The sample-holding door of this instrument was modified to accommodate a strip of gelatin-coated film so that it could be drawn by clockwork across a diffusely reflected surface for automatic scanning. Film moves across the scanner at 4.5 inches per minute. At any given instant, the fluorometer, as modified, responds to the integrated fluorescence from a 3.4 $cm^2$ area (about 1 cm length) of film.

Figures 11 and 12 are views of the modified fluorometer with and without light shield, respectively. During fluorometric analysis the light shield prevents light contamination from external sources. When it is not shielded the gelatin-coated film serves as a lightpipe, routing external light directly into the scanning area and causing erroneous readings.

Recording

Fluorescence sensed by the fluorometer is converted to either a milliampere or a millivolt signal. Either signal can be recorded

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1/ Turner, Model 111, Fluorometer; Manufactured by G. K. Turner, Associates, Palo Alto, California.

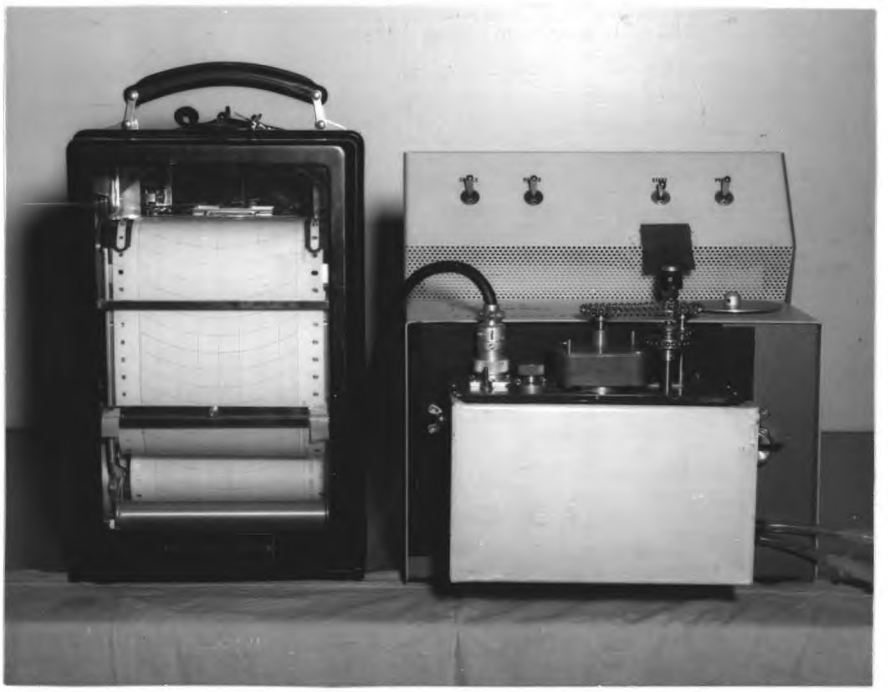

Figure 11. Graphic Ammeter and modified fluorometer, light shield in place.

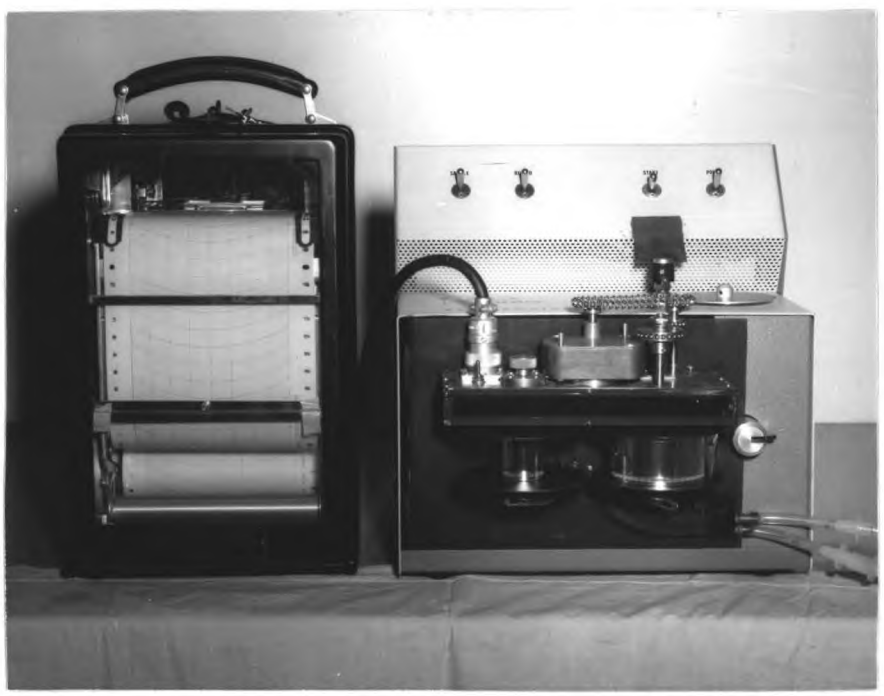

Figure 12. Esterline-Angus AW Graphic Ammeter and Turner 111 Fluorometer with modification to accommodate continuous strip of film under clockwork control, light shield removed.

on a strip-chart or a computer-compatible tape. In either case the records represent a continuous time series of tracer concentrations, $c$, or by polarity reversal, represent $1/c$. Validity of these representations has been documented by Udenfriend (1962). He found that in dilute solutions of fluorescent tracers fluorescence is proportional to concentration.

Fluorometric outputs during this research were recorded on one of two strip-chart recorders[1/] shown in Figures 12 and 13.

Software

The term software includes equipment, supplies, and tools necessary for an efficient laboratory analysis, such as conduits, glassware, plastic gloves, etc.

In many operations the capability of performing instantaneous discharge measurements along with continuous stream gaging is desirable. The laboratory can be equipped for this further capability by the addition of only a few more items to its inventory. If an instantaneous tracer-dilution technique similar to that described by Siverts (1967) is followed, the additional laboratory items include borosilicate glass beakers, dropper pipettes, polyethylene wash and sample bottles,

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1/ Bausch, Model VOM-5, Recorder; Bausch and Lomb Incorporated, Rochester, New York.

Esterline-Angus, Model AW, Graphic Ammeter; Manufactured by Esterline-Angus Co., Inc., Indianapolis, Indiana.


Figure 13. Bausch and Lomb VOM-5 strip-chart recorder and Turner 111 Fluorometer.

stirring rods, a top-loading balance, a water-cooled fluorometer door designed to hold liquid samples, and an ice-water circulation system to cool the latter.

# CHAPTER III

# PROCESSES

Although development and evaluation of a tracer detection system could proceed without complete understanding of the processes involved, a brief review of the phenomenon which occur is of value. An appreciation of the physical and chemical processes will supplement empirical testing of the system by indicating its possible limits and extent of application.

## Stream Sampling Processes

The processes involved in routing a stream aliquot past the gelatin-coated film are basically an extension of the same processes governing the transport of a soluble tracer by flowing water. In natural streams these processes include molecular diffusion, turbulent dispersion and turbulent diffusion.

### Molecular diffusion

Molecular diffusion of a stream-borne tracer results from Brownian movement of molecules. Both tracer and water molecules are in a state of continuous, multidirectional vibration which, according to Kruyt (1930), can be considered as a kinetic motion corresponding to the temperature of the system. The kinetic energy of a colloid or molecule

is characterized by its $(1/2)mv^2$ , where $m$ is the mass and $v$ the velocity of the particle. An equation describing the mean displacement, $\overline{\Delta}_x$ , of a particle in the $x$ direction has been attributed by Jacobs (1935) to Sutherland, van Smoluchowski, and Einstein, independently:

$$\overline{\Delta}_x = \left[\frac{RT}{N} \quad \frac{t}{3\pi\eta r}\right]^{1/2} , \tag{1}$$

where $R$ is the universal gas constant, $T$ the absolute temperature in °K , $N$ the constant of Avogadro, $t$ the time, $\eta$ the dynamic viscosity of the medium, and $r$ the radius of the particle. The $RT/N$ term is connected with the kinetic energy of the particle, while $3\pi\eta r$ denotes the Stokes' law term, where particle velocity is related to fluid viscosity. Although this equation has been verified, most diffusion problems are solved by Ficks' law (Jacobs, 1935):

$$dQ = -DA \frac{\partial u}{\partial x} dt \tag{2}$$

or in a more fundamental form labelled the general diffusion equation,

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2} , \tag{3}$$

where $dQ$ represents the amount of material diffusing in the time $dt$ , across and normal to a plane of area $A$ , $\partial u/\partial t$ and $\partial u/\partial x$ are concentration gradients with respect to time and distance, and $D$ is

the diffusion coefficient. The constant, D , has been the object of considerable investigation. In laminar flow where Stokes' law is valid, equation (1) has been used to define D such that if

$$D = \frac{\overline{\Delta x}^2}{2t}, \text{ then } D = \frac{RT}{N} \frac{1}{6\pi\eta r} .$$

In reference to movement of a tracer in a stream, Sayre and Chang (1968) dismiss the effects of molecular diffusion as being several orders of magnitude lower than the effects of turbulence. Never-the-less, they base development of turbulent diffusion theory on its analogy to the process of molecular diffusion.

Turbulent diffusion and dispersion

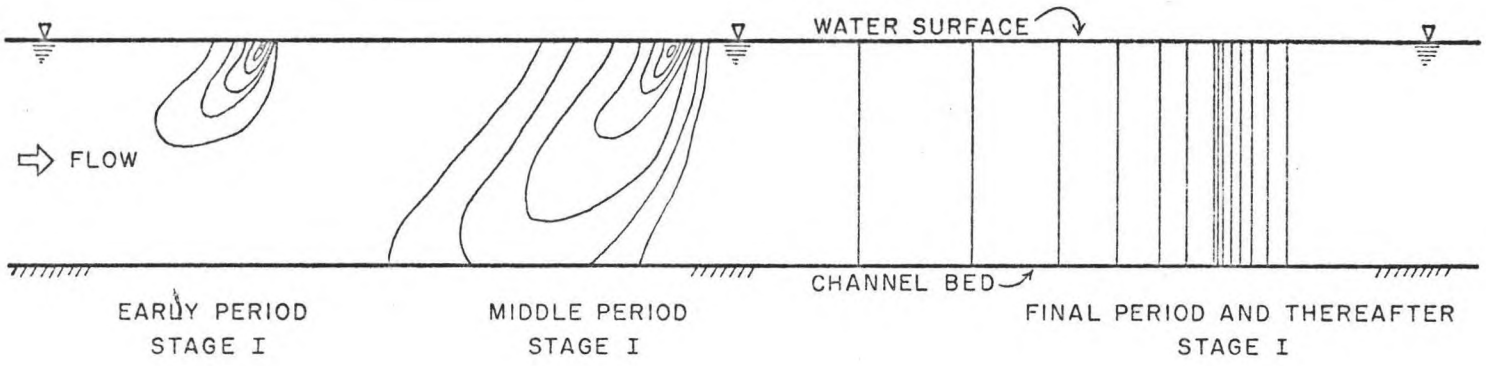
Yotsukura (1967) concisely described the processes which transport stream-borne tracers. The following discussion reviews much of his presentation.

Although transport processes are mainly functions of stream turbulence, they are more clearly viewed as the net result of local and temporal flow velocities. Flow velocity may be divided into a mean part and a fluctuating part. The mean velocity, which may be different from point to point in a cross-section, transports the tracer according to the pattern of velocity distribution. The fluctuating velocity, if it can be represented by a random walk, transports the tracer so that tracer particles are distributed normally with their

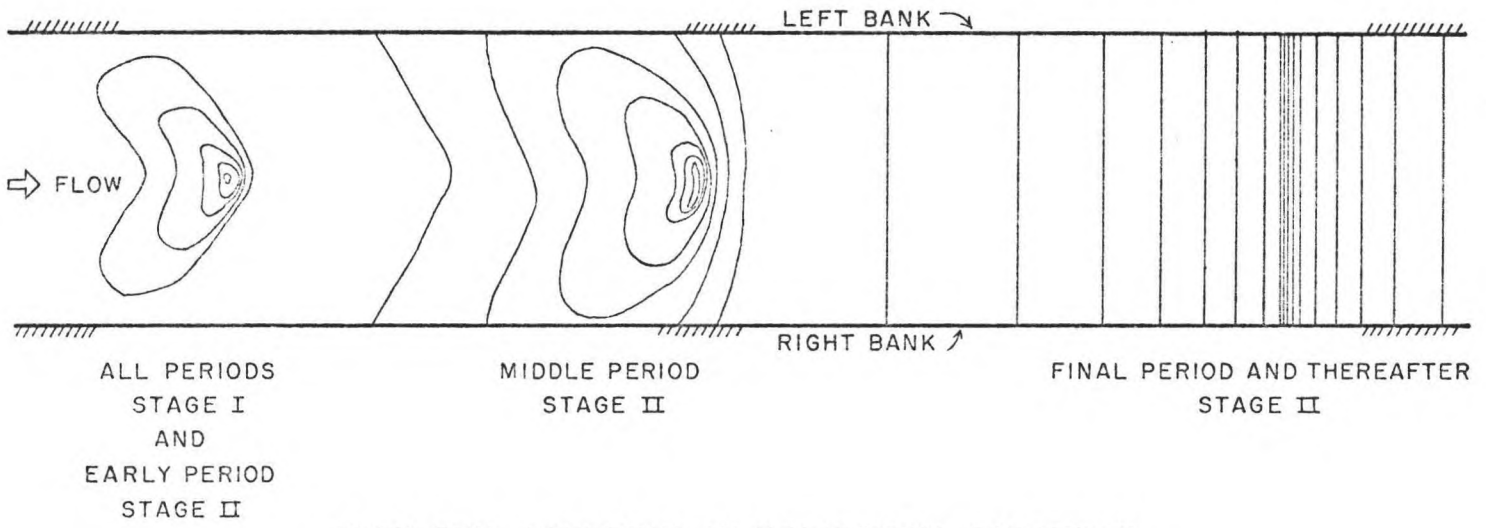
degree of spread (the variance) depending on the scale and the intensity of the turbulence.

Yotsukura (1967) defined turbulent diffusion as the spreading of tracer by the fluctuating velocity only. Turbulent dispersion, on the other hand, combines the effect of mean velocity transport and that of fluctuating velocity. In a steady, uniform flow the tracer will spread in depth and width by turbulent diffusion alone because mean velocities in these directions are zero. The entire mean velocity plus parallel velocity vectors of the fluctuating part are orientated in the longitudinal direction and initiate the turbulent dispersion process.

When a tracer is suddenly released at the surface and midstream into a steady, uniform flow, its spread progresses in a series of three stages as shown by the concentration configurations of Figure 14. The tracer diffuses both vertically and horizontally while it is carried downstream. During the first stage tracer molecules in most streams will arrive at the stream bed much earlier than they reach the banks, because width normally exceeds depth. Tracer molecules oriented in the vertical pick up the prevailing velocity at any given depth while they randomly move about. Initially, a tracer concentration gradient exists from the surface downward. However, as more and more particles diffuse downward, the gradient diminishes and eventually concentration in the vertical becomes uniform. At this point, which marks the beginning of stage II, horizontal diffusion is far from complete.




ISOPLETH PATTERNS IN VERTICAL DIRECTION




ISOPLETH PATTERNS IN HORIZONTAL DIRECTION

Figure 14. Tracer concentration isopleths in vertical and horizontal directions of a tracer slug injected into a stream of steady uniform flow, (Taken from Yotsukura, 1967).

In the horizontal the process is analogous to that in the vertical, except that the tracer molecules are now picking up varying velocities in the horizontal direction. Formation of a uniform tracer concentration in the horizontal completes stage II and infers that the tracer cloud will be travelling with the same velocity as the discharge velocity of the flow. In other words, lateral mixing of the tracer with the stream will be complete.

Yotsukura (1967) presented an equation relating horizontal and vertical diffusion distance,

$$\frac{X_w}{X_d} = \frac{1}{4} \left(\frac{w}{d}\right)^2 \frac{B_d}{B_w} \quad . \qquad (4)$$

If the width - depth ratio, $w/d$ , is assumed 20 and the ratio of horizontal diffusion coefficient to vertical, $B_w/B_d$ , is 3, the distance ratio, $X_w/X_d$ , equals 100/3 or 33.3.

The third stage of tracer transport is characterized by longitudinal dispersion. Distribution of tracer concentrations in the longitudinal direction is non-uniform, with the degree of skewness changing very slowly. Because other dispersion characteristics follow a normal distribution fairly well, time-of-travel, discharge, or other measurements can be obtained in the third stage.

Variations

Superimposed on the idealized form of concentration distribution presented above are many characteristics operating in flow regimes

such as natural streams and the stream sampling component of the tracer detection system. One of these characteristics is the persistence of low tracer concentrations caused by the slow diffusion of tracer from storage pockets or vessels. Another is the retarding effect of sudden expansions in channel or conduit width. In this case tracer molecules near the banks will move longitudinally with speeds less than those of the mean flow. Branched and braided flows also affect longitudinal dispersion. Also, the sorption of tracer molecules on solid surfaces exposed to the flow adds to modification of idealized tracer concentrations.

The effect of tracer sorption is much greater in the case of a single-slug release of tracer than during continuous injection. With tracer source and streamflow both constant, a concentration equilibrium is established at all interfaces of sorption,

$$C_a \rightleftharpoons C_b \quad ,$$

where $C_a$ is the concentration of the tracer in solution or suspension phase and $C_b$ is the tracer concentration on the sorbent. Tracer substances are commonly sorbed on organic matter, stream bed and bank material, conduits and plumbing required in the stream sampler, and stream-borne sediment.

## Gelatin-coated Film

During operation of the tracer detection system the presence and concentration of tracer dyes in the stream aliquot are registered on a gelatin-coated film.

### The support film

As described previously, the dual-layered film consists of a gelatin layer carried on a polyethylene support. Designed use of the film requires that the carrier be impervious to liquids and chemically inert. Drops of Rhodamine WT in a 20% solution placed on the smooth surface of the carrier film are easily washed or blotted away.

### The gelatin layer

Hart (1953) and Bennett (1921) classified gelatin as a fibrous protein which, as a crystal, is colorless, transparent, devoid of taste or smell, usually brittle, optically active, and only slightly soluble or dispersible in water. With water, however, it forms a colloidal gel or sol.

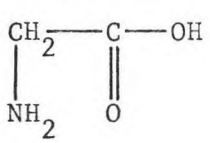
Photographic gelatin consist of amino acids bonded together chain-like by peptide linkages. These molecular chains are thought to form stable three-dimensional coils. The percentage compositions of amino acids found in gelatin and given in Table 1 are not exact; they vary somewhat with source and preparation.

Table 1. Percentages of amino acids in lime-processed gelatin. (Taken from Mees, 1942)

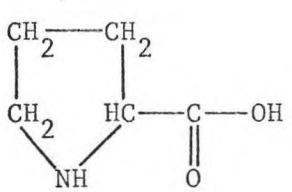
| Amino Acid | Percentage |
|---|---|
| Glycine | 25.5 |
| Proline | 19.4 |
| Hydroxyproline | 14.4 |
| Alanine | 8.7 |
| Leucine | 7.1 |
| Arginine | 6.2-7.8 |
| Lysine | 5.9 |
| Glutamic | 5.8 |
| Aspartic | 3.4 |
| Phenylalanine | 1.2 |
| Serine | 0.4 |
| Histidine | 0.3-0.5 |

Fox and Foster (1957) give the structures for the three most common amino acids in gelatin:

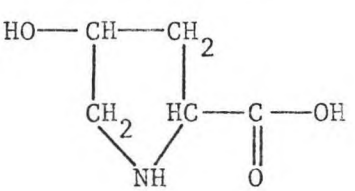
Glycine



Proline



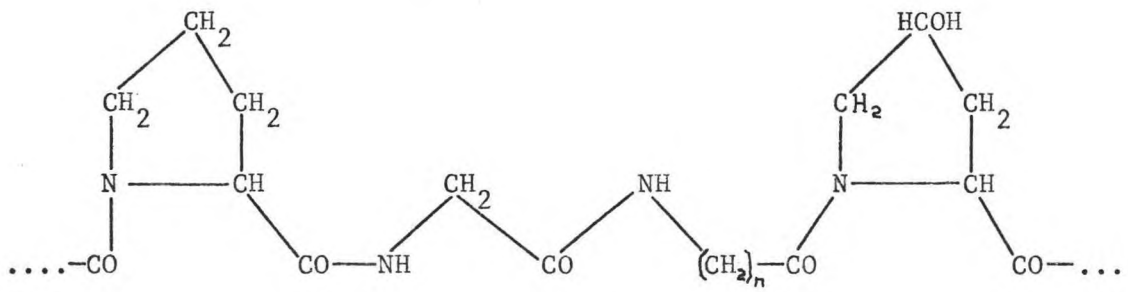
Hydroxyproline



Arrangement of amino acids along the gelatin molecule is suggested by their frequency of occurrence in decomposed gelatin. The most probable arrangement is

.... - P - G - R - P - G - R - P - G - R - ....,

where P stands for either proline or hydroxyproline, G for glycine, and R for one of the other amino acids. Structurally this arrangement is



This grouping repeats itself, forming an average molecular weight of 27,000, a chain length of 838 Å, a sequence of 288 amino acids, or multiples of these values.

The manufacture of gelatin-coated films for photography usually involves a gelatin hardening procedure. Hardening protects the film against softening, excessive swelling, and sticking at high temperature. Hardening can be accomplished by heating, by photochemical means, by inorganic additives, and by organic reagents. Being a commercial product, the film used in this study had been hardened, but as predicted by the manufacturer[1/], no adverse effects were observed from this treatment.

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1/ Personal communication with scientists at Eastman Kodak Co., Rochester, New York.

## Gelatin Swelling

Immersion of the gelatin-coated film in an aqueous solution initiates the process of gelatin swelling. In describing the swelling process, Smith (1921) noted that gelatin in water at 15°C may increase its apparent volume by seven or eight fold. An imbibition of liquid is always associated with the process. Kruyt (1930) was careful to point out that one often describes swelling by a volume change that is more apparent than real. If one compares the total volume of the constituents, the gel and the liquid, before and after sorption of the latter, he will, in fact, observe a volume decrease. This observation follows the theorem of van't Hoff - Le Chatelier, that under uniform pressure on both gel and liquid, the process would favor a decrease in total volume.

### Swelling pressure

The process is also characterized by development of swelling pressures. Initially, the flexible gelatin matrix opposes these pressures only slightly. As liquid imbibition proceeds, however, matrix resistance to the swelling pressures increases. Kruyt (1930) cited a study by Posnjak (1912) supporting the inverse relation between pressure and liquid uptake by a swelling protein. The same study also showed that in early stages of swelling small amounts of imbibed liquid correspond to large pressures of swelling and, conversely, in later stages, large quantities are taken up under small swelling pressures.

Eventually, however, a quasi-limit to matrix expansion is reached and swelling ceases.

Osmotic potential

The nature of the process of swelling has not yet been determined with certainty. One school of thought assumes gelatin to consist of a number of cavities, the walls of which act as semipermeable membranes. These cavities are thought to contain substances, generally salts, which are responsible for the exertion of an osmotic pressure causing the swelling. In describing the process, Mees (1942) referred to the work of Loeb (1922) based on the Donnan membrane equilibrium. If the gelatin membrane is permeable to all ions in the system except the dissolved gelatin located within the cavity, the Donnan theory will predict an influx into the cavity commensurate with the appropriate ion equilibrium.

Adsorptive potential

Kruyt (1930) rejected the conclusiveness of Loeb's argument. Agreement with Donnan's theory also follows just as well for a colloid in adsorption equilibrium with a peptizing electrolyte. This second theory, namely, that a gelatin gel swells in response to an adsorptive potential, stems from the nature and composition of this common protein.

It is usually accepted that a gelatin gel consists of two phases of matter, a protein solid and liquid water, separated by an interfacial region of unknown thickness. Moreover, the water is finely

dispersed within the gelatin frame forming the colloidal gel. Proof that gelatin particles in a gel are of colloidal size came from an observation by Bachmann (1912), as reported by Kruyt (1930). Using an ultramicroscope, Bachmann noticed the development of Brownian movement as a gelatin sol transformed into a gel. Such movement is typical of colloidal particles, which in gelatin, Kruyt suggested, are aggregates of chain-like protein molecules.

Proponents of the adsorptive theory for gelatin swelling occasionally classed the process with capillarity (Bennett 1921; Kruyt, 1930; Banerji, 1953). Doing so, they implied: (1) that the aggregates are sufficiently pliable, for capillarity concerns interfaces that are mobile enough to assume an equilibrium shape (Adamson, 1960), or (2) that an influential number of water-air interfaces also exist in the system. The adsorptive forces generated in either system, (1) or (2) above, can be described by the well-known capillary pressure, Pc , equation,

$$Pc = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \quad , \qquad (5)$$

where $r_1$ and $r_2$ are any two mutually perpendicular radii of curvature at a particular point on the interface, and $\gamma$ is the surface energy per unit area of an interface under constant temperature, pressure, and composition.

Further insight is possible, if the gas-solid relationships presented by Ross and Olivier (1964) can be validly extrapolated to a

water-gel system. The extrapolation results in an equation describing the change in total differential energy for equilibrium adsorption on the gelatin surface taking place isothermally,

$$q = (Pads + Pia) - Evib - \Delta Etr - \Delta Erot \quad , \qquad (6)$$

where $q$ is the heat of adsorption, Pads is the adsorptive potential energy of gelatin surfaces, Pia is the additional potential energy due to molecules already adsorbed, $\Delta Etr$ and $\Delta Erot$ represent the change of translational and rotational energy for the process, respectively, and Evib is the average vibrational energy of a sorbate molecule. According to equation (6), if heat evolves during adsorption, as is the case in all physical adsorption (Osipow, 1962), $q$ is positive and potential energy of the system decreases. Three types of molecular forces lead to the existence of the adsorptive potential, Pads:

(1) induction forces brought about by the operation of a surface field on induced or permanent dipoles of resident molecules,

(2) interaction dispersion forces resulting from specific properties of the sorbate and sorbent, and

(3) dative bonding resulting from a chemical reaction between sorbate and surface atoms, (Ross and Olivier, 1964; Zimon, 1969).

Swelling temperature

An increase in temperature affects gelatin swelling negatively (Bennett, 1921). The adsorptive theory of swelling offers a ready

explanation for the inverse relation. Adamson (1960) presented an equation,

$$\gamma = E_s \left(1 - \frac{T}{T_c}\right) \quad , \qquad (7)$$

which indicates that the free surface energy, $\gamma$ , is inversely related to absolute temperature, $T$ , provided total surface energy, $E_s$ , and critical temperature, $T_c$ , remain invariant. These assumptions are usually valid, resulting in a negative derivative, $d\gamma/dT$ , of equation (7).

pH of swelling

Figure 15 shows the effect of hydrogen ion concentration, expressed as pH , of the liquid phase on gelatin swelling. The pH value at minimum swelling corresponds to the isoelectric point of lime-processed gelatin, which ranges between 4.7-5.3 (Mees, 1942). Explanations of the phenomenon are incomplete, but probably involve the viscosity of gelatin. Viscosity plotted as a function of pH results in a curve similar in shape to the swelling-pH relation with the low value again occurring at the isoelectric point.

Rate of swelling

The time rate of gelatin swelling depends on the forces causing swelling and the elastic limit of the gelatin matrix. Kruyt (1930) suggested a theoretical time-swelling curve (Figure 16) for gelatin in

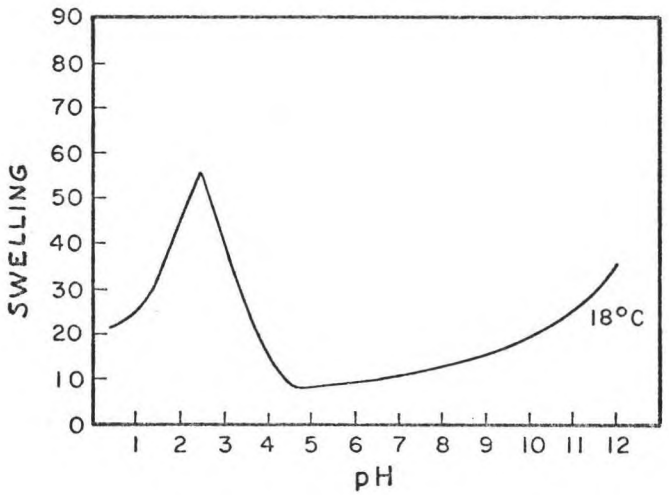


Figure 15. Swelling of gelatin in water in relation to pH; Swelling is expressed as grams of water held per gram of gelatin, (Taken from Mees, 1942).

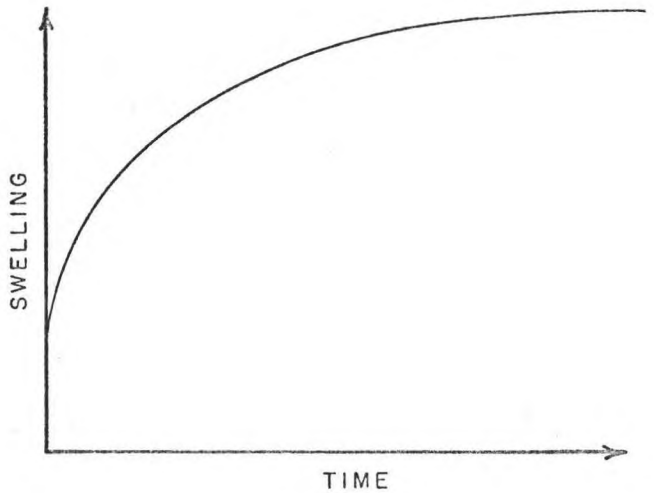


Figure 16. Swelling as a function of time when imbibing liquid is in constant supply, (Taken from Kruyt, 1930).

water at a given temperature. The initial rapid rate of swelling gradually slows to an asymptotic value. Dumanskii, Mezhennii, and Nekryach (1947) confirmed experimentally the shape of this curve for swelling gelatin. Their data fit a curve of the form

$$i = Bt^n \quad , \tag{8}$$

where $i$ represents the amount of liquid uptake, $B$ and $n$ are constant, and $t$ is immersion time.

Swelling stress

Swelling is complicated by many factors. One of these relates to thickness of the gelatin layer. If a very thin gelatin layer is carried on a non-swelling support film, swelling is limited mainly to a direction normal to the surface of the support. Some lateral swelling occurs which exerts a force opposing the constrain of the support. If not controlled, this stress can cause permanent deformation of the gelatin framework. Swelling is controlled by adjusting the thickness of the gelatin layer and by applying suitable film hardening.

## Tracer Diffusion

Swelling of the gelatin-coated film allows ready access of the tracer solution into the gelatin matrix. Molecular diffusion is the most likely mechanism by which tracer molecules migrate from the bulk

solution into the gel and approach the sorptive surface of the gelatin. Diffusion occurs as swelling progresses and reaches its maximum development when swelling is completed. Friedman (1930) was one of the first to show that the movement of a non-electrolyte in a gelatin gel followed a molecular diffusion process for which Fick's law (equation 2) is applicable.

Fick's equation contains a term for the solute concentration gradient, $\partial u/\partial x$ , which is related to rate of diffusion. Any action which increases the absolute value of the concentration gradient should increase diffusion and, in the case of gelatin immersed in a tracer solution, should increase tracer uptake. This possibility was tested in a laboratory experiment. Gelatin-coated films were immersed in a non-flowing supply of Rhodamine WT solution at a concentration of 20 parts per billion (ppb). Conditions were uniform except that half of the time the solution was mechanically agitated, the other half not. Agitation increased tracer uptake by 62 to 100%.

## Gelatin Sorption

Gelatin swelling and solute diffusion bring the tracer molecules in proximity to gelatin surfaces. When a given tracer molecule is close enough to one of these surfaces, attractive forces can be sufficient to cause adherence of the molecule to the surface. This process is termed sorption.

The colloidal system

The process of sorption occurs within colloidal systems which are specific in composition. For the sorption of an organic tracer from a dilute solution by gelatin, the following constituents can be described:

| | |
|---|---|
| three components: | -water, tracer, and gelatin; |
| two bulk phases: | -gelatin solid and liquid solution; |
| m plus n surface phases: | -tracer sorbed on gelatin (m) and water sorbed on gelatin (n); and |
| m plus n interfaces: | -tracer-gelatin and water-gelatin. |

For a colloidal system constituted as above, Ross and Olivier (1964) suggested the following phase rule:

$$F = C + 2 + i - P \quad , \qquad (9)$$

where $F$ denotes degrees of freedom, $C$ the components, $i$ the interfaces, and $P$ the phases. For the gelatin system described above

$$F = 3 + 2 + (m + n) - (2 + m + n)$$

and $F = 3$ degrees of freedom. This implies that of all the variables involved, only three need be specified to define the system. Based

on experience, these are taken to be temperature, tracer concentration in solution, and sorbate concentration.

Gelatin solubility

The possibility that a significant portion of the gelatin enters into solution during registration processes was investigated. Eight lengths of gelatin-coated film at uniform moisture content were weighed and immersed in standard volumes of distilled water at 1.0°C for 10, 25, 35, and 60 minutes. After immersion, these films were dried to their original moisture content and again weighed. The residual distilled water was analyzed in a spectrophotometer. Both weighing and spectrophotometry indicated that gelatin loss, presumably to solution, amounted to less than 1%.

Sorption

The sorption of an organic molecule onto a solid gelatin surface is caused by forces grouped into five classes (Osipow, 1962): non-polar van der Waals, electrostatic attraction, ion exchange, hydrogen bonding, and covalent bonding. Forces in the first three classes are thought to originate from physical phenomena, while forces in the latter two classes are of a chemical nature. Physical sorption involves relatively weak forces, while chemical sorption, or chemisorption, arises from the actual formation of a chemical bond with the surface. These latter bonds, being rather strong, evolve reaction heats in the 10 to 100 kcal range.

Physical sorption requires little, if any, activation energy typical of chemisorption. Osipow (1962) introduced a Lennard-Jones diagram (Figure 17) to clarify differences in activation energies. Curve I represents potential energy according to physical sorption. As a molecule first approaches the surface, there is a small attraction and a corresponding exothermic heat of sorption, $H_w$ . At closer distances, the attraction is replaced by repulsion. If sorption is accompanied by bond formation, the potential energy curve is that of Type II, with the heat of sorption indicated by $H_a$ . The activation energy for chemisorption, E , will depend on where the two curves intersect; the crossing also indicates the change from physical to chemical sorption.

Chemisorption

The nature of chemisorption of organic substances by proteins is poorly understood. Fox and Foster (1957) referred to a process of ion binding which involves chiefly dissociative groups of amino acids and hydrogen ions. They also suspected that large protein molecules bind other ions as well. For example, the precipitation of proteins from aqueous solution by certain complex acids, such as trichloroacetic acid and phosphotungstic acid, can be regarded as the formation of an un-ionized salt, the protein acting as a cation and the acid providing the anion according to the reaction

$$P^{n+} + nA^{-} \rightleftharpoons PA_n \quad . \qquad (a)$$

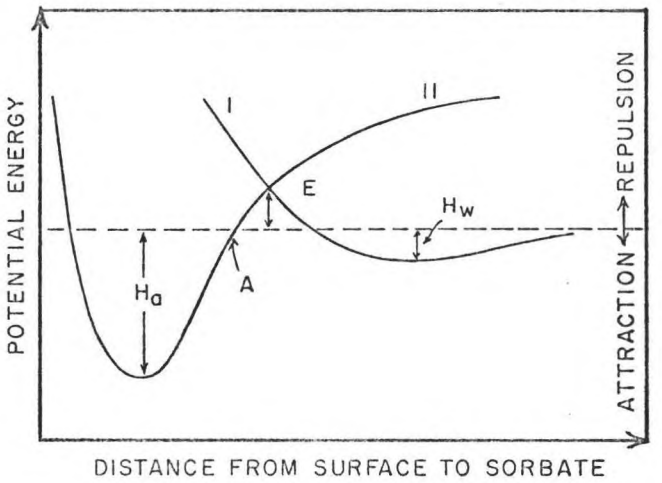


Figure 17. Potential energy as a function of distance between surface and sorbate molecule, (Taken from Osipow, 1962).

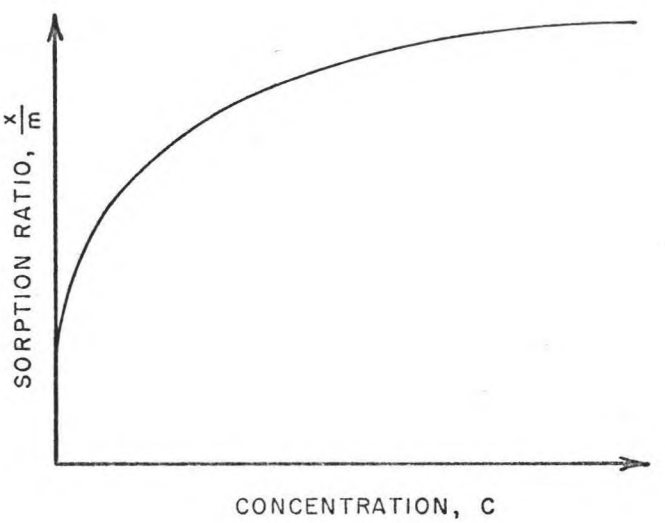


Figure 18. Sorption ratio, x/m as a function of solute concentration, where x denotes amount sorbed and m the quantity of sorbent, (Taken from Kruyt, 1930).

Other protein reactions occur in which the protein seems to act as an anion,

$$P^{n-} + nR^{+} \rightleftharpoons R_nP \quad . \qquad (b)$$

A study by Sheppard, Houck, and Dittmar (1942) supported the suspicions of Fox and Foster when they found that gelatin took up a soluble dye from a dilute solution according to reaction (a).

Physical sorption

The nature of physical sorption of a solute on to a solid surface was first described theoretically in 1916 by Langmuir (Ross and Olivier, 1964). He stated that the rate of adsorption is proportional to the number of molecules that strike a surface, to the fraction of that number that remain on the surface long enough for an exchange of kinetic energy to occur, and to the fraction of the surface not already occupied by adsorbed molecules.

The parameters in Langmuir's relationship are difficult to measure. Consequently, physical sorption data have usually been more successfully analyzed empirically using the so-called Freundlich approach. The quantitative form of this approach is

$$\frac{x}{m} = KC^{n} \quad , \qquad (10)$$

where $x/m$ designates the ratio of the amount sorbed, $x$, to the amount of sorbent, $m$, $K$ is a constant, $C$ stands for the solution concentration, and $n$ is a constant less than 1.0. Equation (10) is graphically represented in Figure 18.

The curve in Figure 18 indicates that the rate of sorption is greatest in very dilute solutions. In fact, if solutions were dilute enough, the initial portion of the curve would approach an infinite sorption rate; more important, much of the curve would approach a straight line.

Initial tests using gelatin-coated film and Rhodamine WT indicated that tracer concentrations used in this study were sufficiently dilute to be sorbed linearly. To confirm these indications, a controlled test was conducted in the actual tracer registration device. Temperatures were kept at 10°C; only solution concentration was varied. Figure 19 shows test results with relative fluorescence, which is considered equivalent to the amount sorbed, as a function of concentration. A regression analysis resulted in an $R^2$ value of 99.8%, an error mean square of 1.42, and a highly significant F-test.

The shape of the curve in Figure 18 has been used to support the contention that tracer sorption is mainly a physical process. Kruyt (1930) reasoned that if adsorption dominated and its effect decreased with concentration as shown in the figure, adsorptive power would depend on the value of $d\gamma/dC$, recalling that $\gamma$ is the free energy of the sorbing surface. More specifically, $d\gamma/dC$ would have to be

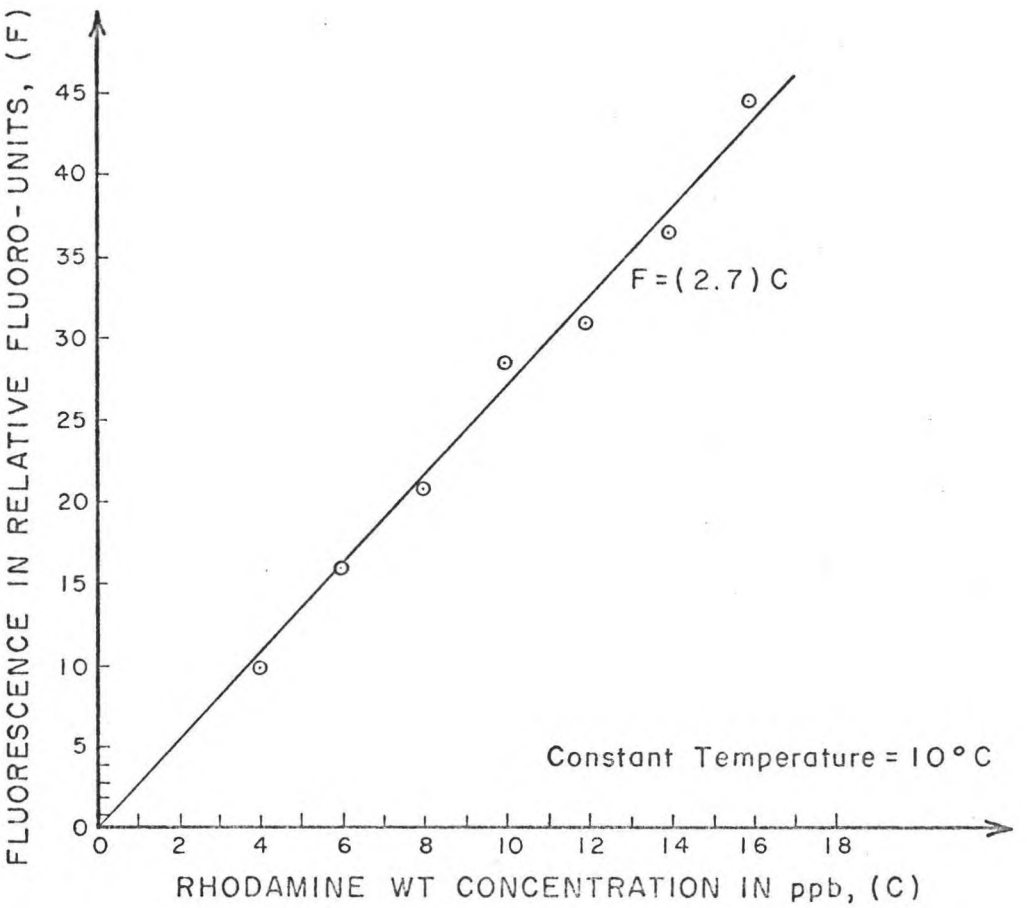


Figure 19. Tracer uptake by gelatin-coated film (measured by fluorescence) from 19 minutes immersion in aqueous Rhodamine WT solutions of varying concentrations.

less than 1.0. Banerji (1953) measured surface energies for a gelatin sol and found that they were inversely related to concentration, that is, $\gamma = f(1/C)$ . This relation dictates that the inequality, $(d\gamma/dC) < 1.0$ , must be true, which supports the physical sorption theory.

Solution temperature is a significant variable affecting the uptake of a dissolved tracer. Its influence was reported by Kruyt (1930) to be negative to solute adsorption. If tracer uptake by gelatin stems primarily from physical sorption and if, as Kruyt stated, increasing temperature decreases adsorption, it is not surprising to find that the relation plotted in Figure 20 has a negative slope. The figure shows the results of a test where gelatin-coated films were immersed in uniform Rhodamine WT solutions of 10 ppb under varying temperatures. The inverse linear relation between tracer uptake, as measured by fluorometry, and temperature was confirmed by a regression analysis, where $R^2 = 99.2\%$, error mean square = 0.675, and the F-test was highly significant. The effect of temperature on gelatin swelling was included in this test. However, its effect, being negative, was additive.

## Tracer Uptake

### Theoretical

From the relationships discussed above, a hypothesis may be formed describing the tracer uptake process. Immersion of the

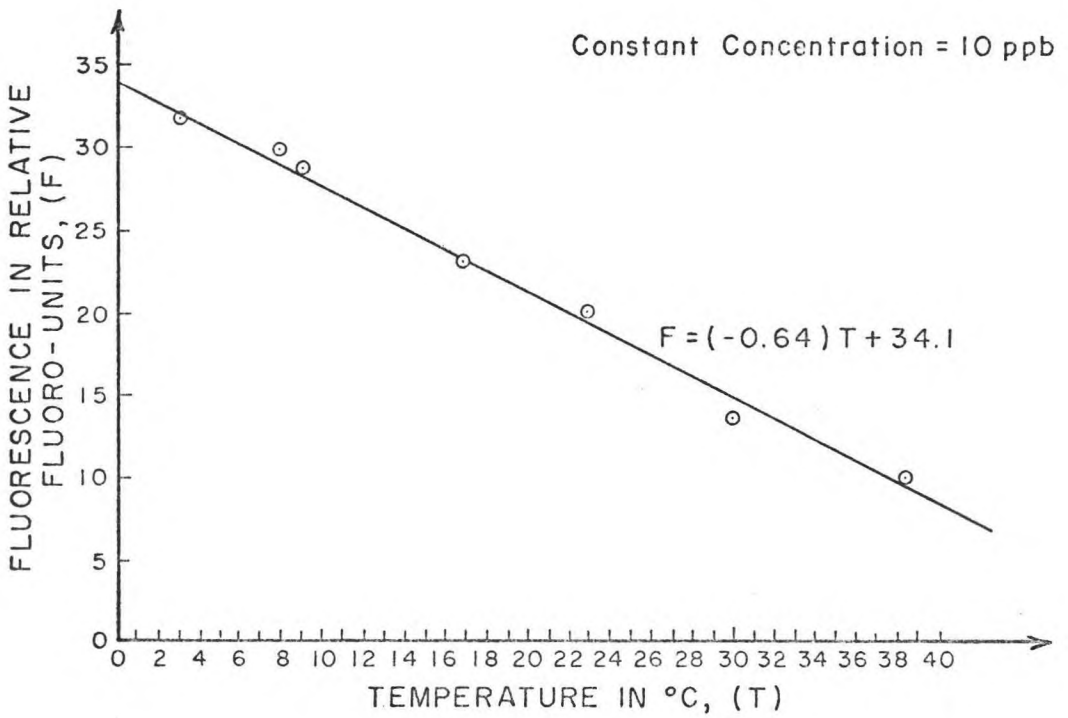


Figure 20. Tracer uptake by gelatin-coated film (measured by fluorescence) from 19 minutes immersion in aqueous Rhodamine WT solutions at varying temperatures.

gelatin-coated film into the tracer solution initiates gelatin swelling probably by a surface energy process. Swelling is not immediate and probably requires at least five minutes for full development. The swelling allows tracer molecules to diffuse into the activated gelatin gel under a concentration gradient controlled by tracer concentration in solution. Then, surface energy forces act to sorb tracer molecules in the liquid phase of the gel on to solid surfaces of the gelatin. Kruyt (1930) emphasized the rapidity with which this sorption is usually observed to occur. From this, one might suspect that during the latter part of gelatin film immersion, a rapidly responding concentration equilibrium is established between the solution and the gelatin. A rapid sorption phenomenon suggests chemisorption. This possibility is explored further.

Experimental

One indication of the nature of the sorption process would be its comparison with desorption. If the sorbed tracer showed little sign of returning to solution from its sorbed state, an irreversible chemical reaction would be suspected.

An experiment was performed to test this possibility. Two clean containers were filled with 55.5 Kg of distilled water. To one container, sufficient Rhodamine WT was added to form a solution of 8 ppb. The second container received no dye. Both liquids were stirred and maintained at 25°C throughout the experiment. One set of film strips was immersed in the 8 ppb dye solution for 30 minutes and then

quickly transferred to the distilled water for another 30-minute period. A second set was immersed for 30 minutes in the dye solution only. Fluorometric analysis of both sets resulted in data of Table 2.

Table 2. Uptake and release of Rhodamine WT by gelatin-coated film.

| Treatment | Uptake in Fluorometric Units |
|---|---|
| 30-min. solution exposure only | 102 |
| 30-min solution exposure followed by 30-min water exposure | 37 |

Thus, of the dye taken up by the film 63.7% was removed after exposure to distilled water. The occurrence of a significant chemical reaction is doubtful. The results could be explained either by a reversible chemical reaction or a physical sorption process. In neither case is it expected that all dye would be removed by the distilled water treatment.

A second experiment was initiated and again directed toward separation of processes causing tracer uptake by gelatin-coated films. The experiment was based on the Arrhenius equation which relates the rate parameter of a chemical reaction to temperature (Gucker and Siefert, 1966),

$$\text{Log}_e \; k = B - \frac{\Delta E}{RT} \quad , \qquad (11)$$

where k is the rate parameter for each reaction,

T is the absolute temperature of the reactants in °K

R is the universal gas constant

B is a mathematical constant, and

$\Delta E$ is the energy of activation characteristic of the reaction.

This analysis is based on the supposition that the occurrence of a low $\Delta E$ value will eliminate chemisorption as an influential process. Unfortunately, the converse is not true, for a large $\Delta E$ will not exclude the possibility of physical sorption.

Experimental data came from two sources. The first source was a tracer sorption test (Oct., 1969) where a number of 30-inch strips of gelatin-coated film were submerged in an agitated, 4 ppb solution of Rhodamine WT. The strips were exposed to the solution for a series of time intervals of 1, 5, 10, 20, and 30 minutes duration. Film immersions were repeated at temperatures of 3, 10, 20, 30, and 40 degrees Celsius. Strips were air-dried, fluorometrically analyzed, and the results plotted with tracer uptake (measured by fluorometry) as a function of exposure time (Figure 21). Curves fitted to these plotted data were used to form temperature-based equations of the form,

$$L = (100-U) = At^{-n} \quad , \qquad (12)$$

where U represents the percent of Rhodamine WT taken up per $cm^2$ of the gelatin-coated film, L the percent of Rhodamine WT remaining in

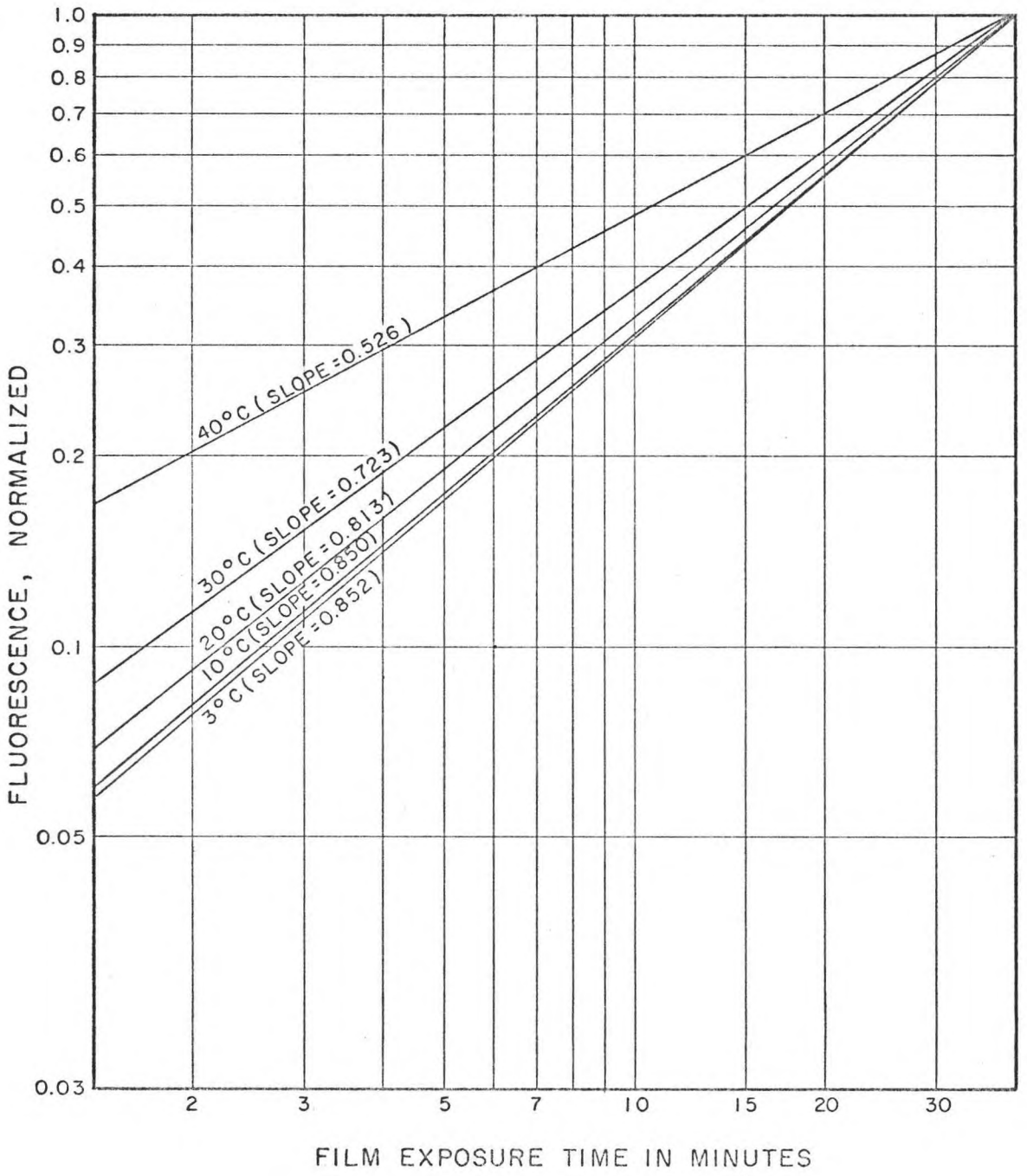


Figure 21. Normalized fluorescence as a function of film exposure time according to temperature of the aqueous Rhodamine WT solution, (Data from sorption test of 5 October 1969).

solution but eventually taken up, A a constant, t the exposure duration in minutes, and n the power constant of the relation.

Curves from above data were not directly used in the Arrhenius analysis because unexplainable effects of this immersion technique negated their reliability. However, because other data were lacking and because the curve slopes were thought to be good indicators of changes in tracer uptake with time for different temperatures, the n-values were used. These n-values are tabulated in Table 3.

The major source of data for the Arrhenius analysis came from the temperature test (March, 1970) previously described, the results of which are plotted in Figure 20. That experiment was conducted with the tracer registration device and yielded data thought to be more reliable and analogous to field operations. Gelatin exposure time was kept constant at 19 minutes. To render the relation in Figure 20 more useful, a tracer uptake value at 0°C was determined by extrapolation and used to scale abscissa values into units of percent tracer uptake. This scaled temperature-uptake relation is given in Figure 22.

Rate parameters, k's , were determined for each temperature from successive evaluations of equation (12). Determinations were based on the assumptions that maximum Rhodamine WT uptake occurred at 0°C and that the n-values were reasonable. Combined data for each temperature reaction are recorded in Table 3.

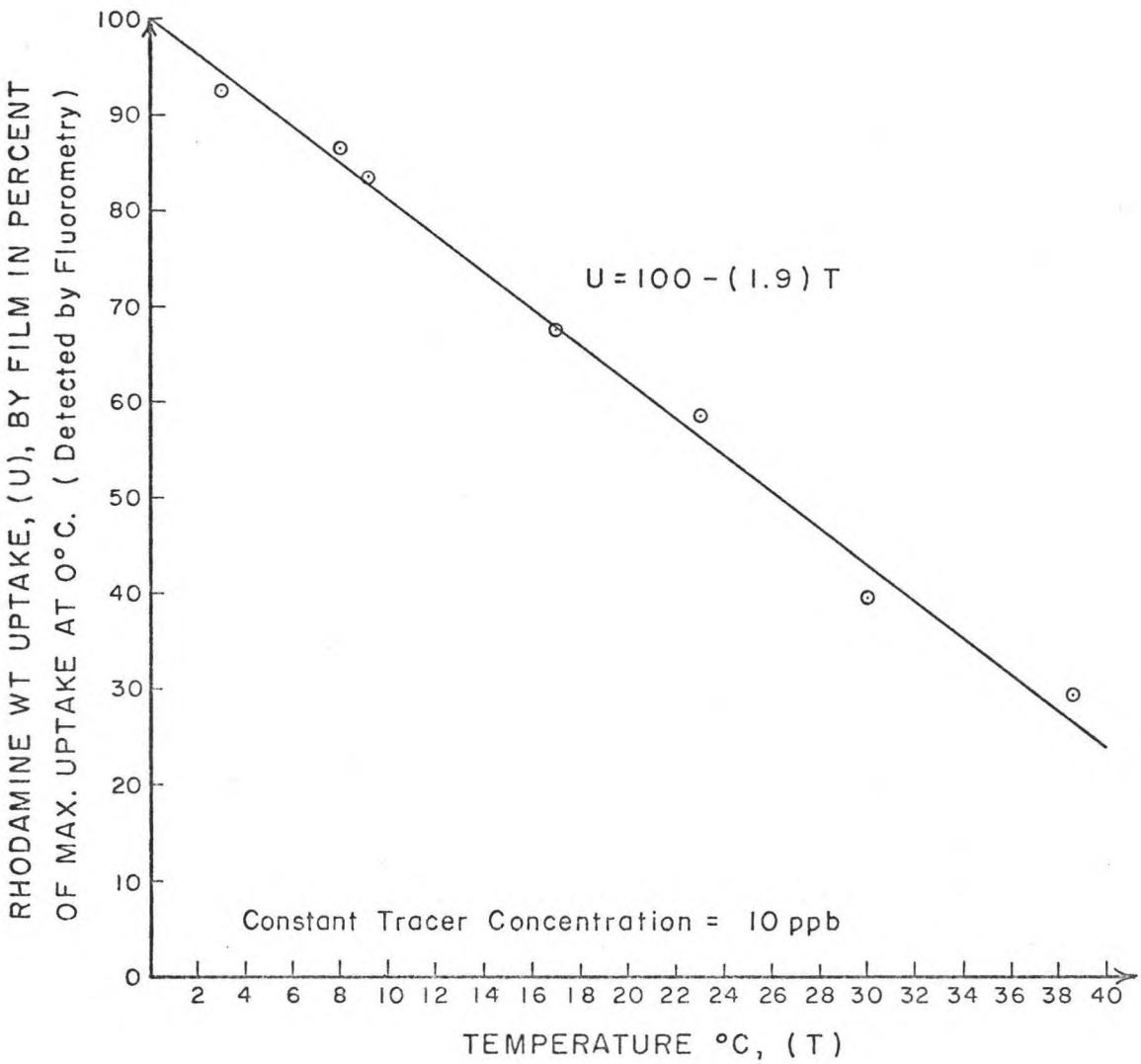


Figure 22. Percentage uptake of Rhodamine WT by gelatin-coated film as a function of solution temperature, based on uptake at 0°C, (Data from sorption test of March 1970).

Table 3. Data required to evaluate rate parameters, k's , for each reaction at given temperatures.

| T[1] °C | n[2] 1/min | t[3] min | $t^n$ | d[4] | U %/cm² | L[7] % | A[8] %/min |
|---|---|---|---|---|---|---|---|
| 0 | 0.852 | 100 | 50.5 | | 100.0 | 0 | |
| 0 | 0.852 | 19 | 12.28 | 1.000 | 24.2[5] | 75.8 | |
| 3 | 0.852 | 19 | 12.28 | 0.944 | 22.8[6] | 77.2 | 901 |
| 10 | 0.850 | 19 | 12.21 | 0.812 | 19.6[6] | 80.4 | 982 |
| 20 | 0.813 | 19 | 10.95 | 0.624 | 15.1[6] | 84.9 | 970 |
| 30 | 0.723 | 19 | 8.405 | 0.436 | 10.6[6] | 89.4 | 751 |
| 40 | 0.526 | 19 | 4.706 | 0.248 | 6.0[6] | 94.0 | 442 |

1/ Temperature of the tracer solution.

2/ Power values from sorption test of October, 1969.

3/ Duration of film immersion.

4/ Temperature adjustment coefficient where

$d = \frac{U}{U_o}$ and $U_o$ is the percent uptake at 0°C and $t = 19$ min.

5/ Percentage uptake, $U_o$ , at $T = 0°C$, $t = 19$ min , and $G = 1.98$, where $G$ is a constant of uptake at any $t$ for $T = 0°C$ calculated from $G = 100\ t^{-n}$ when $T = 0°C$, $t = 100$ min , and $U = 100\%$.

6/ Percentage uptakes, $U_3$ , $U_{10}$ , $U_{20}$ , $U_{30}$ , $U_{40}$ at their respective temperatures calculated as a product of $dU_o$ .

7/ Percentage of tracer remaining in solution, $L = 100 - U$.

8/ Coefficients of tracer remainder computed for each temperature by $A = Lt^n$ .

Data from Table 3 are sufficient to evaluate equation (12) for each temperature condition. These evaluations are listed in Table 4 below:

Table 4. Base equations describing percentage of tracer remaining in solution but eventually taken up by gelatin film at selected temperatures.

| Temperature °C | Equation |
|---|---|
| 3 | $L_3 = 901\ t^{-0.852}$ |
| 10 | $L_{10} = 982\ t^{-0.850}$ |
| 20 | $L_{20} = 970\ t^{-0.813}$ |
| 30 | $L_{30} = 751\ t^{-0.723}$ |
| 40 | $L_{40} = 442\ t^{-0.526}$ |

The rate parameter, $k$, is a coefficient in the equation expressing the rate of a chemical reaction, such that

$$R' = k\,L^m \quad , \tag{13}$$

where $R'$ is the time rate of the reaction, $L$ is any reactant and $m$ is a constant. Equation (13) can be solved for $k$ by taking the derivative of the base equation (12) with respect to time,

$$\frac{dL}{dt} = -nAt^{-(n+1)} \quad . \tag{14}$$

Also from equation (12)

$$t = \left[\frac{L}{A}\right]^{-(1/n)} \quad . \tag{15}$$

Substitution of equation (15) into equation (14),

$$\frac{dL}{dt} = -nA\left[\left[\frac{L}{A}\right]^{-(1/n)}\right]^{-(n+1)} ,$$

and simplifying to

$$\frac{dL}{dt} = -nA^{-(1/n)}L^{\left(\frac{n+1}{n}\right)} , \tag{16}$$

results in a rate equation in the form of equation (13),

where $\frac{dL}{dt} = R'$

$\frac{n+1}{n} = m$ , and

$-nA^{(-1/n)} = k$ .

Table 5 contains temperatures and rate parameters evaluated by the above procedure. The rate parameters are given in units of tracer percentage remaining in solution per minute, based on total uptake occurring at $T = 0°C$ and $t = 100$ min.

Table 5. Rate parameters for selected temperatures.

| $\frac{T}{°C}$ | $\frac{T_A}{°K}$ [1] | $\frac{10^3/T_A}{1/°K}$ | $\frac{-10^4 k}{\%/min}$ [2] | $\frac{-\text{Log}_e\ k}{\%/min}$ |
|---|---|---|---|---|
| 3 | 276 | 3.623 | 2.97 | -8.120 |
| 10 | 283 | 3.533 | 2.50 | -8.292 |
| 20 | 293 | 3.413 | 1.40 | -8.872 |
| 30 | 303 | 3.300 | 0.778 | -9.462 |
| 40 | 313 | 3.195 | 0.495 | -9.913 |

[1] Absolute temperature.

[2] Computed from $k = -nA^{(-1/n)}$.

Values from Table 5 were used to construct the $\text{Log}_e\ k - (1/T)$ relation plotted in Figure 23.

The curve in Figure 23 can be described by a straight line equation of the same form as the Arrhenius equation,

$$\text{Log}_e\ k = B - (\Delta E/R)\ (1/T_A) \quad ,$$

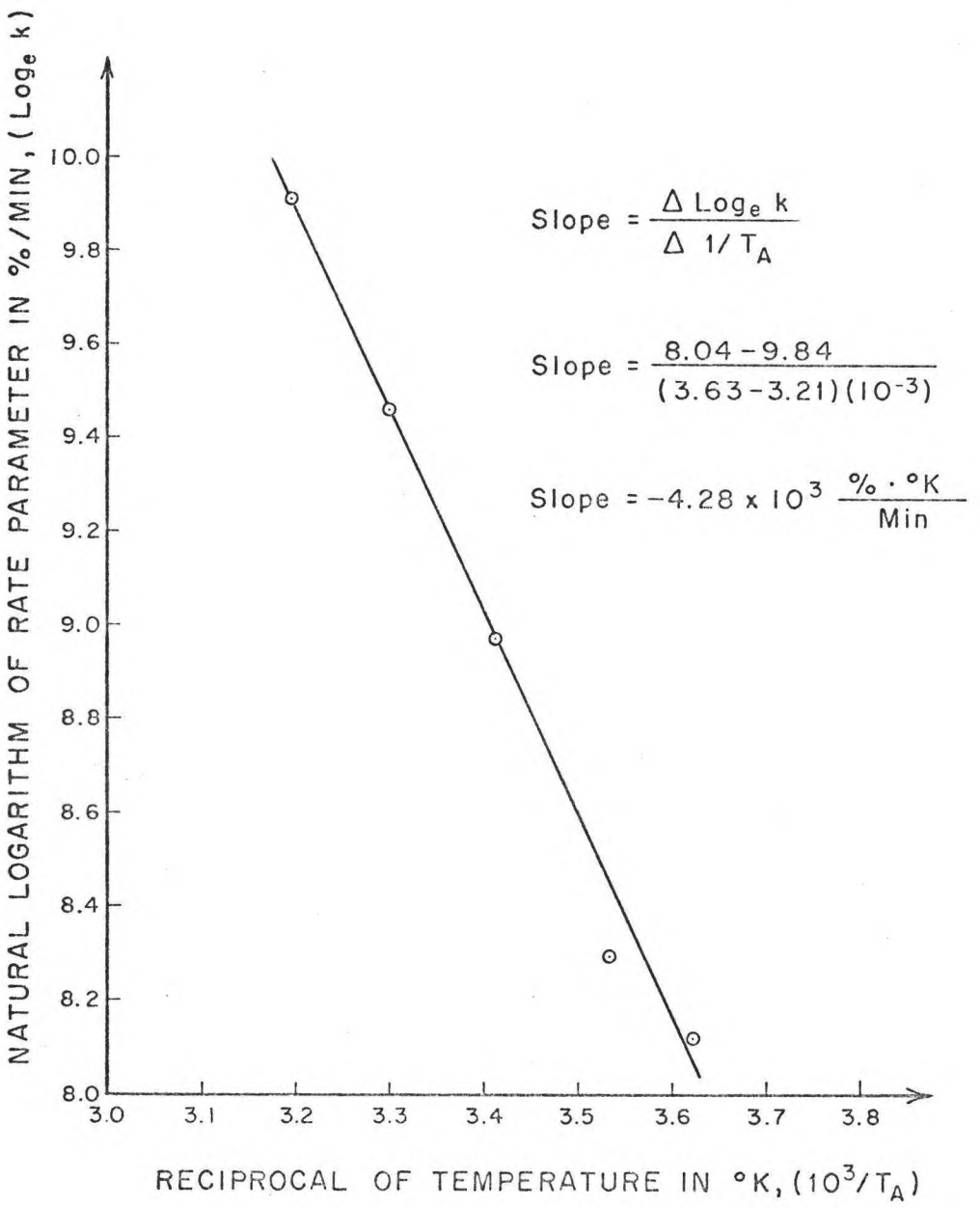


Figure 23. Arrhenius Relation, $\text{Log}_e\ k = B + (-\Delta E/R)(1/T_A)$ .

where $(-\Delta E/R)$ is the slope of the curve. Derived graphically, the slope is $-4.28 \times 10^3$% · °K per min. If the gas constant, R , is 1.987 cal per mole per °K ,

$$\Delta E = R \text{ (slope)} = 8520 \text{ cal per mole of}$$

Rhodamine WT remaining in solution but eventually taken up by the gelatin-coated film. The relatively low value of $\Delta E$ lends major support to the premise that chemisorption plays a minor role in tracer uptake processes.

## Gelatin Drying

Immediately upon removal from the registration reservoir, the gelatin-coated film begins to lose water to its ambient atmosphere. During drying, vapor pressures in the film must exceed those of the atmosphere. Increasing the rate of film drying accentuates this vapor pressure difference. Zorich (1966) concluded that a hexahydrate of magnesium chloride ($MgCl_2 \cdot 6H_2O$) in a super-saturated aqueous solution was the best means of increasing the vapor pressure gradient. Except for a brief, unsuccessful attempt with anhydrous calcium sulfate, Zorich's recommended desiccant was used exclusively during this study.

The film drying process involves the relative water vapor pressures of the desiccant, Pd , drying chamber, Pa , and the film, Pf . During efficient drying $Pf > Pa > Pd$ . It is important to

effective desiccation that these inequalities are maintained at all temperatures. Figure 24 shows that the inequality, Pf > Pd , for $MgCl_2$ and water is maintained over a wide temperature range, assuming that vapor pressures in the film remain equal to those of free water.

The drying of gelatin is often considered the reverse of swelling, and is termed syneresis (Kruyt, 1930). The process is two-fold; water must first diffuse to the surface of the gelatin gel and then evaporate from the surface. The gel responds by decreasing in apparent volume, but remains a gel. Even at low air humidities, the gel contains about 10% moisture (Mees, 1942).

Rapid evacuation of moisture from the gelatin-coated film causes stresses in the gelatin layer which lead to deformation. Because stresses in the gelatin during syneresis are not necessarily the reverse of those caused by swelling, new strains develop in the material. If any such strains developed during the research reported here, they were accounted for during fluorometery.

## Fluorometry

Fluorometry, or fluorometric analysis, utilizes the physical phenomenon called fluorescence. Fluorescence is a form of luminescence, a broad term for any emission of light not directly ascribable to heat. Fluorescence is a property of many substances and can be described as the emission of radiation immediately and only during irradiation from

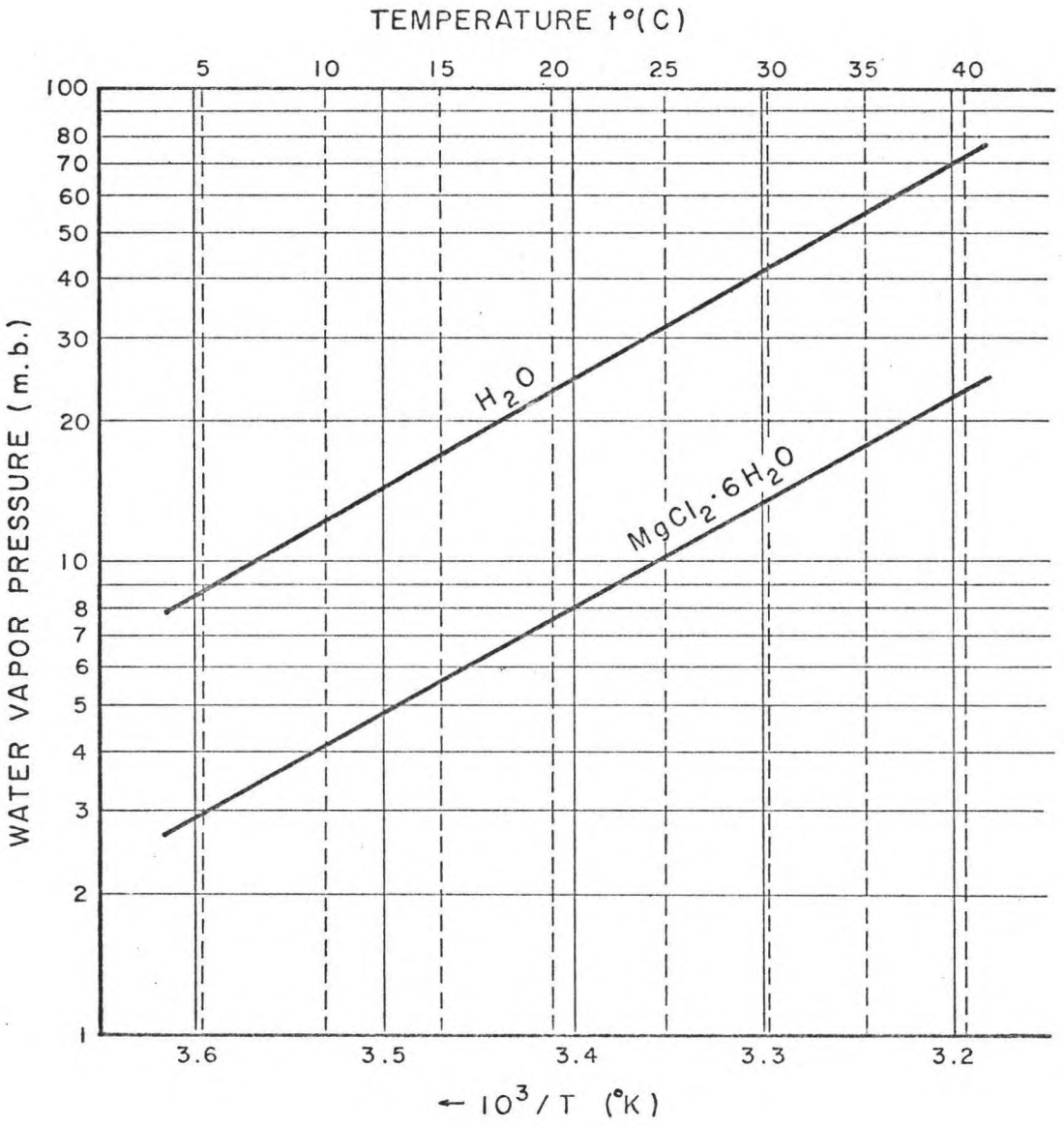


Figure 24. Vapor pressure above free water and super-saturated solution of magnesium chloride, (Taken from Zorich, 1966).

an external source (Feuerstein and Selleck, 1963). Wilson (1968) has outlined the following "split-second sequence of events in fluorescence":

(1) irradiation of a fluorescent substance by the sun or an ultraviolet lamp,

(2) absorption of this energy by the substance,

(3) excitation of electrons in the substance, some of which enlarge their orbits and form the "excited state",

(4) return of some electrons to the "ground state" by reducing the scale of their orbits, and

(5) emission of energy from the substance caused by events in (4).

Energy emitted by a fluorescing substance is nearly always of lower energy and longer wave length than the radiation that excites it (Stokes' law).

The fluorometer used in this study incorporates the sequence outlined above. In an instant, it measures the fluorescence intensity of the sample by irradiating it with standard energy at a specific wave length and monitoring fluoresced energy emitted at a longer wave length. Watt (1965) and Zorich (1966) investigated and reported many of the basic fluorometric aspects of the fluorometer and fluorescent tracers in aqueous solution.

The effect of gelatin-coated film on fluorometry was researched. Gelatin sols of 2, 5, and 10% were prepared with distilled water and analyzed in fluid form with the fluorometer. At the wave lengths

normal to stream tracing with rhodamine dyes, the gelatin sols fluoresced significantly in direct proportion to their concentration. Similarly, aqueous gelatin solutions were obtained when strips of gelatin-coated film were boiled in distilled water. These "boiled off" gelatin solutions also fluoresced significantly.

The greatest difficulty with the film, however, stems from its reflectance. During scanning, source radiation reflects off the film's smooth surface into the fluorometer's sensing element. By instrument design much of this "cross-over" radiation is blocked, yet enough is admitted to require a strong background adjustment during operation. Background adjustment is an instrument feature which enables the operator to monitor true tracer fluorescence above the effects of gelatin fluorescence, reflectance, and the undesired fluorescence of gelatin-sorbed, tracer-like substances.

As previously reported, Udenfriend (1962) stated that in dilute solutions fluorescence of a substance is proportional to its concentration. Wilson (1968) agreed, but presented a number of conditions deviating from the ideal relation. These are outlined in Figure 25. Figure 19, resulting from fluorometrically analyzed tracer uptakes by gelatin-coated film, verifies the linear concentration relation, which is the basis of film use in this study.

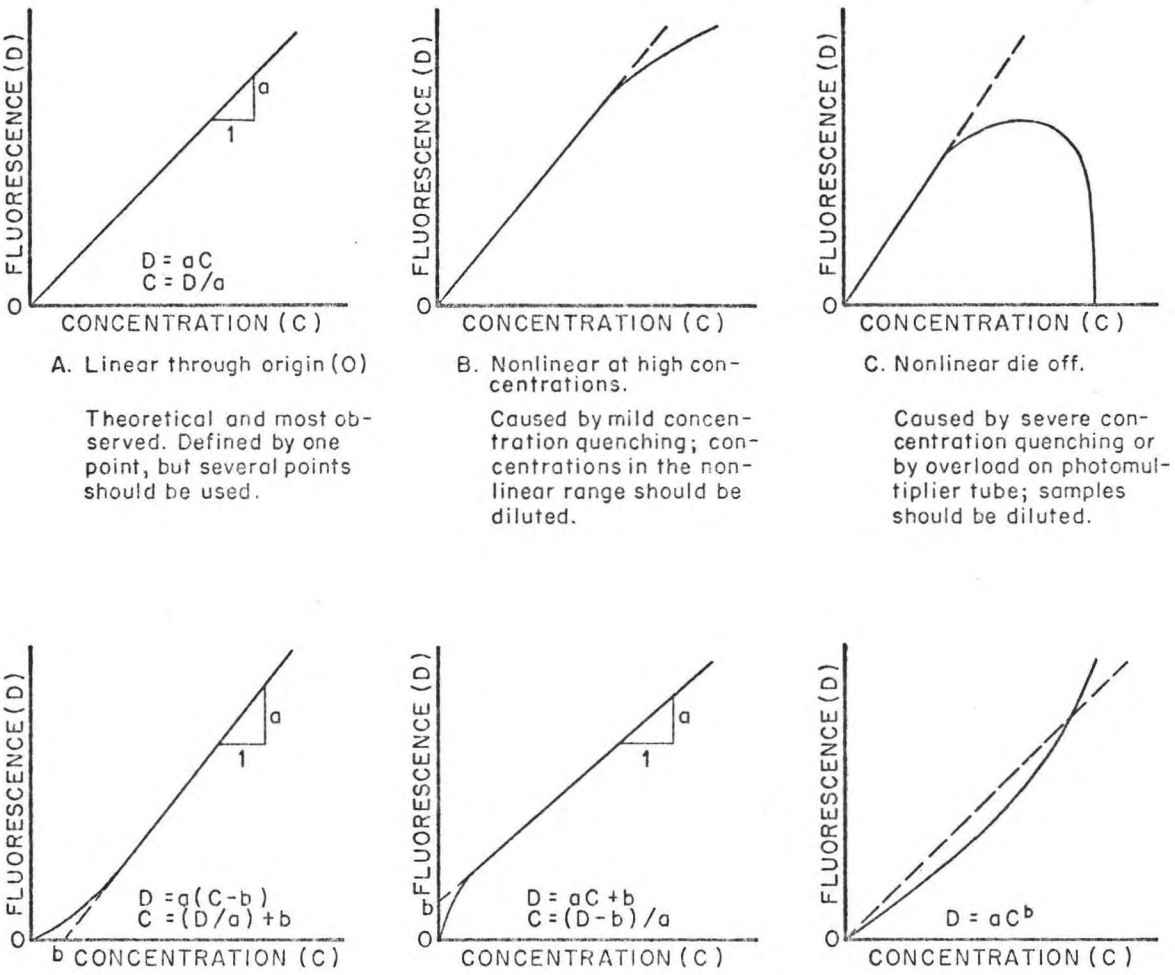


Figure 25. Types of fluorometer calibration curves relating fluorescence to tracer concentration of the sample, (Taken from Wilson, 1968).

# CHAPTER IV

# APPLICATIONS

## Possible Uses of the Detection System

A system capable of continuously monitoring the concentration of a fluorescent tracer in water is potentially applicable to any study involving the use of such a tracer. Although tracing itself is not new, the combination of a fluorescent tracer with greatly improved fluorometers was first reported by Pritchard and Carpenter (1960) in estuarine studies. Since then the same combination has been employed in numerous hydrologic studies.

The most common application has been in studying the dispersive properties of contaminants in natural waters, such as in oceans, lakes, harbors, estuaries, and large rivers. Workers who have conducted dispersion studies using a fluorescent tracer and a highly sensitive fluorometer include Hela and Voipio (1960), Nickerson (1961), Conte (1961), Kisiel et al. (1964), Costin (1964), Foxworthy (1964), Csanady (1964), Joseph et al. (1964), Okubo (1964), Merritt (1964), Pritchard (1964), Isayeva and Isayev (1964), Breidenstein and Thomas (1965), Bailey (1966), Sayre and Chang (1968), Fischer (1968 and 1969).

The downstream movement of water as timed by water-borne particles has been generally termed time-of-travel. Buchanan (1964) reported his

use of a rhodamine dye and a highly sensitive fluorometer to trace the travel time of streams. Wilson and Forrest (1965) described a time-of-travel measurement performed in the Potomac River between Cumberland, Maryland and Washington, D. C. Their technique paralled that of Buchanan's and obtained results equally satisfying.

Other time-of-travel measurements have been conducted on the Mississippi River by Stewart (1967), on the Missouri River by A. Homyk as reported by Wilson (1967), on the Umpqua River in Oregon by Harris (1968), on the Great Miami River in Ohio by Bauer (1968), and according to Stall and Hiestand (1969) on the Kaskaskia and Vermilion Rivers in Illinois by Thomas Butts and on the West Fork of the White River in Indiana by U. S. Geological Survey personnel.

The combination of a sensitive fluorometer and fluorescent dye tracers for gaging streamflow was initially lauded by Wright and Collings (1964). In (1965) Cobb and Bailey wrote a manual which explains practical methods of employing the above combination to measure rates of streamflow. Replogle, Myers, and Brust (1966) followed a similar technique in measuring discharge from two Arizona canals. In a discussion of the Arizona study, Kilpatrick, Sayre and Richardson (1967) also reported success using fluorescent dyes to measure streamflow in turbulent and unsteady streams, beneath ice, in rating in-situ weirs, orifices, etc., and in waters laden with considerable sediment. In another Arizona study, Werrell (1967) also combined a fluorescent tracer with a sensitive fluorometer. After

comparing instantaneous discharge measurements from four streams, obtained by using Pontacyl Pink and a current meter simultaneously, he concluded that methods of dye-dilution hold promise. Goodell, Watt, and Zorich (1967) reported tracer-dilution techniques using fluorescent dyes to measure streamflow volumes for durations of a week or longer.

Fluorescent tracers have found use in numerous other investigations. Dole (1906) measured ground water flow with fluorescein; Reynolds (1966) traced rain water through soil using 12 fluorescent tracers; Robinson and Donaldson (1967) followed the movement of water in two species of woody phreatophytes with Pontacyl Pink; and, as mentioned by Wilson (1967), fluorescent tracers have been used to determine circulation times of well-drilling muds.

With specific mechanical adaptations the tracer detection system developed during this research could probably be employed in all of the tracer studies reviewed above. Here however, testing of the system was limited to measurements of mountain stream discharges, continuous and instantaneous, and to the evaluation of time-of-travel in these upland streams.

## Continuous Measurement of Stream Discharge

Perhaps the most useful application of the detection system is to produce a stream hydrograph. The system can provide part of a continuous stream gaging technique which is inexpensive and applicable

to remote mountain streams. Equipment can be quickly installed, left self-operative under weekly servicing, and readily removed to a new site.

Technique theory

The technique of continuous stream gaging by the use of a fluorescent tracer rests on the physical relationship, that the degree of dilution of a given volume of tracer is directly proportional to the volume of the dilutant. In the case of a stream into which a fluorescent tracer is continuously injected, the relationship is expressed by:

$$qC_1 = (Q + q)(C_2 - C_o) \qquad \text{or}$$

$$Q = q\frac{C_1}{C_2 - C_o} - q \quad , \qquad (17)$$

where $Q$ is the rate of stream discharge,

$q$ is the rate at which the tracer solution is injected into the stream,

$C_1$ is the tracer concentration in an injected solution,

$C_2$ is the tracer concentration in the stream after complete mixing, and

$C_o$ is the naturally occurring concentration of the tracer and tracer-like substances in the stream.

In practice, when suitable tracers are employed, $q$ is negligibly small relative to $Q$. Also, $C_o$ is commonly zero. Thus, equation (17) may be simplified to

$$Q = q \frac{C_1}{C_2} \quad . \qquad (18)$$

If for an appropriate duration $q$ and $C_1$ were invarient, equation (18) would be applicable to the continuous gaging of streamflow. With $q$ and $C_1$ known and $C_2$ continuously sampled, repeated evaluations of equation (18) result in a time-dependent series of $Q$, or specifically, a stream hydrograph.

If the ratio, $C_1/C_2$, can be evaluated as a single term, absolute determinations of concentrations are unnecessary. To do this, one usually assumes that in fluorometric tracing, tracer concentration is linearly related to fluorescence, $F$, such that $C_1/C_2$ can be approximated by $F_1/F_2$.

Ideally, $C_1$ and $C_2$ should be evaluated by identical analyses. That is, if one measures $C_2$ by analyzing fluorescent information stored on gelatin-coated film, he should also register $C_1$ on gelatin-coated film and make a comparable analysis. Such registration of $C_1$ would be inconvenient at best and is not necessary; two circumventions are possible.

One substitute method would be to obtain a $C_1/C_2$ ratio from liquid samples taken from the stream. This ratio would be used to derive gelatin-registered values of $C_1$ from the equation:

$$\frac{C_{1\ liquid}}{C_{2\ liquid}} = \frac{C_{1\ film}}{C_{2\ film}} \qquad \text{or}$$

$$C_{1\ film} = C_{2\ film} \cdot \frac{C_{1\ liquid}}{C_{2\ liquid}} \quad . \qquad (19)$$

Another method involves calibration of $C_2$ - values registered in the gelatin film directly in terms of stream discharge. Calibration is accomplished by measuring stream discharge at specific times using any instantaneous gaging technique (current meter, tracer-dilution, etc.). Measurement is most convenient at the time when stream-side components are serviced. This provides calibration points for the beginning and ending of each tracer-dilution gaging period.

To develop the basis of calibration, equation (18), $Q = q\ (C_1/C_2)$, is utilized. If a constant of proportionality, $K$, replaces the product of $q$ and $C_1$, equation (18) becomes

$$Q = K \frac{1}{C_2} \quad . \qquad (20)$$

Furthermore, if $C_{2i}$ designates any tracer concentration, $C_2$, registered in the gelatin film at the time the instantaneous discharge measurement is made, equation (20) at that instant becomes

$$Q_i = K \frac{1}{C_{2i}} \quad , \qquad (21)$$

where $Q_i$ is the measured instantaneous stream discharge. Equation (21) solved for K yields

$$K = Q_i C_{2i} \quad , \tag{22}$$

where K is defined as the calibration factor.

In theory, K during a given gaging period is constant. In practice, however, K , being a product of $C_1$ and q , may vary slightly as these quantities fluctuate minutely. With two instantaneous discharge measurements, beginning and ending the gaging period, the average K parameter can be approximated by

$$K = 0.5 (K_b + K_e) \qquad \text{or}$$

$$K = 0.5 (Q_{ib} C_{2b} + Q_{ie} C_{2e}) \quad , \tag{23}$$

where the subscripts b and e represent the beginning and the ending of the gaging period, respectively.

Technique description and operation

Two systems are needed for continuous, tracer-dilution stream gaging: an injection system and a detection system. The stream-side installation of these systems are diagrammed in Figure 26.

The injection system must be capable of delivering a constant flow of a concentrated tracer solution throughout the gaging period.

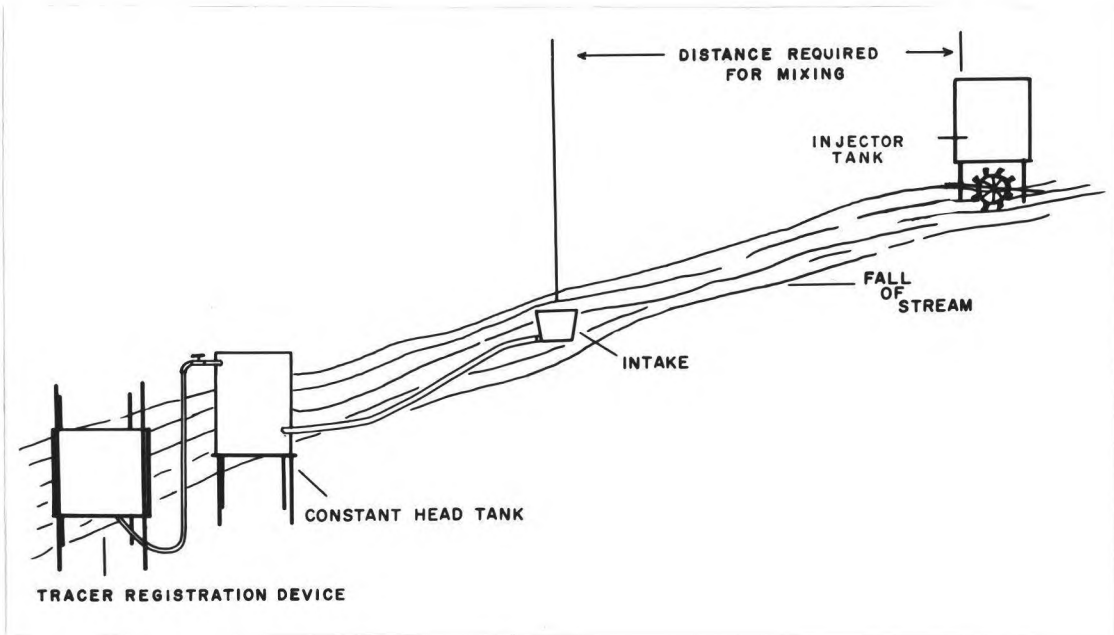


Figure 26. Illustration showing placement of stream-side components including tracer injector.

It should dose the stream sufficiently to produce a stream-tracer concentration of 5-10 ppb. In addition, the injection system should be reliable, simple to operate, compact, as free from dependence on electrical power as possible and adaptable to various rates of delivery demanded by stream size.

André (1964) listed three types of injection systems based on (1) a mariotte vessel, (2) a micropump, and (3) a constant level vessel. Barsby and Cole (1963) used a 60-liter polyethelene aspirator arranged as a mariotte vessel for successful constant rate injection. Kilpatrick et al. (1967) adapted a chlorine feeder to discharge a constant flow of tracer solution. Its rate of flow is adjustable and storage capacity is sufficient for several instantaneous discharge measurements. None of these systems are designed for long-term, tracer injection.

Goodell et al. (1967) described an injection system designed to discharge a tracer solution at a constant rate for periods up to one week. Siverts (1967), in his detailed description of the same system, achieved injection rates over a seven-day period which varied no more than 0.5% about the mean. The system consists of a water-cooled mariotte vessel, either bank or stream mounted, which is capable of delivering a 12.6% Rhodamine WT solution at a rate as low as four grams per minute. Siverts established the reliability of this injection system in extensive field tests. This is the system used in this study.

After injection, the tracer mixes with the stream water by diffusion and dispersion. The tracer is carried downstream while

lateral and vertical mixing proceed. The stream distance required for lateral mixing usually dictates the location of the sampling intake; complete lateral mixing usually lags complete vertical mixing.

Barsby, Delannoy and Watt (1967) studied the problem of mixing lengths in rivers thoroughly. In rivers whose width, $b$, greatly exceeds its depth, $d$, they suggested estimating the mixing length, $L$, by using a modified Rimmar's formula,

$$L = \frac{(0.13)\ b^2\ v^2}{g\ d^2\ S} \quad , \tag{24}$$

where $v$ is the mean stream velocity in feet per second,

$S$ is the water surface slope,

$g$ is the gravitational acceleration in feet per second squared, and variables $L$, $d$, and $b$ are all expressed in feet.

Other equations to determine mixing distances have been suggested: Hull (1962); Yotsukura, cited in Cobb and Bailey (1965); and André, cited in Barsby et al. (1967). Their applicability is limited by uncertainty of coefficients appropriate to a given stream.

Experience in tracer dilution gaging of small, turbulent mountain streams leads this author to suggest a dye-slug trial to indicate an adequate mixing length. The trial consists of dumping a slug of dye (approximately 3 grams of a 20% Rhodamine WT solution per cubic-foot per second of estimated streamflow) into the stream at the tentatively chosen injection point. By following the moving dye-cloud

one can observe its course, its lag caused by backwater and pools, and its color uniformity across the channel width. If behavior of the dye-cloud indicates a poor mixing reach, a second reach can readily be tested by another dye-slug trial. The final reach selected should, of course, be scrutinized for flows or seeps leaving or entering it. As a precaution, the sampling section should be chosen somewhat downstream of the apparent point of complete lateral dispersion. Andre´ (1964) supported the use of dye-slug trials; however, he stated that they are second-best to the knowledge of well-trained operators who are experienced with the stream.

Once continuous injection of the tracer begins, adequate tracer mixing at the chosen sampling section can be verified by analyzing liquid samples obtained across the section. Equality of concentration across the stream is evidence of adequate mixing. The percent mixing, M (%) may be determined by applying Schuster's (1965) equation,

$$M\ (\%) = \left\{ 1 - \left[ \frac{\left( \left| N_1 - \overline{N} \right| + \left| N_2 - \overline{N} \right| + \cdots \left| N_x - \overline{N} \right| \right)}{\overline{N}_x} \right] \right\} 100 \quad , \qquad (25)$$

in which $N_1$ , $N_2$ , $\cdots$ $N_x$ are dye concentrations from respective samples, $x$ is the number of samples in the section, and $\overline{N}$ is the mean concentration in the section. Schuster, along with others, has arbitrarily accepted 99% mixing as sufficient, while Cobb and Bailey (1965), using a similar mixing equation, suggested that satisfactory results can be obtained with 95% mixing.

The mixing length locates the sampling section from which a segment of flow (approximately 10 liters per minute) is diverted to the detection system. As previously described, the system will produce a continuous record of stream-tracer concentrations, $C_2$ . This record can be converted to a stream hydrograph by appropriate calibrations as previously described.

Excluding transportation time to the site, one can install the gaging equipment and prepare for operation in about four hours. The frequency of servicing is a function of stream size and injection tank capacity. In the trials conducted under this study, one week was the nominal period between complete servicings. Complete servicing includes:

(1) obtaining liquid stream samples at the sampling section to test for adequate tracer mixing and to instantaneously gage discharge for calibration purposes;

(2) measuring the rate of tracer injection and co-incidentally obtaining a sample for $C_1$ determination;

(3) checking the equipment, especially stream intakes, for malfunctions;

(4) renewing the supply of tracer in the injection vessel (procedural suggestions are listed in appendix);

(5) removal of the exposed gelatin-coated film and installation of a fresh supply.

Film is brought to the laboratory and analyzed when convenient. Analysis consists of scanning the film in a modified fluorometer, obtaining an appropriate record, and converting the information into a stream hydrograph.

Stream types to which technique is most applicable

Appropriately applied and instrumented, the technique will in theory record a stream hydrograph of any stream regardless of size or character.

Mountain streams, however, are especially applicable, because their turbulent flows and tortuous channels are unsuited to accurate use of velocity control sections (and to a current meter as well), but favor the tracer technique because of their potential for rapid mixing. Turbulence reduces mixing lengths which, in turn, diminishes opportunity for tracer sorption on sediment and organic matter. Also, because mountain streams typically carry little sediment, sorption potentials are minimal. Mountain streams, however, often flow through reaches rich in organic debris, which tend to increase sorption potentials. The value of tracer-gaging for mountain streams has been recognized by many investigators from earlier times (Neuzil, 1929) through the present (Keller, 1968).

The continuous gaging technique can also be used to produce a hydrograph on streams whose bed configuration varies excessively with flow rate and renders its stage-discharge relation inconstant. This problem is particularly acute for gaging cross-sections adjacent to bridges supported on piers which obstruct flow. In tracer-dilution gaging local scour or fill does not negate accurate measurement.

Field trials

Field trials of the tracer-dilution, continuous-gaging technique were conducted during the summers of 1967 and 1968 on the Fraser Experimental Forest near Fraser, Colorado. Test sites were chosen near sharp-crested weirs that continuously gage discharge from two high mountain streams: Deadhorse and East Saint Louis Creeks. Pertinent data on the two gaged streams are listed in Table 6.

Table 6. Pertinent data for two gaged streams.

| Stream | Type of Weir | Range of Discharge During Dilution Gaging(cfs) | Times of Dilution Gaging |
|---|---|---|---|
| Deadhorse | 120° V-notch | 0.4 - 1.1 | Sept. 1967 |
| East St. Louis | 8-foot Cippoletti | 1.9 - 7.0 | Aug. - Sept. 1968 |

Boulders, logs, and organic debris clutter both test streams and promote rapid mixing. However, their large wetted perimeters relative to their rates of flow favor tracer loss. Melted snow supplies a majority of the flow-volume in each stream. Peak flows occur in early summer and are followed by gradually diminishing flows, which produce relatively uniform summer hydrographs.

Tests were designed to evaluate the performance of the detection system and to compare stream hydrographs compiled by tracer-dilution and by weir techniques. Tests during 1967 were mainly concerned with

evolution and improvement of detection equipment and procedures. Results served as a guide for testing during 1968. Although procedural and equipment improvement continued in 1968, major emphasis was placed on production and evaluation of stream hydrographs derived from tracer-dilution gaging.

In accordance with recommendations by Replogle et al. (1966) and Cobb and Bailey (1965) and spurred by the success Siverts (1967) obtained, Rhodamine WT was used exclusively. Dye concentrations in the stream varied with the concentration and rate at which the dye was injected into the stream, as well as with stream discharge. Stream-dye concentrations ranged from 2 to 14 ppb, but more commonly averaged 6 to 8 ppb.

Because instrument and technique development was contemporaneous with many of the field trials, recognizable failures in performance were numerous. Data from time periods encompassing such failures were excluded from statistical analyses. There remained 640 hours of record from 18 discrete gaging periods that were free of known and vitiating faults, (Table 7).

Figures 26, 27 and 28 show representative stream-side positioning of the tracer injector and the tracer detection unit as used during stream gaging trials. Relative tracer concentrations, $C_2$ , sampled from the streams were registered on gelatin-coated film, fluorometrically analyzed, recorded on a strip-chart as functions of time, and converted to stream hydrographs using equation (20), $Q = K\ (1/C_2)$.

Table 7. Tracer-dilution gaging periods, Deadhorse and East St. Louis Creeks.

| Period | Period Interval | | | | | | Duration |
|---|---|---|---|---|---|---|---|
| | Beginning | | | Ending | | | |
| | Month | Day | Hour | Month | Day | Hour | Hours |
| Deadhorse, 1967 | | | | | | | |
| 1 | September | 10 | 2200 | September | 12 | 1300 | 39 |
| East St. Louis, 1968 | | | | | | | |
| 2 | August | 1 | 1800 | August | 3 | 0400 | 34 |
| 3 | August | 9 | 1500 | August | 12 | 0300 | 60 |
| 4 | August | 12 | 1900 | August | 14 | 1100 | 40 |
| 5 | August | 14 | 1215 | August | 15 | 0500 | 17 |
| 6 | August | 15 | 1200 | August | 16 | 0700 | 19 |
| 7 | August | 16 | 2000 | August | 17 | 0600 | 10 |
| 8 | August | 17 | 1500 | August | 20 | 1200 | 69 |
| 9 | August | 24 | 1000 | August | 25 | 1100 | 25 |
| 10 | August | 25 | 2000 | August | 26 | 2300 | 27 |
| 11 | August | 27 | 1400 | August | 28 | 1300 | 23 |
| 12 | August | 30 | 1800 | September | 1 | 0800 | 38 |
| 13 | September | 2 | 2100 | September | 5 | 1400 | 65 |
| 14 | September | 5 | 1700 | September | 6 | 0700 | 14 |
| 15 | September | 6 | 2200 | September | 8 | 1400 | 38 |
| 16 | September | 12 | 1200 | September | 14 | 1700 | 53 |
| 17 | September | 15 | 1300 | September | 16 | 1300 | 24 |
| 18 | September | 18 | 1300 | September | 20 | 1000 | 45 |
| | | | | | | TOTAL | 640 |

Figure 27. Field installation of tracer injector, bank-mounted.

Figure 28. Field installation of tracer registration unit.

Equation (23), $K = 0.5\ (Q_{ib}\ C_{2b} - Q_{ie}\ C_{2e})$ was the primary means employed to compute the calibration factor, $K$, for each gaging period. For expedience, values for instantaneous discharge beginning and ending each gaging period, $Q_{ib}$ and $Q_{ie}$, were obtained from records of nearby weirs and entered in equation (23).

Weir records also provided stream hydrographs with which to compare tracer-dilution hydrographs. The congruity of the dilution-based and the weir-based hydrographs within each period was studied. Figures 29 through 46 show the congruity for all periods. Table 8 presents a summary of comparisons within all 18 gaging periods. Although one instantaneous deviation of -10% occurred, tracer-dilution-based measurements differed from weir-based measurements by an algebraic average of only +0.32% of the latter and by an absolute average of only 1.83%. Algebraic and absolute refer to a regard and disregard, respectively, of the sign of the values of discharges recorded by the two systems at a given time. A positive sign indicates an overestimate of discharge by tracer gaging relative to weir gaging.

Results by the two systems were also compared by a regression analysis based on 916 pairs of streamflow values taken from the 18 periods. To hourly values were added values at smaller intervals of time when discharge change was rapid. Figure 47 represents a plot of the regression equation. Slope of the regression equation is 1.00059; the coefficient of determination, $R^2$, equals 99.9%; the error mean square is 0.006 cfs. At a tracer-dilution discharge of 7.0 cfs, where the

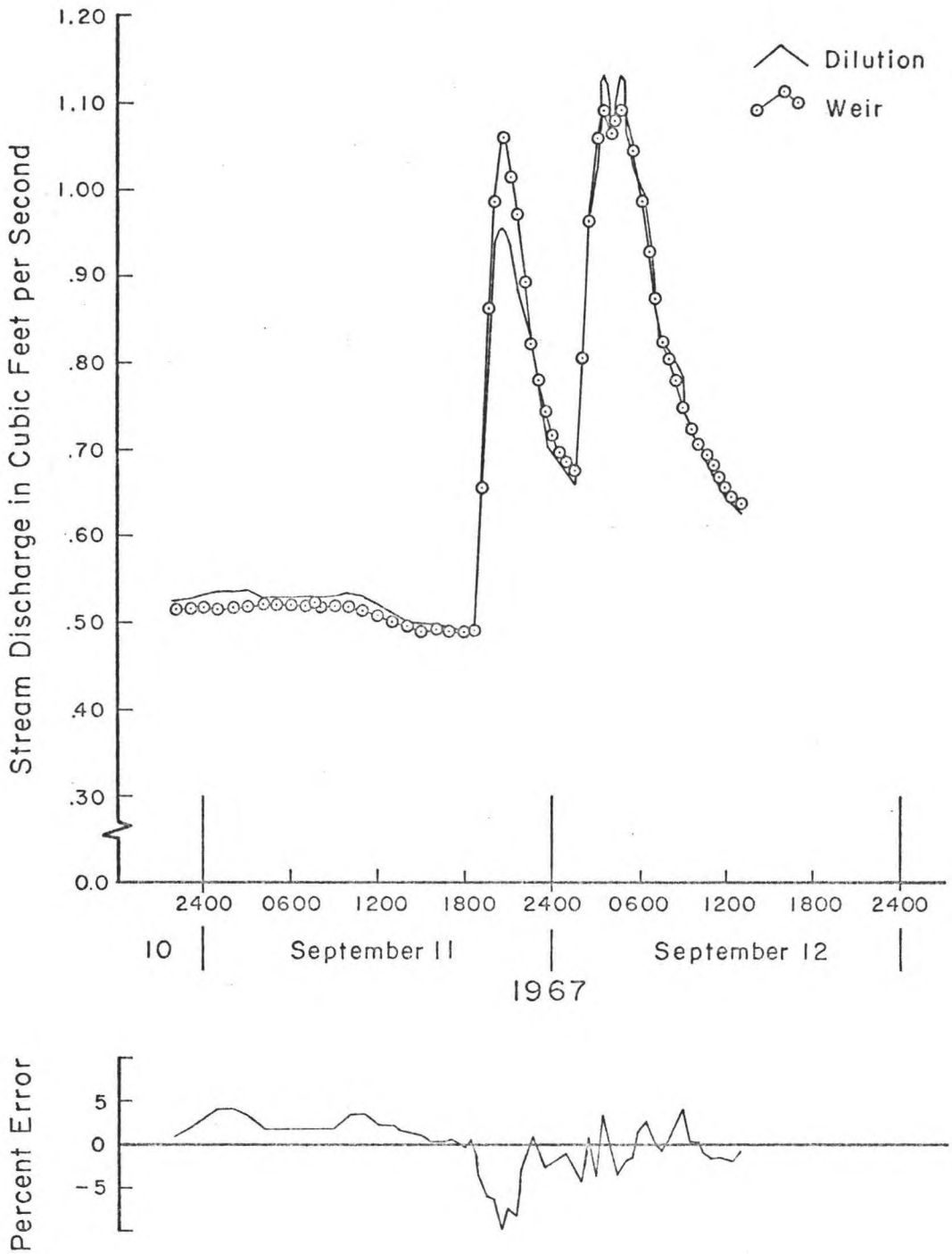


Figure 29. Hydrograph Comparison Period 1, Deadhorse Creek; Comparison of hydrographs computed from tracer-dilution and weir measurements.

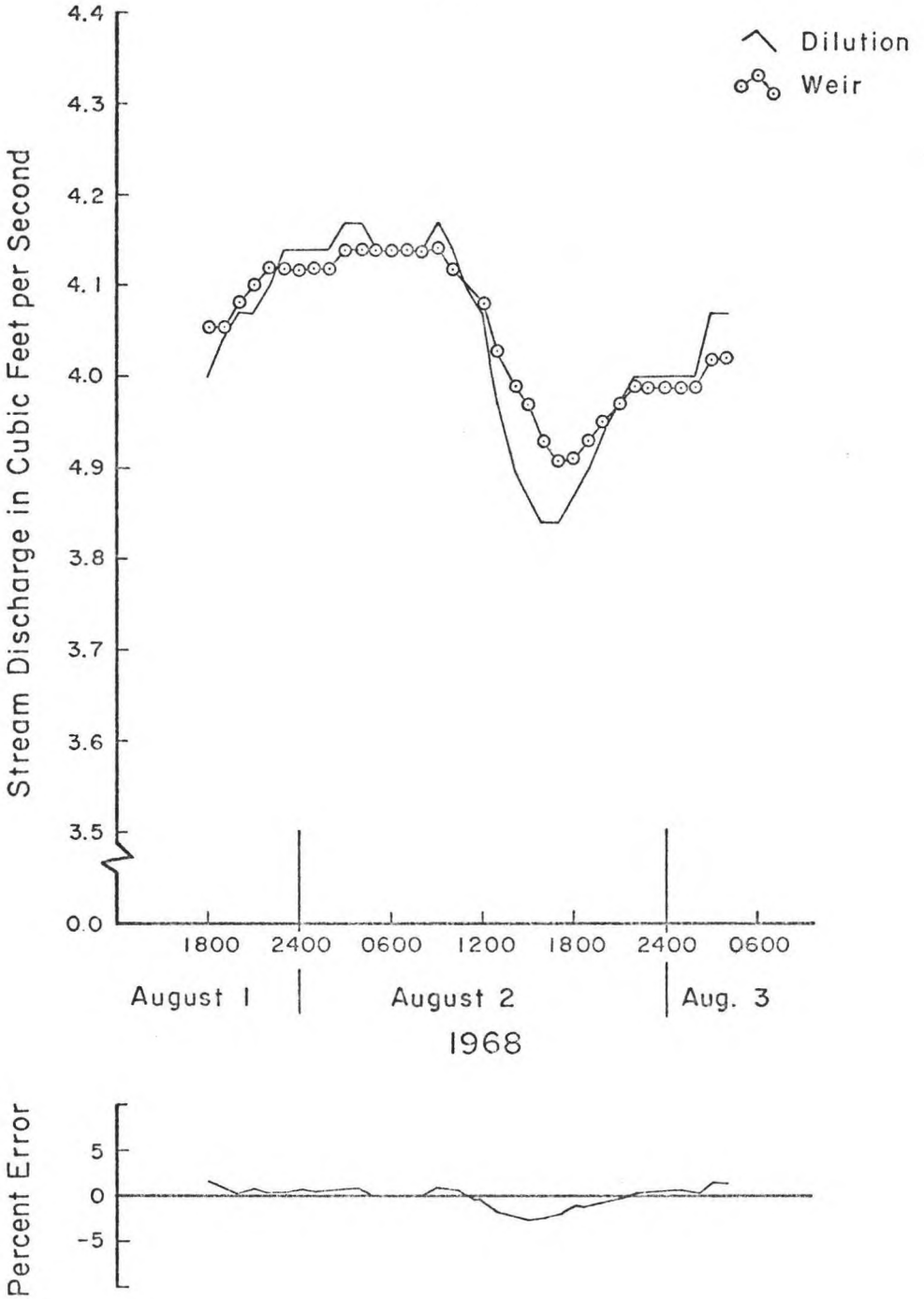


Figure 30. Hydrograph Comparison Period 2, East Saint Louis Creek

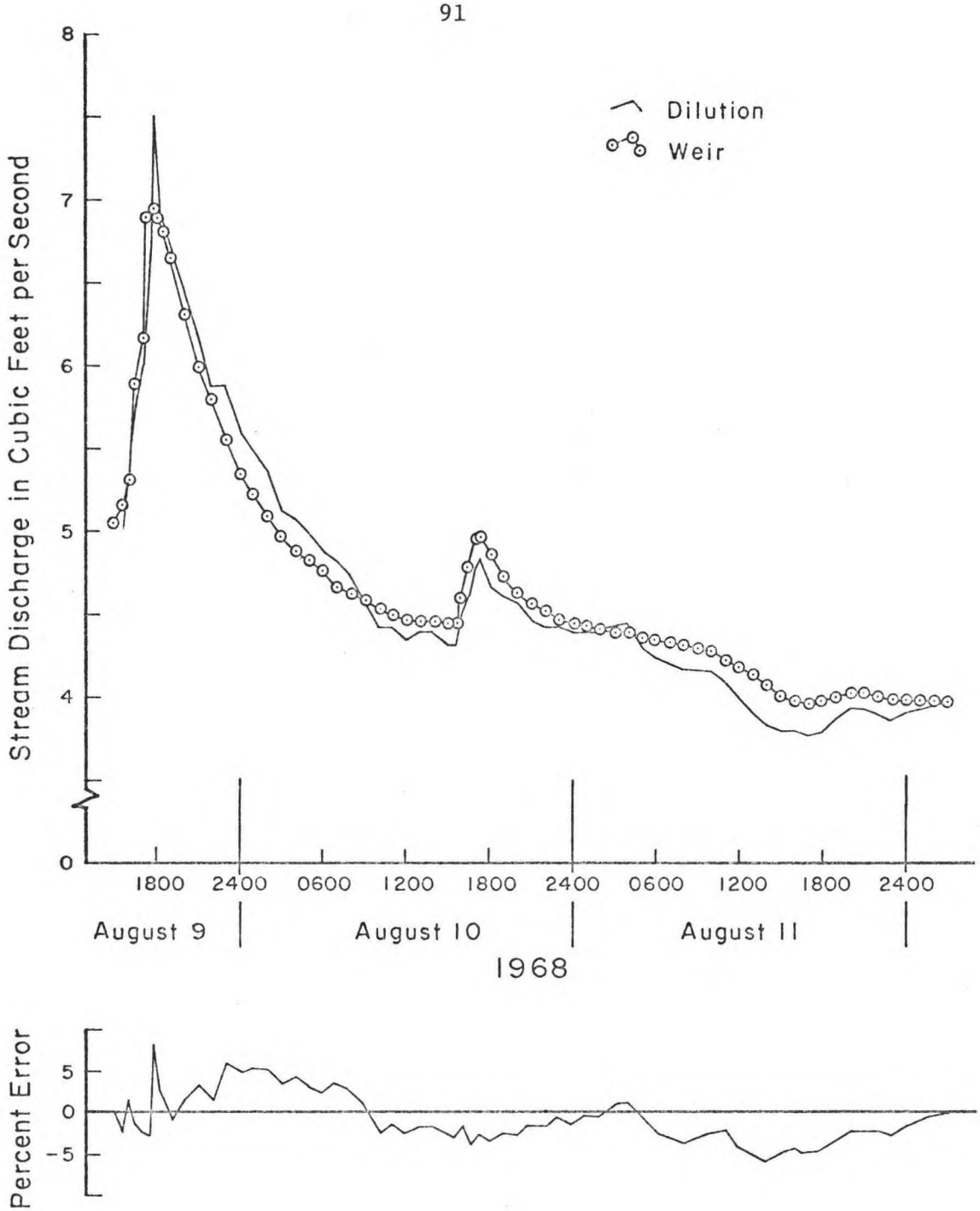


Figure 31. Hydrograph Comparison Period 3, East Saint Louis Creek

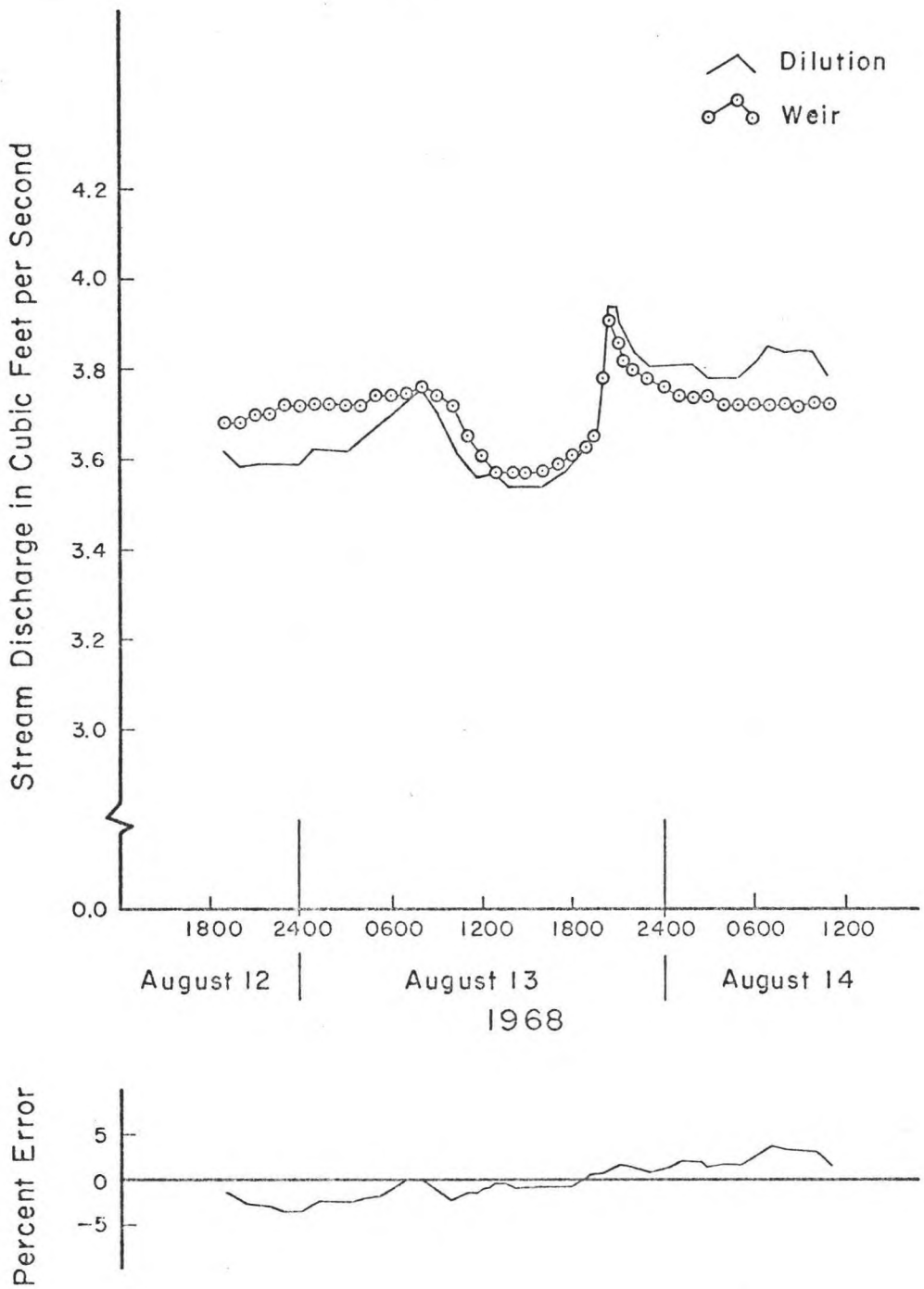


Figure 32. Hydrograph Comparison Period 4, East Saint Louis Creek

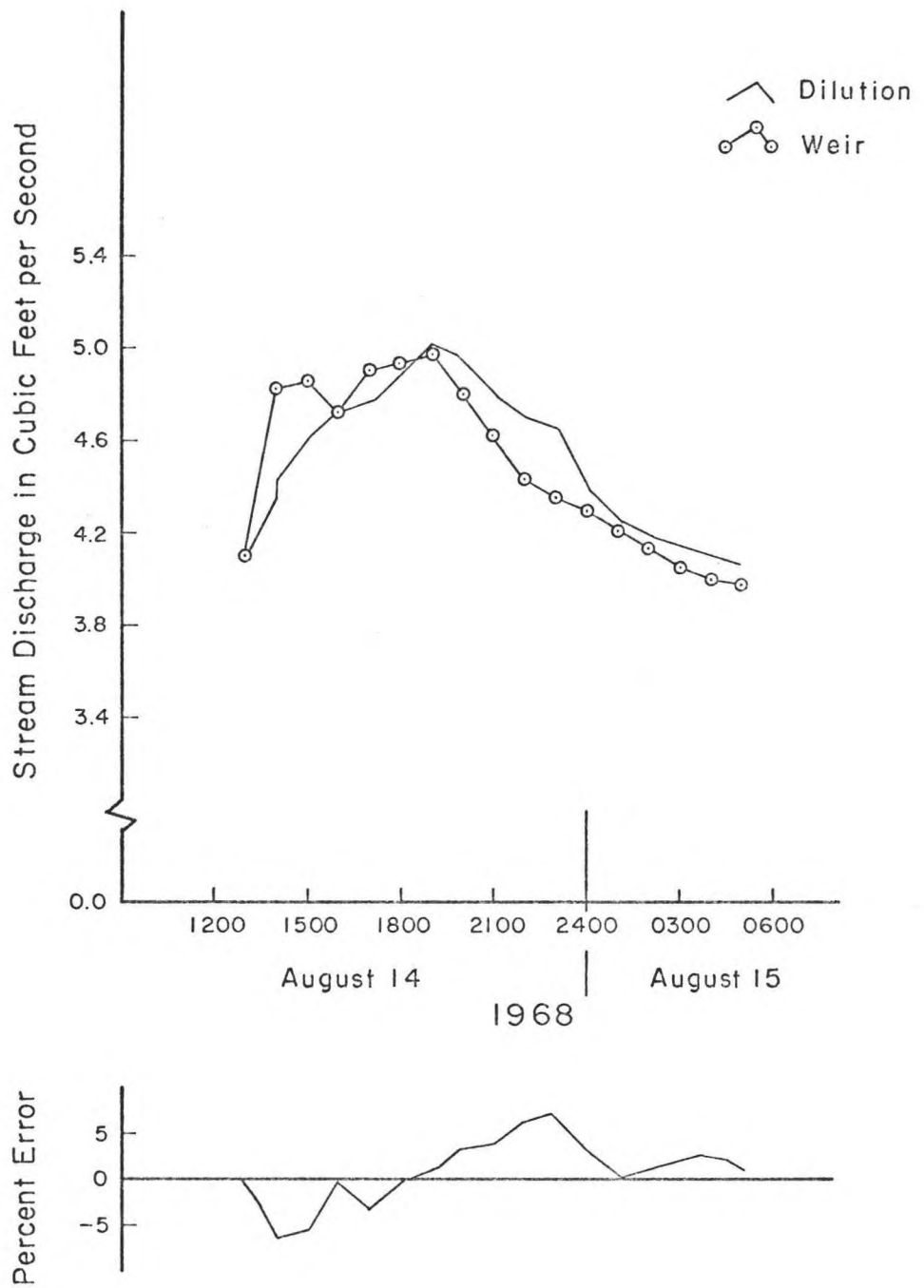


Figure 33. Hydrograph Comparison Period 5, East Saint Louis Creek

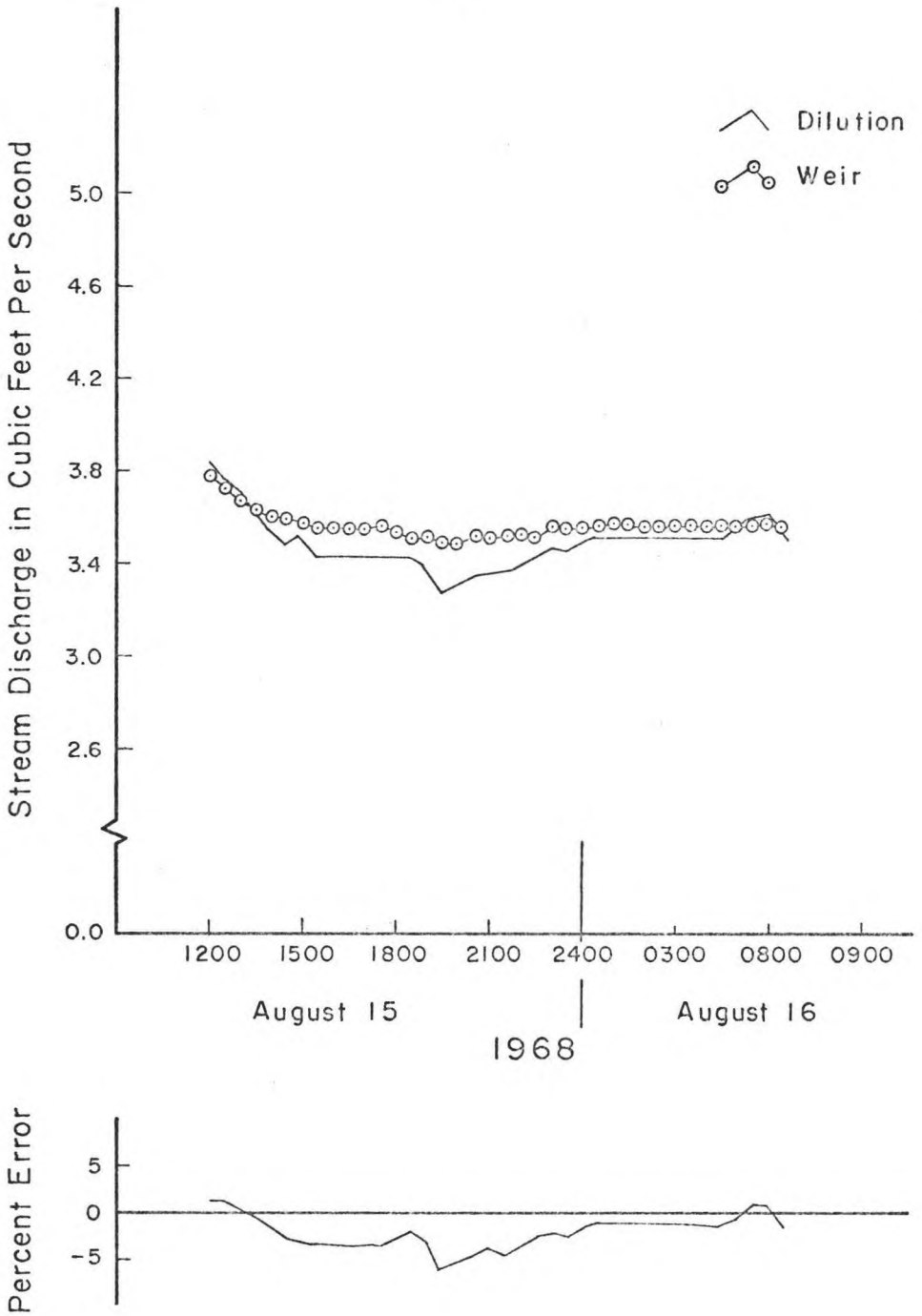


Figure 34. Hydrograph Comparison Period 6, East Saint Louis Creek

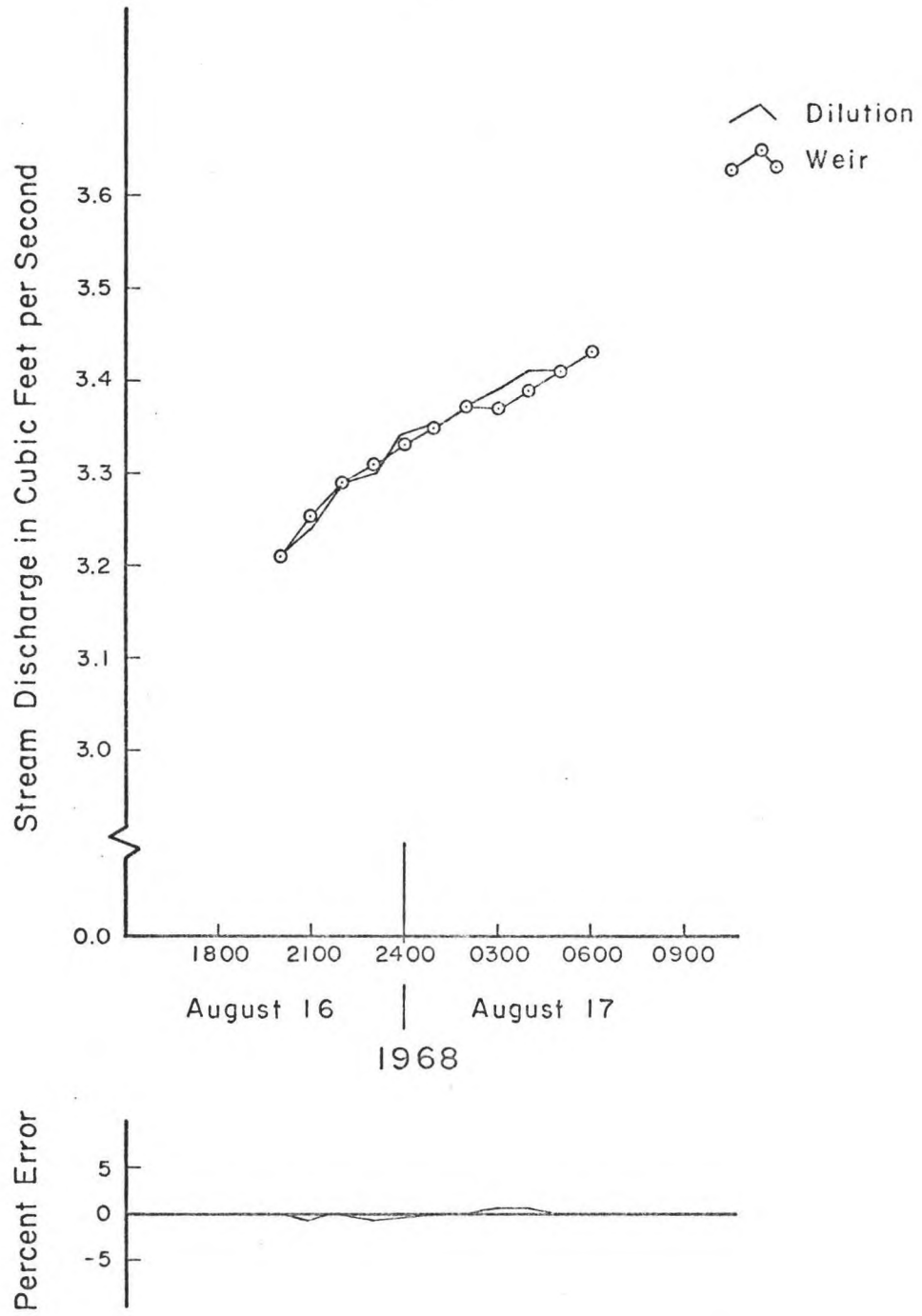


Figure 35. Hydrograph Comparison Period 7, East Saint Louis Creek

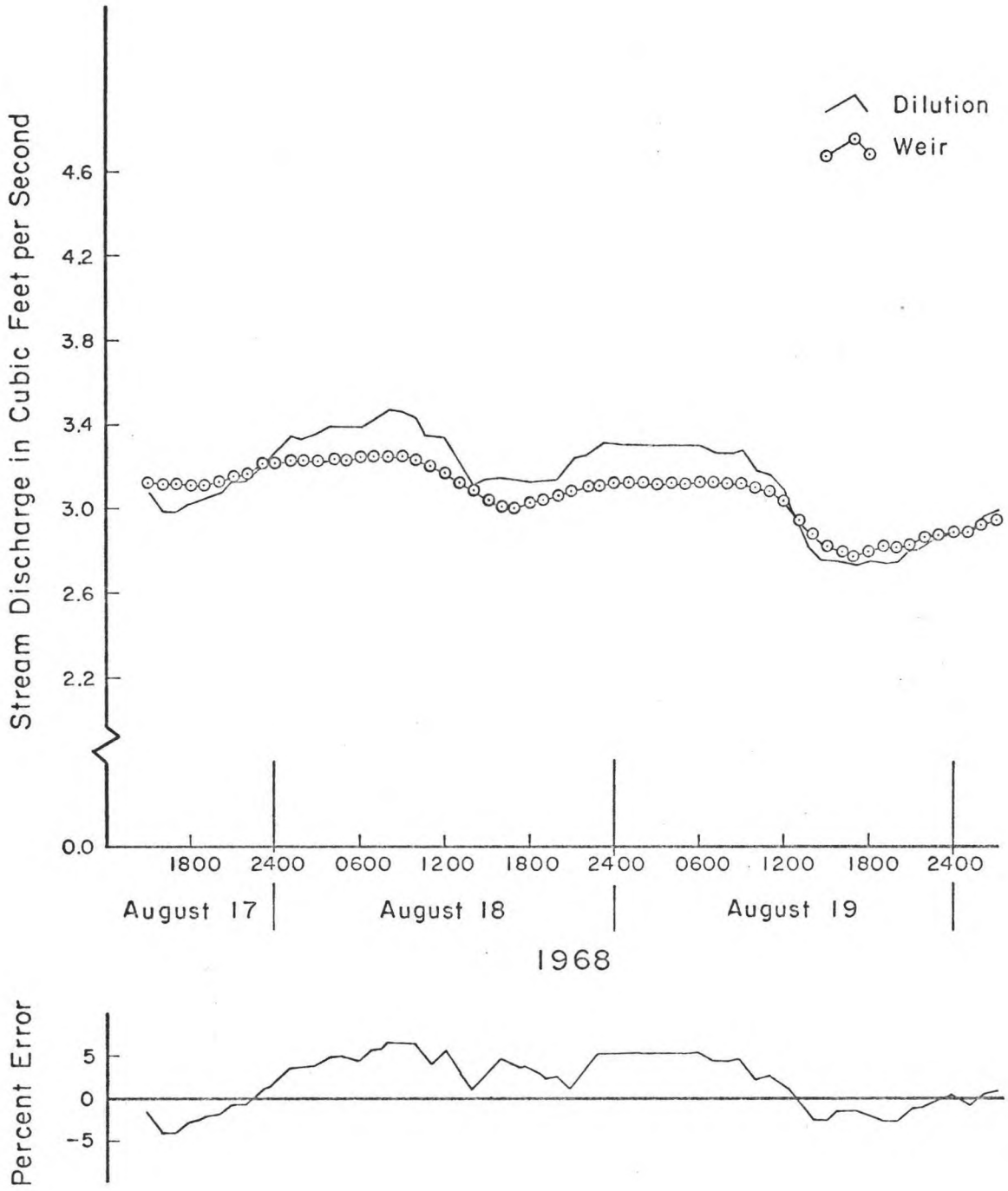


Figure 36. Hydrograph Comparison Period 8, East Saint Louis Creek

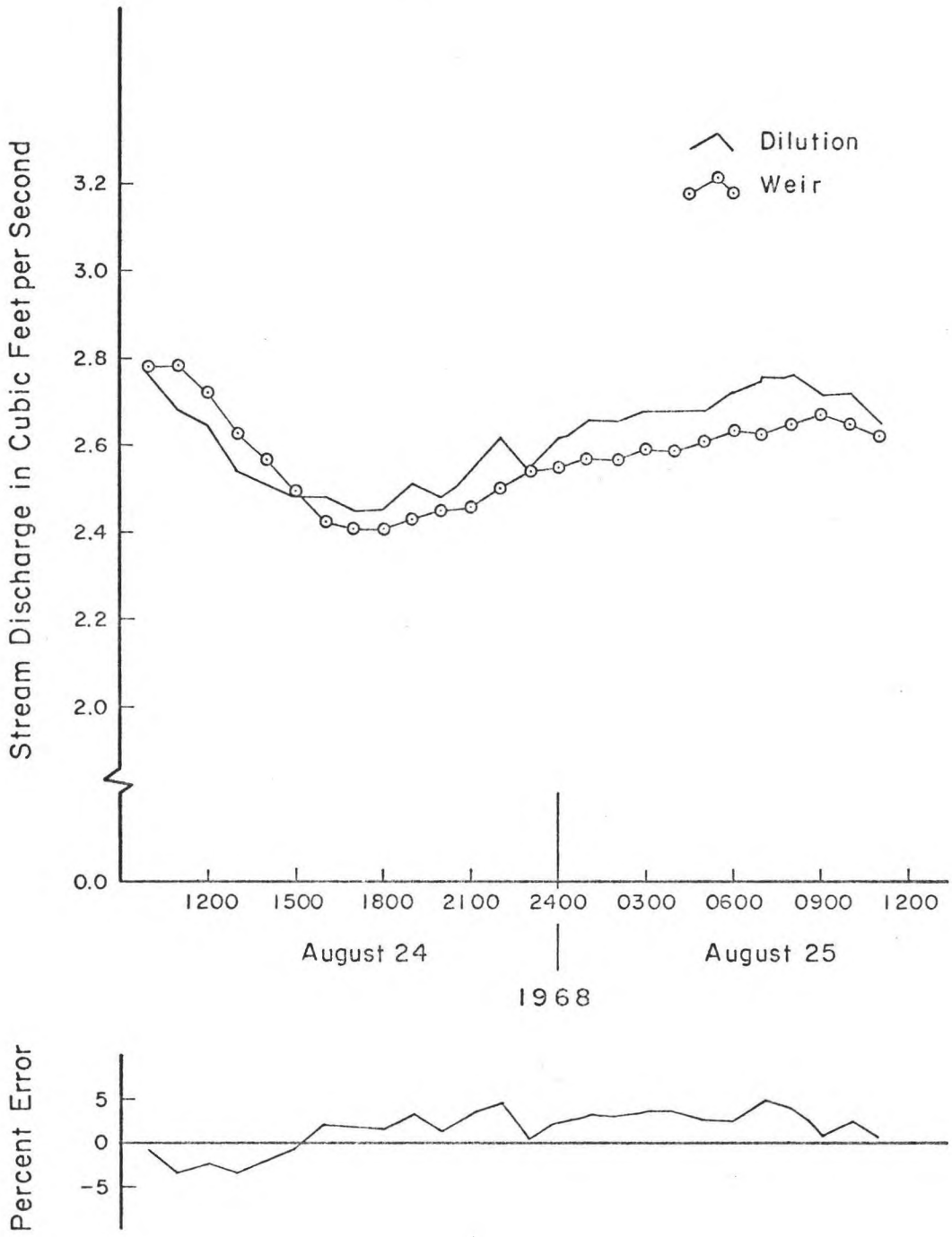


Figure 37. Hydrograph Comparison Peroid 9, East Saint Louis Creek

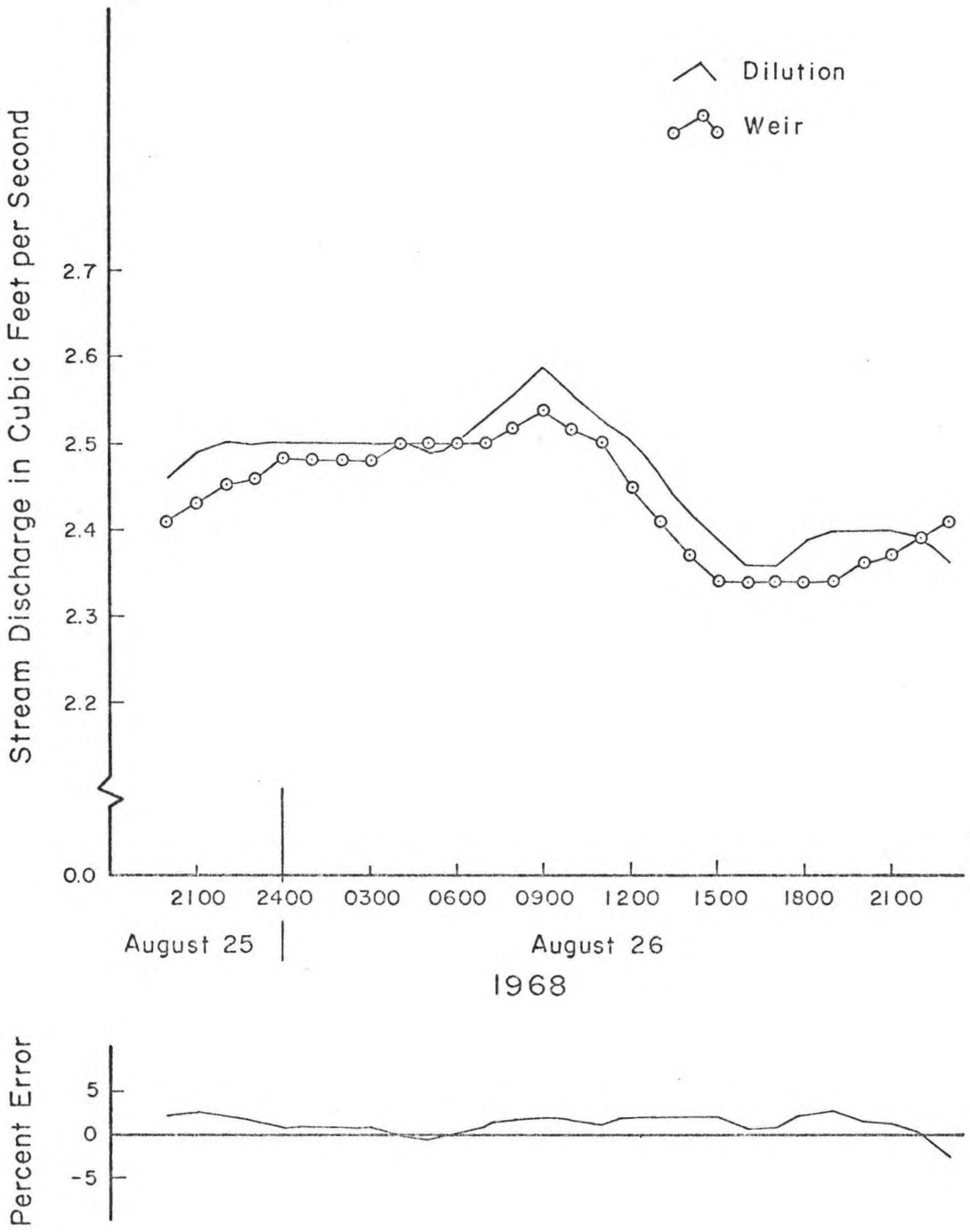


Figure 38. Hydrograph Comparison Period 10, East Saint Louis Creek

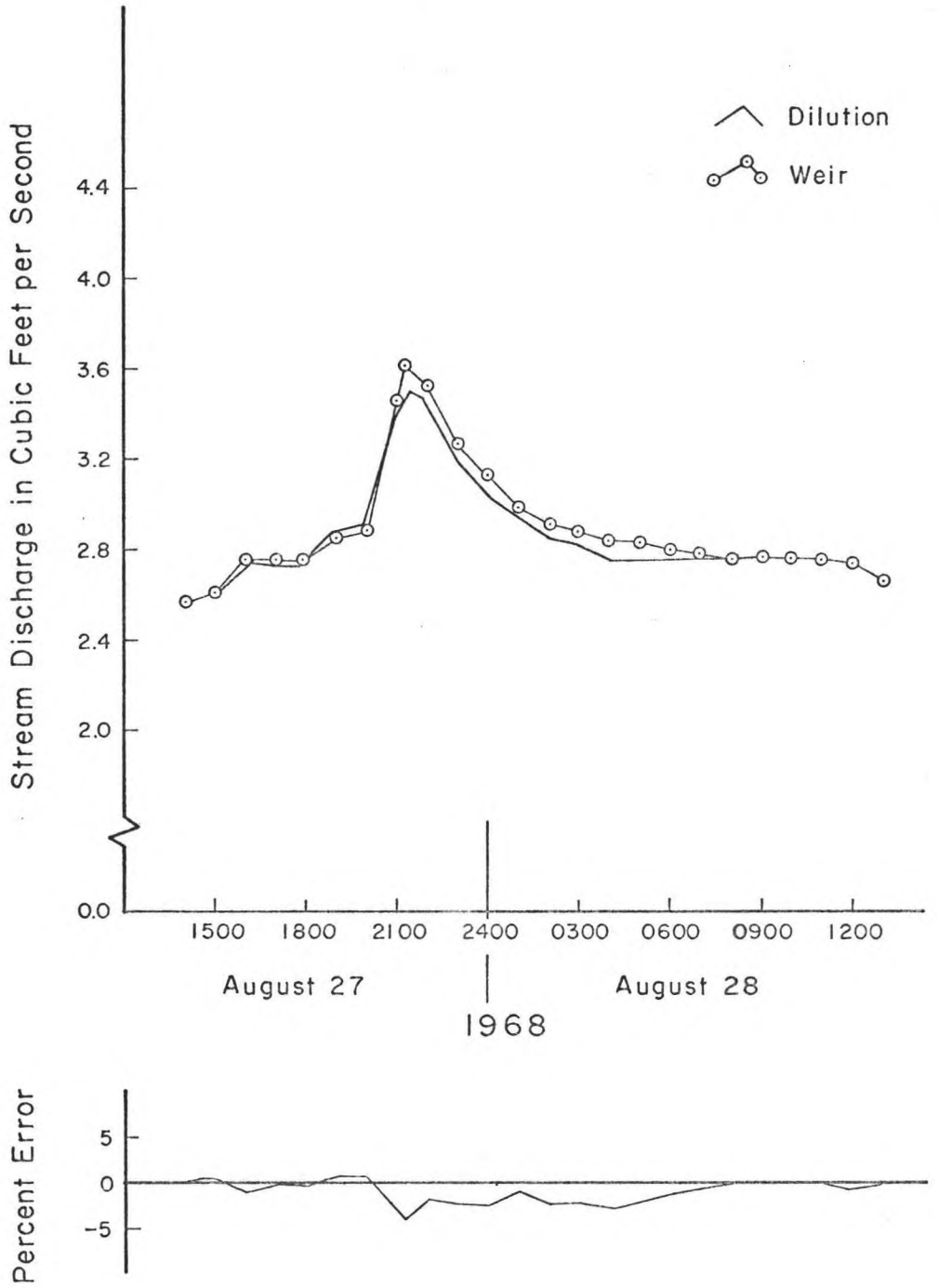


Figure 39. Hydrograph Comparison Period II, East Saint Louis Creek

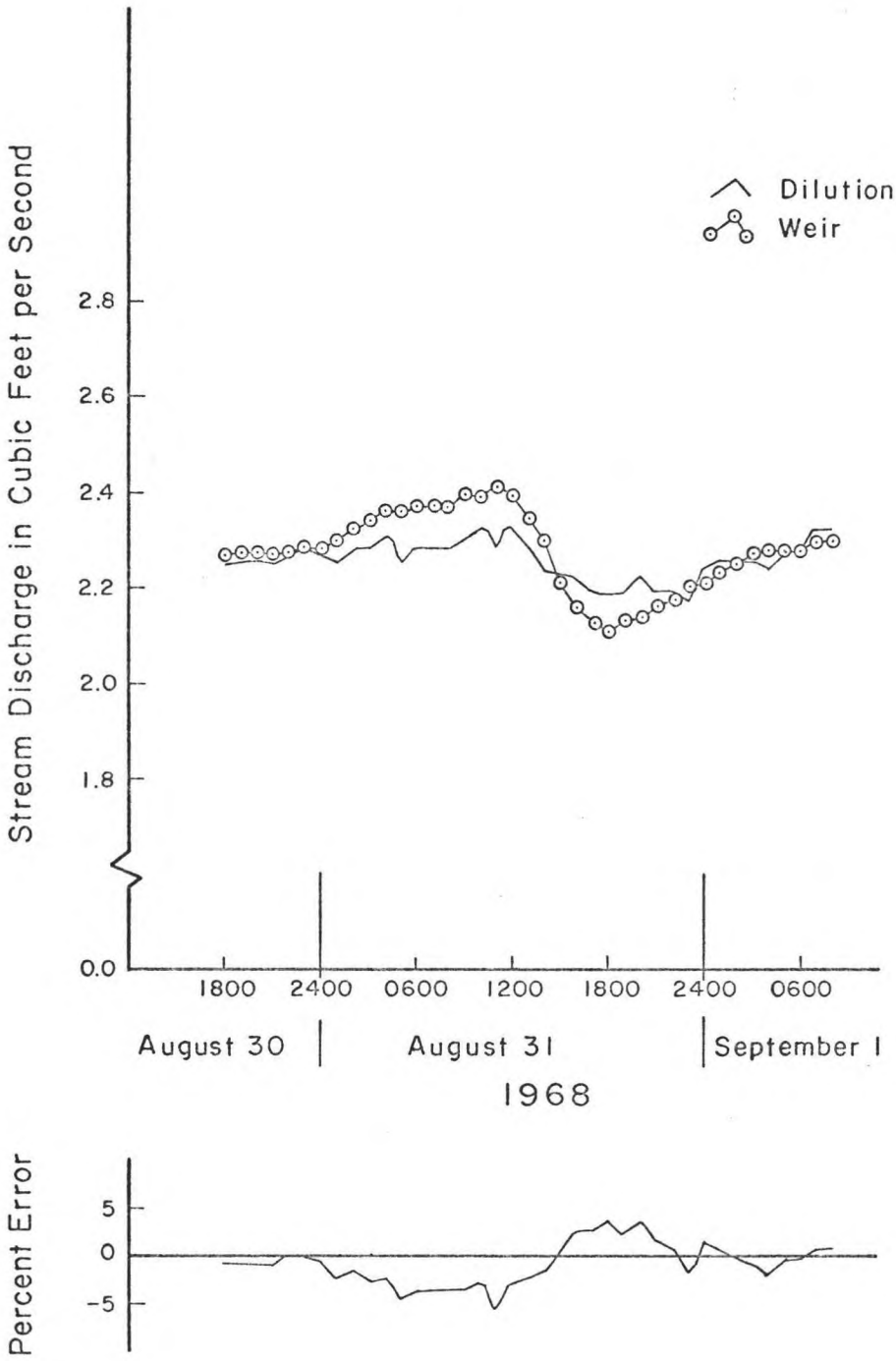


Figure 40. Hydrograph Comparison Period 12, East Saint Louis Creek

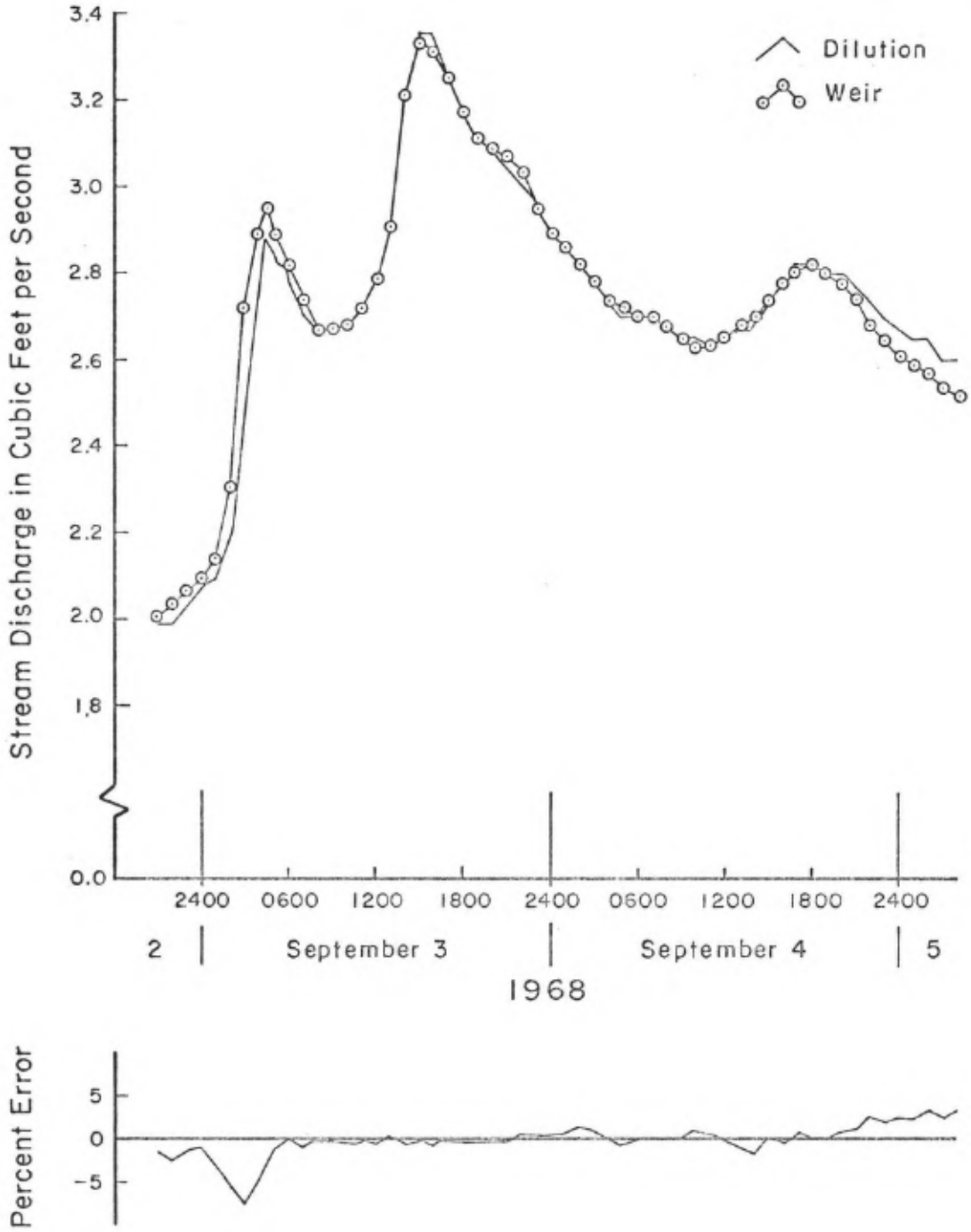


Figure 41. Hydrograph Comparison Period 13, East Saint Louis Creek

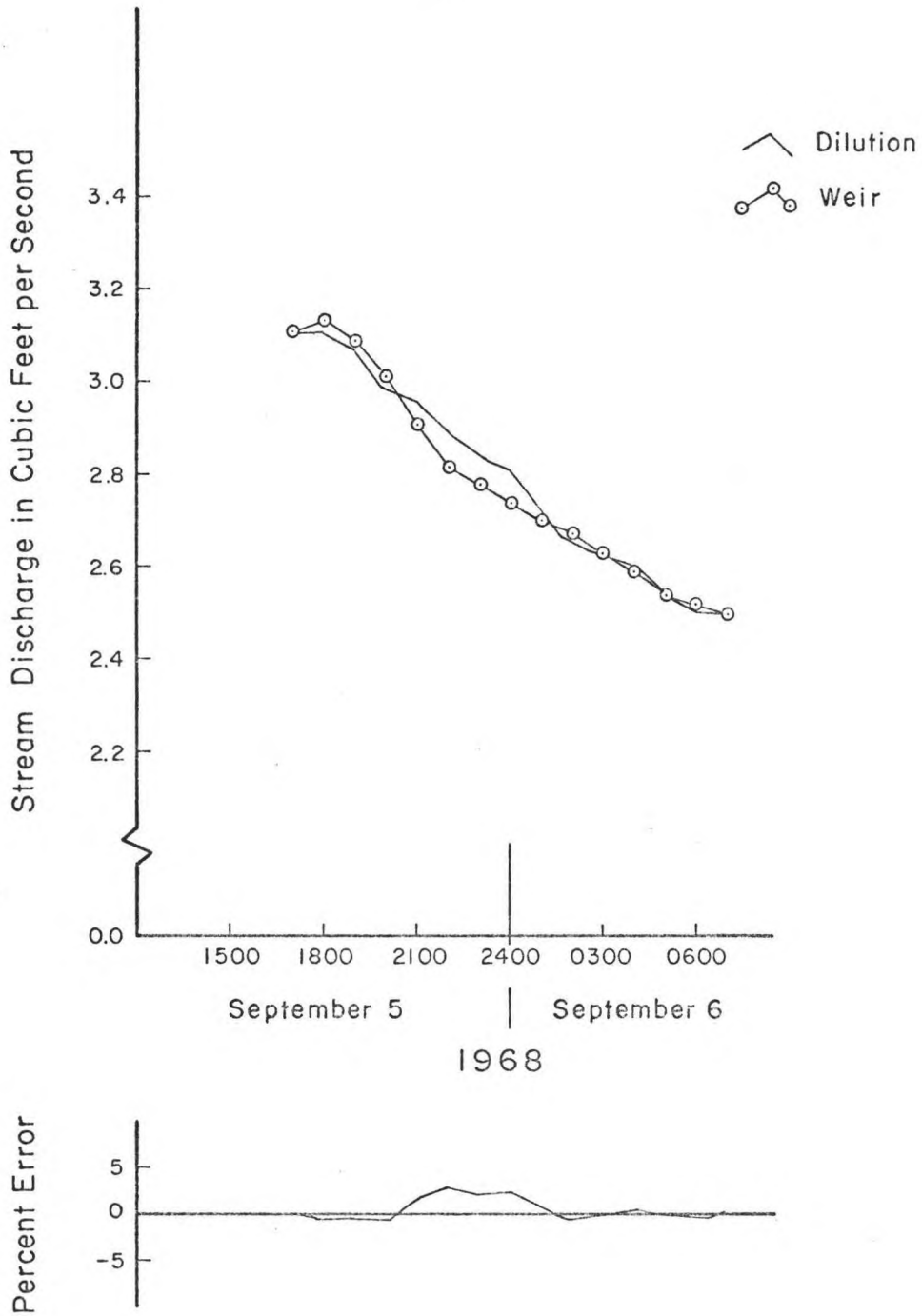


Figure 42. Hydrograph Comparison Peroid 14, East Saint Louis Creek

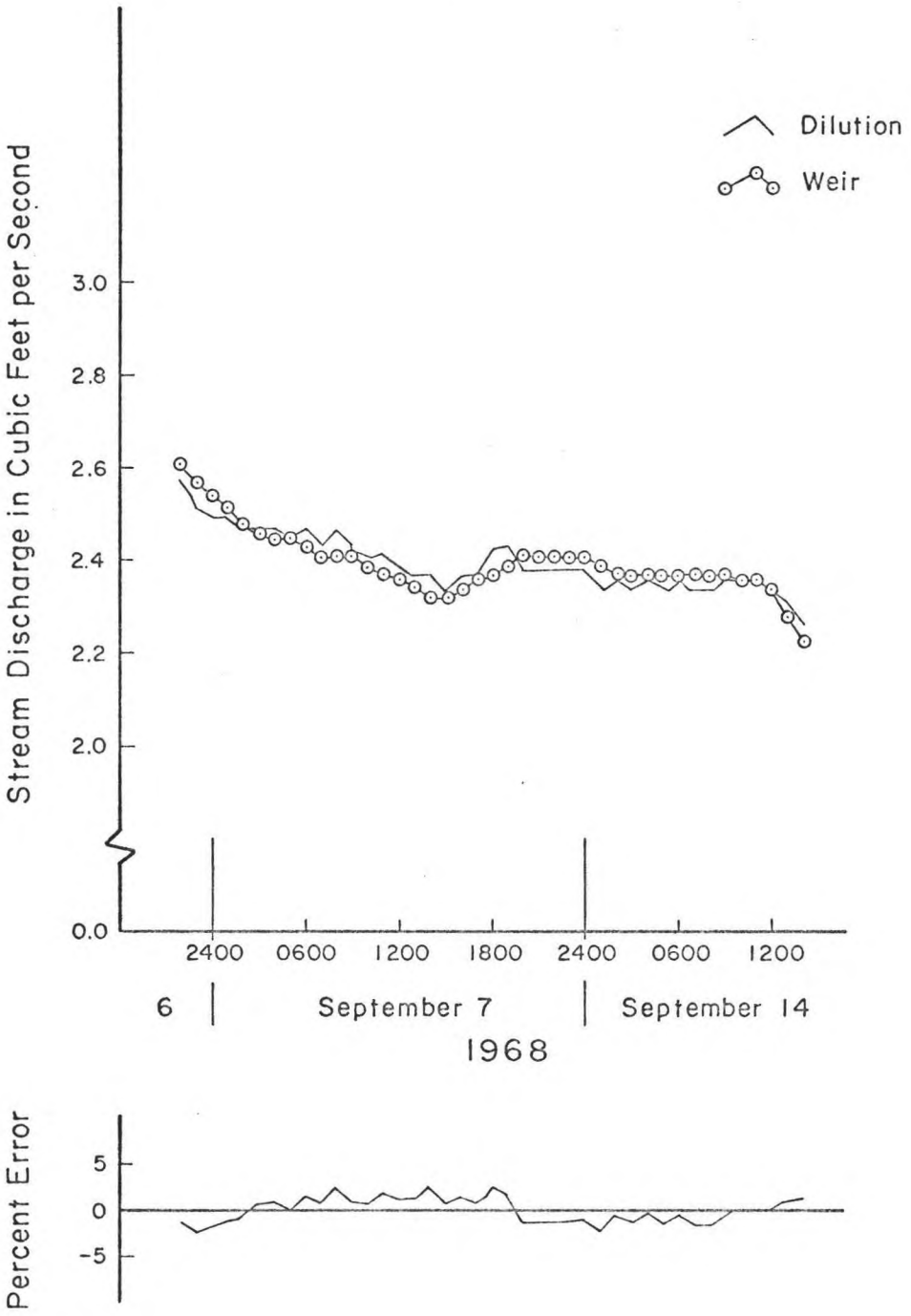


Figure 43. Hydrograph Comparison Period 15, East Saint Louis Creek

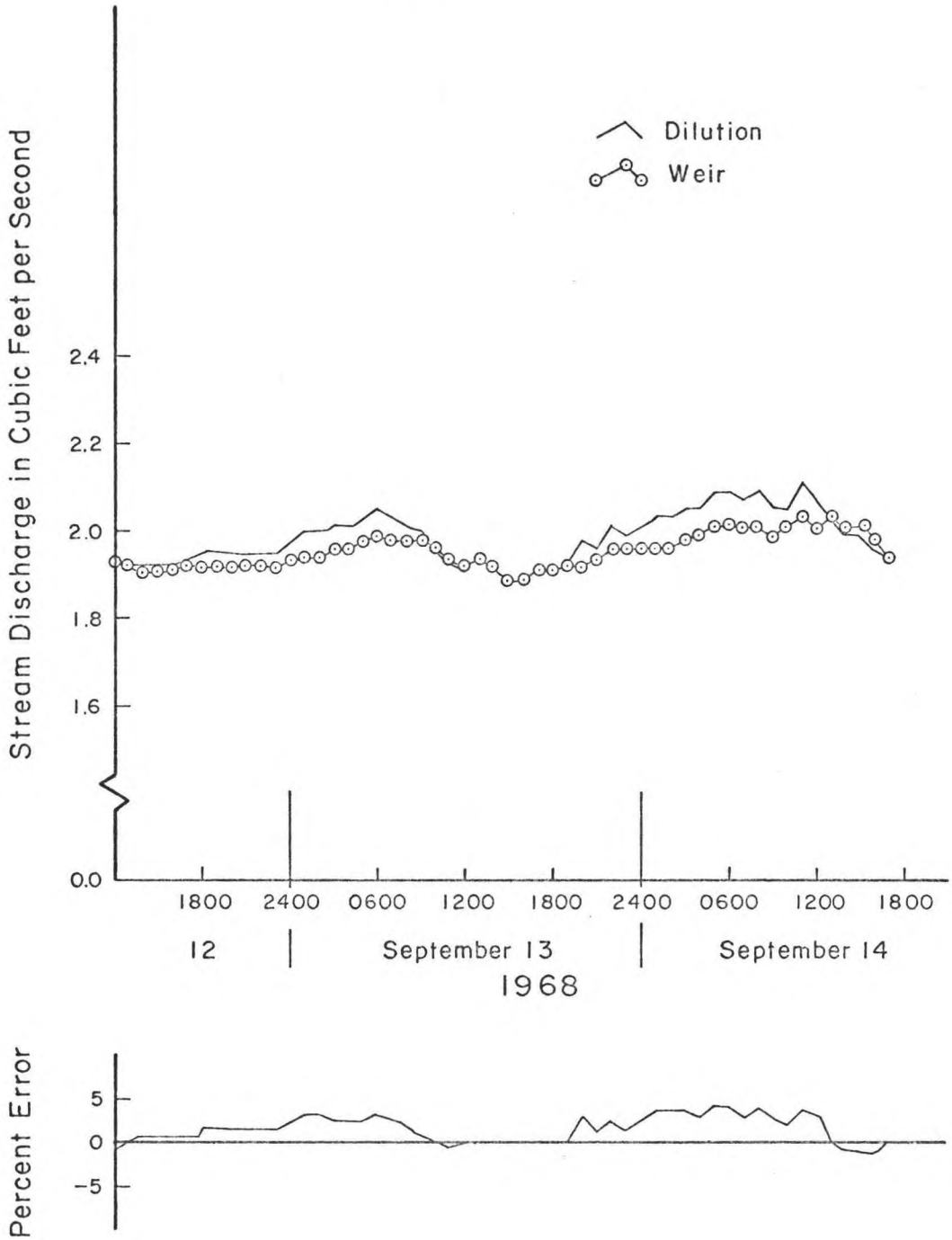


Figure 44. Hydrograph Comparison Peroid 16, East Saint Louis Creek

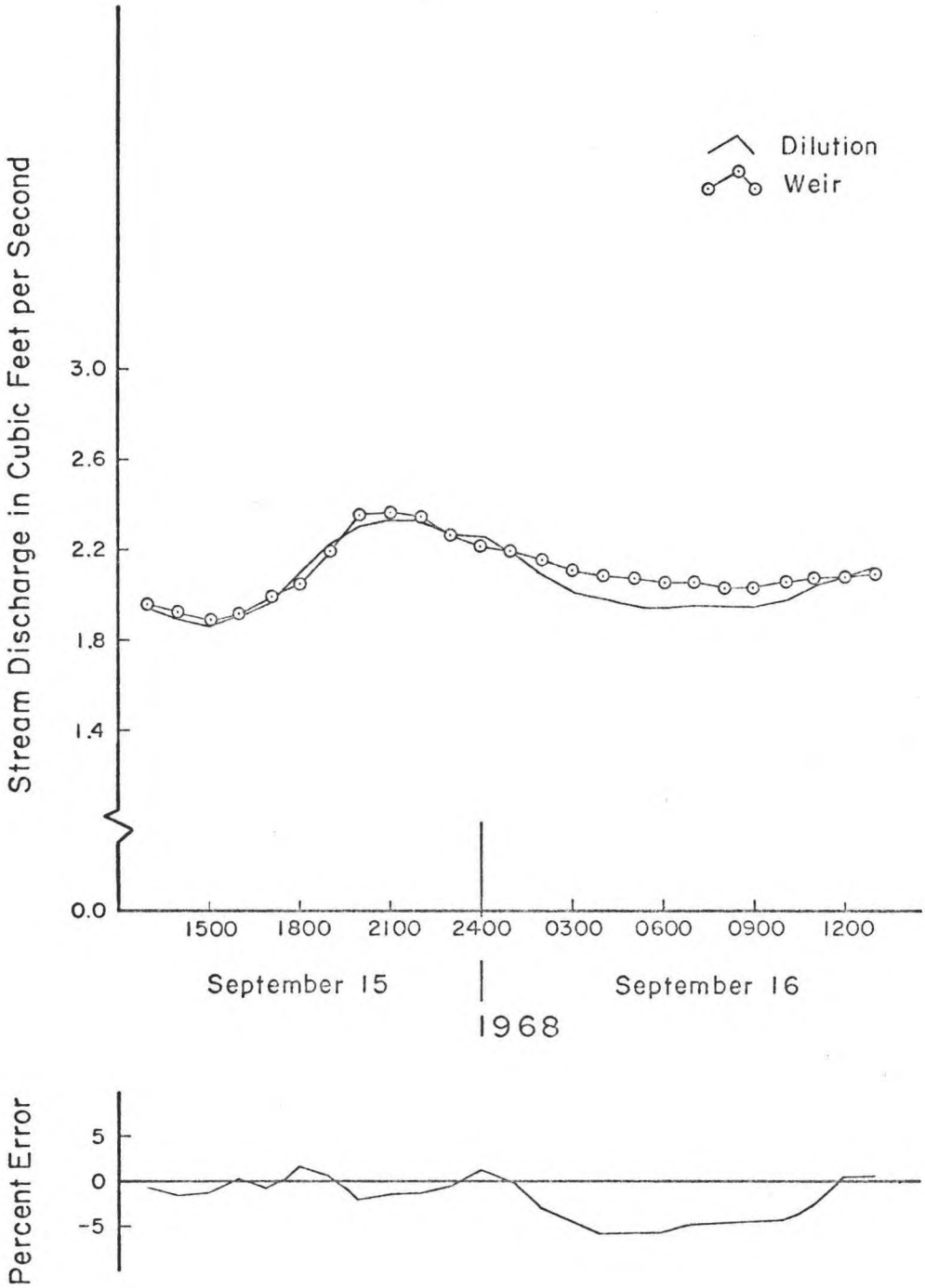


Figure 45. Hydrograph Comparison Peroid 17, East Saint Louis Creek

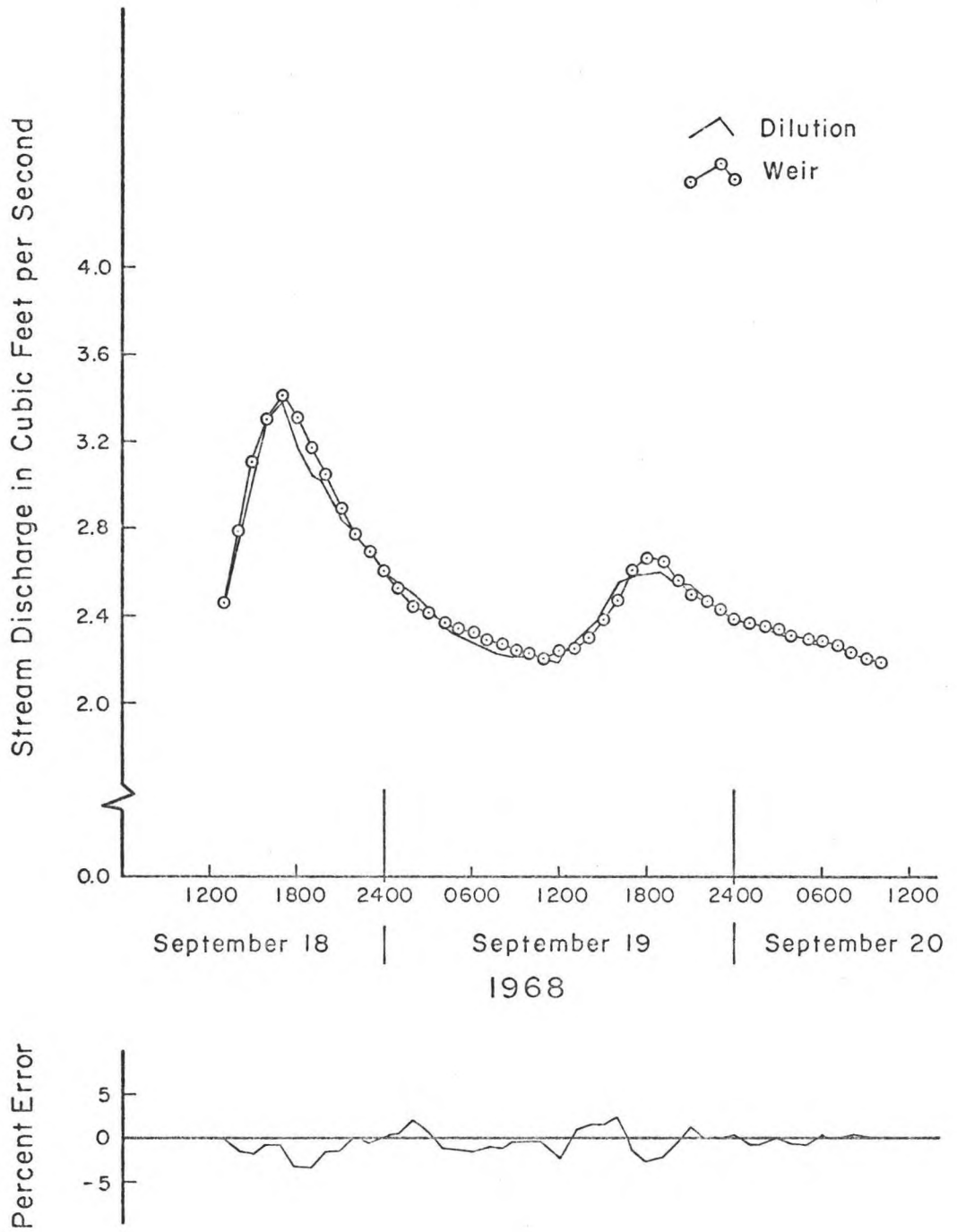


Figure 46. Hydrograph Comparison Period 18, East Saint Louis Creek

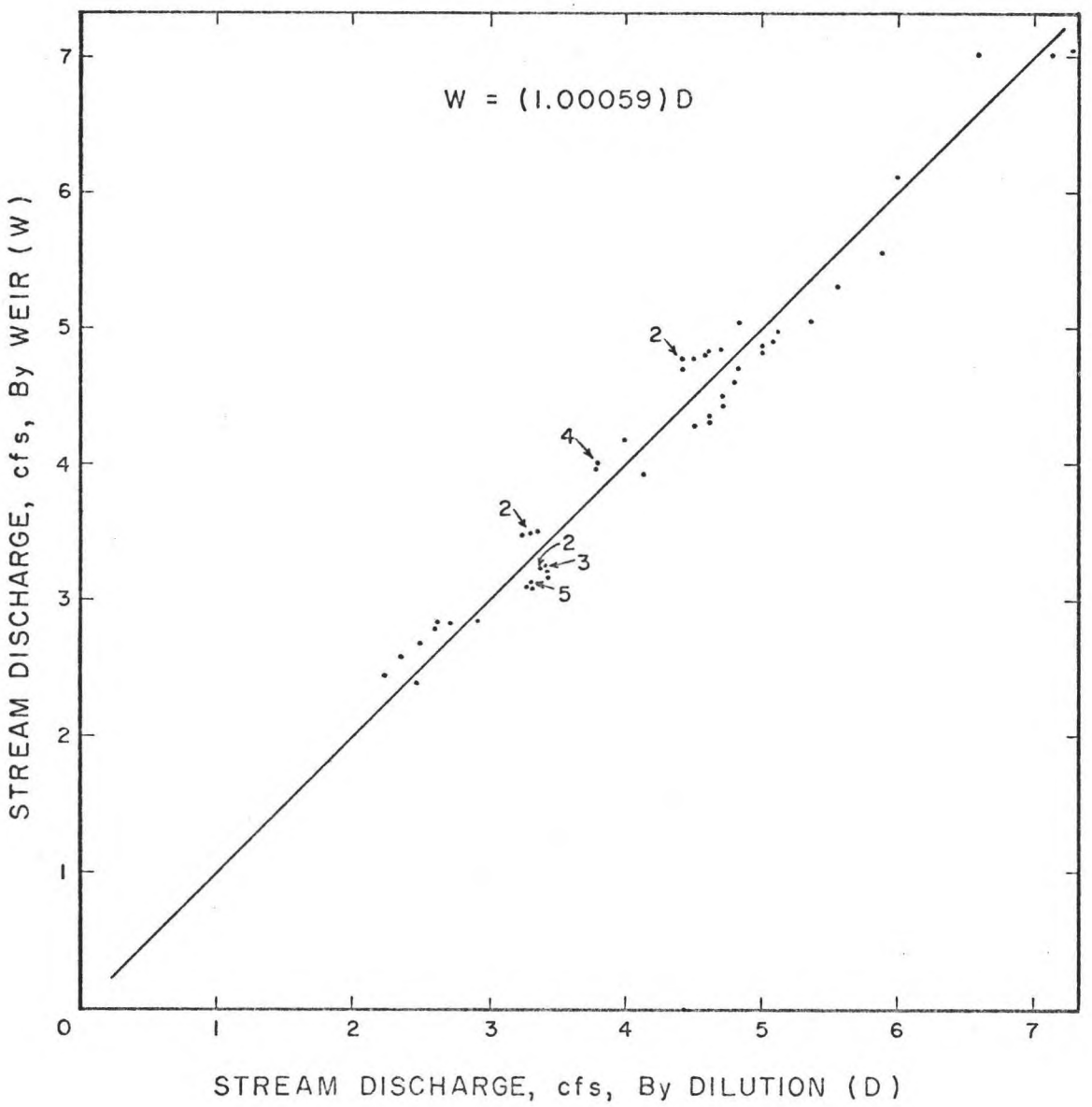


Figure 47. Regression of 916 pairs of stream discharge values recorded by weir and tracer-dilution systems; plotted data points are those that deviate from the model by more than two standard deviations.

Table 8. Summary of hydrograph comparisons, Deadhorse and East Saint Louis Creeks.

| Gaging Period[1/] | Duration | Deviation between tracer-dilution and weir systems | | |
|---|---|---|---|---|
| | | Instantaneous | Averages[2/] | |
| | | Maximum | Absolute | Algebraic |
| | Hours | % | % | % |
| Deadhorse Creek | | | | |
| 1 | 39 | -10.0 | 2.29 | 0.34 |
| East Saint Louis Creek | | | | |
| 2 | 34 | - 2.5 | 0.69 | -0.23 |
| 3 | 60 | 8.2 | 2.66 | 0.78 |
| 4 | 40 | ± 3.5 | 1.76 | -0.24 |
| 5 | 17 | 6.8 | 2.45 | 0.80 |
| 6 | 19 | - 6.0 | 2.31 | -2.10 |
| 7 | 10 | ± 0.5 | 0.19 | 0.01 |
| 8 | 69 | 6.5 | 2.84 | 1.94 |
| 9 | 25 | 4.9 | 2.48 | 1.96 |
| 10 | 27 | ± 2.1 | 1.43 | 1.25 |
| 11 | 23 | - 4.2 | 1.14 | -1.01 |
| 12 | 38 | - 5.4 | 1.93 | -0.78 |
| 13 | 65 | - 8.9 | 1.43 | 0.31 |
| 14 | 14 | 2.8 | 0.86 | 0.48 |
| 15 | 38 | 2.5 | 1.12 | 0.01 |
| 16 | 53 | 4.0 | 1.69 | 1.54 |
| 17 | 24 | - 5.8 | 2.26 | -1.92 |
| 18 | 45 | - 4.4 | 1.09 | -0.61 |
| Grand Average | 640 | | 1.83 | 0.32 |

1/ Identifying data given in Table 7.

2/ Based on deviations at hourly intervals or less.

confidence interval is at a maximum, the estimated weir discharge at the 1% level is 7.0 $\pm$ 0.03 cfs.

## Instantaneous Measurement of Stream Discharge

Instantaneous measurements of streamflow rates using the principle of tracer-dilution are commonly obtained either by the constant-rate-injection method or the total-recovery method.

### Constant-rate-injection method

The constant-rate-injection method is simply a shortened application of the continuous, tracer-dilution gaging technique previously outlined. A tracer-solution of known and uniform concentration is injected at a constant rate into the stream. Injection is continued just long enough for the tracer-concentration downstream, where mixing is complete, to reach an equilibrium dilution.

If a fluorescent rhodamine dye were used as a tracer, the concentration detection system described in this study could facilitate sampling downstream dye concentrations. The detection system might be useful in conjunction with liquid stream sampling. Analysis of the gelatin-registered dye concentrations would serve only to define when a dye-stream equilibrium had been established.

Application of the detection system to measure instantaneous stream discharge by the constant-rate-injection method was automatically

included during the field trials to evaluate the continuous gaging technique. No specific difficulties are envisioned in future applications of the detection system to this method of instantaneous stream gaging.

Total-recovery method, theory and operation

The total-recovery method depends upon the ability to monitor the total tracer cloud as it passes a cross-section of the stream. A measured quantity of tracer is suddenly dumped into the stream (Figure 48). At a point, $S$, downstream, where good mixing is assured, a cross-section, $A$, is chosen where the time-concentration of the tracer will be monitored. Let $dA$ be an incremental area of the cross-section, $A$, through which passes a flow, $dQ$. If $T_A$ is the time of passage of the tracer cloud through area, $dA$, and if $C_2$ is the tracer mass concentration in this area element at any instant, the mass of tracer, $m$, crossing this area, $dA$, during the time, $T_A$, is

$$m = \int_0^{T_A} dQ\, C_2\, dt \quad . \tag{26}$$

If $T$ is the total time required for passage of the tracer-cloud through the cross-section, $A$, the total tracer-mass, $M$, carried through the entire section during time, $T$, is

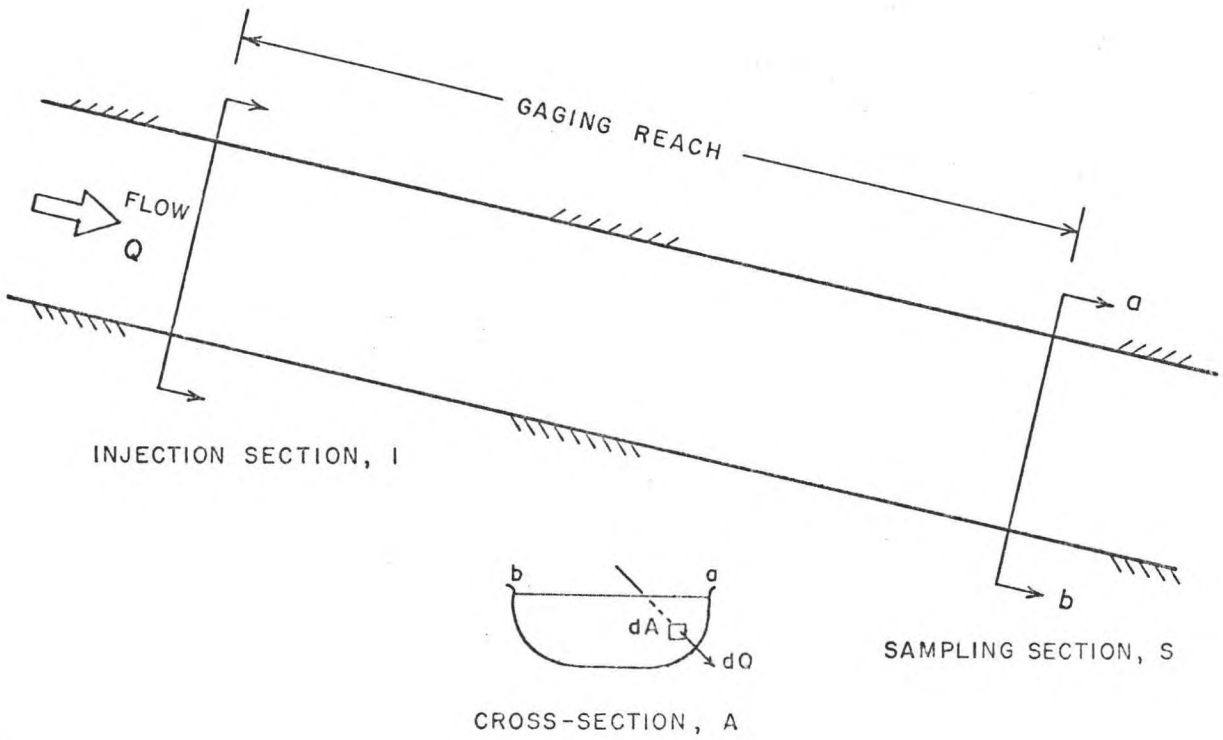


Figure 48. Stream gaging reach for the total-recovery method.

$$M = \int_A \int_o^T dQ\, C_2\, dt \quad , \tag{27}$$

assuming complete mixing of the tracer. If concentration is uniform across $A$, equation (27) can be written

$$M = \int_o^T C_2\, dt \int_A dQ \qquad \text{or}$$

$$M = Q \int_o^T C_2\, dt \quad . \tag{28}$$

The mass of an injected tracer solution is equal to the product of its volume and mass concentration; that is, $M = V\, C_1$. Therefore, according to the conservation of mass

$$M = V\, C_1 = Q \int_o^T C_2\, dt \qquad \text{or}$$

$$Q = \frac{V\, C_1}{\int_o^T C_2\, dt} \quad . \tag{29}$$

The integral in equation (29) represents the area under the time-concentration curve, obtained from the stream at the sampling point, S , (Figure 49).

Four conditions are necessary to validly gage streamflow by this method:

(1) the rate of streamflow must remain constant during the gaging period, T ,

(2) tracer-mass, M , must be conserved between points of injection and sampling,

(3) the background concentration of indigenous, tracer-like substances, if any, must be evaluated, and

(4) tracer concentration must be uniform in the cross-section.

The concentration detection system developed during this study may be used to define the time-concentration curve at the sampling point, S . Changes in the downstream concentration, $C_2$ , of a rhodamine tracer can be continuously registered on gelatin-coated film. Fluorometric analysis of the film produces a time-concentration curve in fluorometric units. Integration of the area under this curve provides the denominator required in equation (29) for discharge determination. Concentration $C_1$ of the injected solution is difficult to obtain by direct film analysis. It is, however, easily derived when liquid samples of $C_1$ and $C_2$ are collected and analyzed. Equation (19),

$$C_{1\ \text{film}} = C_{2\ \text{film}} \frac{C_{1\ \text{liquid}}}{C_{2\ \text{liquid}}} .$$

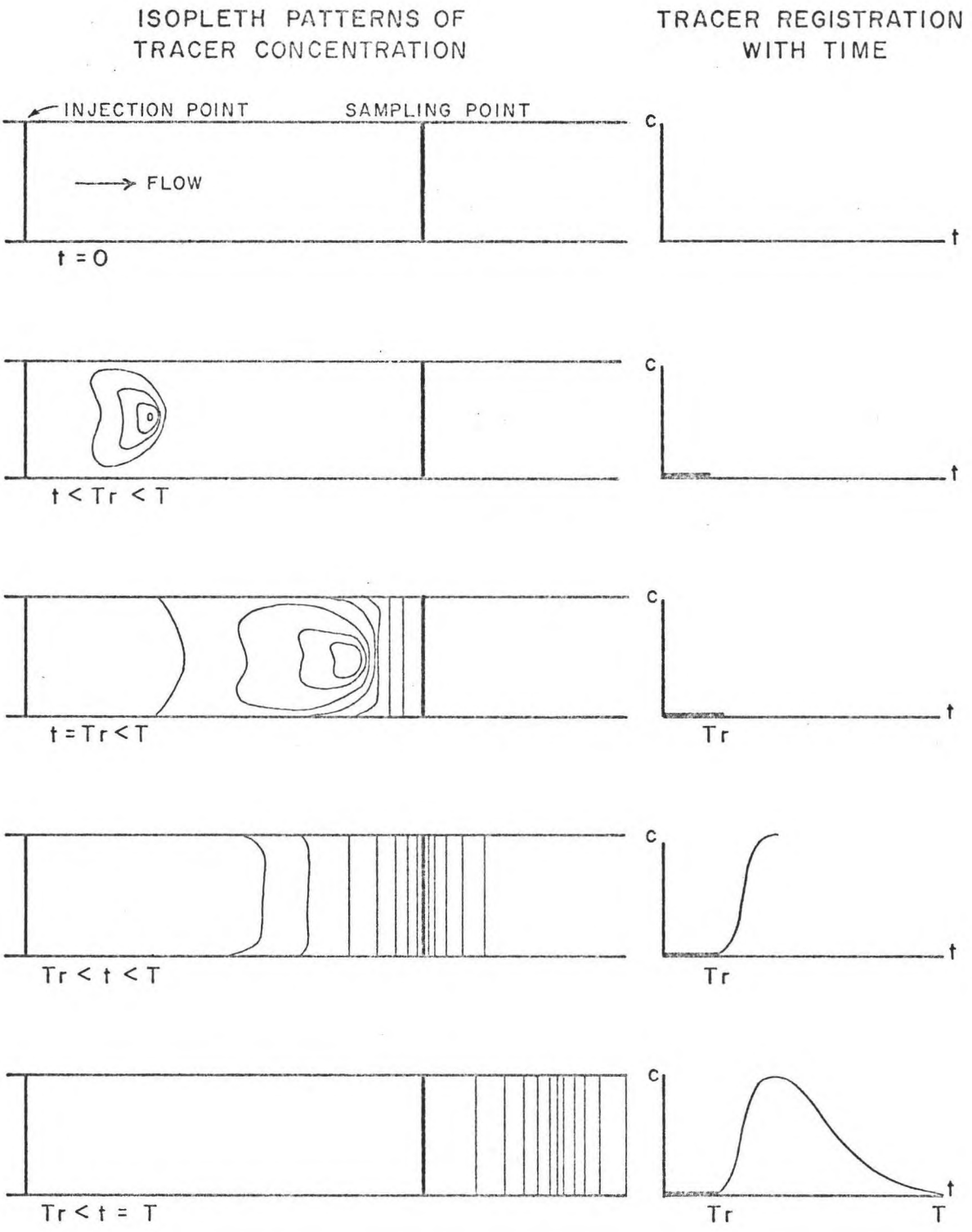


Figure 49. Passage of idealized tracer cloud through a sampling section in a steady, uniform flow and its concentration, c , as a function of time, t ; (Tr = travel time of leading edge of tracer cloud and T = total travel time).

is evaluated to compute a compatible $C_{1\ film}$ which can be substituted for the numerator in equation (29).

Total-recovery method, field trials

Three streams in the Rocky Mountains of Colorado were gaged by the instantaneous tracer-dilution, total-recovery method during the summers of 1968 and 1969. Stream discharge in Deadhorse Creek within the Fraser Experimental Forest was measured twice in 1968, while Hourglass and Little Beaver Creeks were each gaged twice in 1969. The latter two streams are located in the Cache La Poudre River Basin and drain a snow zone of the Front Range in the Rocky Mountains. Segments of these streams are shown in Figures 53, 55 and 56.

Normally, measurements were executed by releasing a massed-quantity of Rhodamine WT dye into the stream and registering its dilution on gelatin-coated film within the detection system. The quantity of dye and the length of the gaging reach were varied with each stream and its estimated discharge. These ranged from 2.0 to 12.0 grams, and 106 to 325 feet, for dye quantities released and gaging reach lengths, respectively. Liquid samples from the dye cloud were also extracted from the stream to facilitate analysis with a compatible $C_1$ concentration.

The above procedure was followed during all measurements except those taken on Deadhorse Creek. Here the procedure deviated only in that the automatic detection system was replaced by a manual technique outlined in Figure 50. A spool of fresh gelatin-coated film was mounted on a wooden stake driven into the left bank of the stream so that film

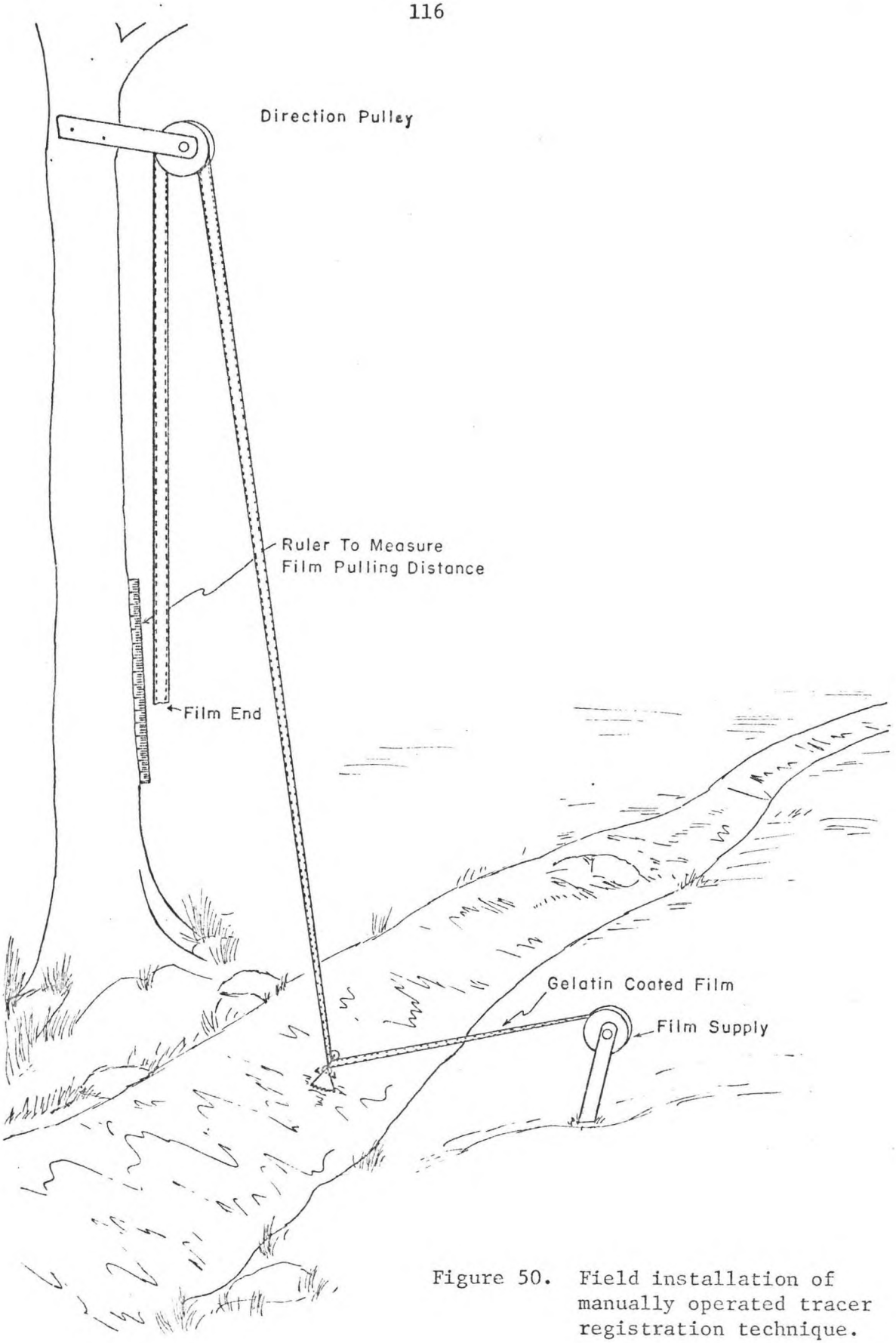


Figure 50. Field installation of manually operated tracer registration technique.

rolled off the spool freely but tautly. This assured a relatively constant tension on that portion of the film extending from the supply spool to a quiet pool of the stream. A small loop of the film was immersed into this pool by a directional pulley secured to the stream bed. From the stream the film extended about 15 feet upward to another pulley attached to a tree on the right bank. From this tree-supported pulley the film hung freely, with its lead end positioned along side of a ruler. During operation, the film was moved by manually pulling the film a discrete distance measured by the stationary ruler, per unit time.

As with the automatic detector, the manually-handled film was initially marked with reference to time. After the dye was dumped into the stream, the film-end was pulled three inches, every five seconds, the length of film immersed in the stream, which resulted in discrete 5-second samples as the cloud passed. The "exposed" film was allowed to air-dry for 30 minutes.

Figure 51 exhibits the equipment used in manual, total-recovery, tracer-dilution gaging on Deadhorse Creek. Itemized, this equipment includes: a one-gallon plastic bucket to dump dye; at least one polyethylene bottle to sample the stream for $C_1$ evaluation; a watch with a second hand; one spool of fresh gelatin-coated film; one empty spool to serve as a pulley; a pre-massed quantity of dye tracer plus a small amount for time marking; the pulley with which to immerse film; knife to cut film; a 30-foot length of string to thread film over

Figure 51. Display of items used to manually measure stream discharge by the total-recovery tracer gaging method.

the tree-supported pulley; a stake and lag screw to support supply spool; and a ruler.

Regardless of the manner in which the gelatin-coated film was exposed to the dosed stream, laboratory procedures necessary to produce a time-concentration curve were similar. As usual the exposed film was fluorometrically analyzed and results recorded on a strip-chart. Integration of the area under the strip-chart curve by planimeter yielded the denominator, $\int_0^T C_2 \, dt$ , of the discharge equation (29). Concentration values, $C_2$ , were integrated in film-based units, $(C_{2\ film})$. Compatible $C_1$ concentrations, $(C_{1\ film})$, were derived using equation (19), and the liquid $C_2$ samples taken during measurement. The lone exception occurred with the measurement of June 29, 1968 on Deadhorse Creek. Liquid samples were unavailable, resulting in the necessity of a film-analyzed $C_1$ concentration. Evaluation of equation (29) resulted in the stream discharges listed in Table 9 together with concurrent weir measurements.

## Measurement of Time-of-Stream-Travel

### Technique description and operation

Buchanan (1964) and Wilson (1967) have discussed the methods and procedures necessary to measure travel times of rivers and streams by a rhodamine tracer. They list four basic steps: (1) the tracer is released into the water, (2) liquid water samples are collected in

Table 9. Instantaneous discharge measurements - total-recovery method, Deadhorse, Hourglass and Little Beaver Creeks.

| Stream and Type of Weir | Date | Discharge Measured by weir cfs | Discharge Measured by dilution cfs | Deviation % |
|---|---|---|---|---|
| Deadhorse (120° V-notch) | | | | |
| | June 29, 1968 | 3.73[a] | 1.78[b] | 50.9 |
| | August 22, 1968 | 0.73[a] | 0.88[b] | 20.6 |
| Hourglass (6-foot Cippoletti) | | | | |
| | July 18, 1969 | 13.9 | 14.2 | 2.1 |
| | July 20, 1969 | 15.3 | 14.9 | - 2.6 |
| Little Beaver (6x10-foot Broad-crested) | | | | |
| | July 22, 1969 | 10.8 | 10.6 | 1.8 |
| | July 23, 1969 | 5.2[c] | 7.9 | 15.2 |

a Weir located 3600 feet downstream of tracer dilution reach.

b Obtained by gelatin-coated film immersed directly in stream.

c Estimated from records by two weirs sited 15,000 feet upstream and 14,400 feet downstream of the tracer dilution reach.

a manner to define either the temporal distribution of the tracer concentration at specific locations or the spatial distribution at specific times, (3) the liquid samples are analyzed in a fluorometer to determine tracer concentrations, and (4) these data are plotted for further analysis.

Both authors suggested using rhodamine B or Rhodamine BA in a 40% acetic acid solution for time-of-travel measurements. Although somewhat sorptive on sediment, these tracer solutions possess a cost and density (specific gravity = 1.03) advantage.

The technique involved in measuring time-of-stream-travels through use of the tracer detection system is simple. Stream-side components of the system are set up at the sampling sites of interest. Then, tracer solutions are released into the stream at desired locations. Downstream at the sampling section the automatic units are prepared to monitor the passing tracer cloud without further attention by the operator. Later, when convenient, the exposed film is brought to the laboratory and fluorometrically analyzed and recorded in the usual manner. A valuable feature of the record is that it is a continuous trace of the time-tracer-concentration curve. This allows accurate and ready description of peak and centroid points on the curve, from which tracer arrival times can be determined.

Field trials

Time-of-travel measurements using the tracer-detection instruments were made on five mountain streams during the summers of 1968 and 1969: East Saint Louis and Deadhorse Creeks in the Fraser Experimental Forest; and Hourglass, Little Beaver and Little South Fork Creeks within the Cache La Poudre River Basin. All are fed by melted snow and exhibit white-watered, tumultuous flows. Figures 52 through 56 show various reaches of the streams.

All measurements of stream travel time followed a basic pattern. Tracer-detection components were placed stream-side and stream lengths of 1000, 2000, 3000, 4000 and 5000 feet were measured upstream of the detection unit. During measurements, a 100-foot steel tape stretched parallel to the stream's edge assured reasonable measurement precision. Distances of two lengthy reaches on Little Beaver Creek were, however, taken from topographic maps (scale 1/24,000) and adjusted by a factor of 1.1. This is a ratio of a measured length of stream to the length of the same reach determined from the map.

During dosing of the stream a small quantity (approximately 2 grams per cubic foot of estimated discharge per second) of Rhodamine WT 20% solution was released at the location and time of interest. Arrival time of the dye-cloud at the sampling site was automatically registered on gelatin-coated film in the shape of a time-concentration curve. Actually, a number of dye-cloud arrivals were registered on a single film strip.

Figure 52. A segment of the time-of-travel reach, East Saint Louis Creek.

Figure 53. A segment of the time-of-travel and total-recovery gaging reach, Deadhorse Creek.

Figure 54. A segment of the time-of-travel reach, Little South Fork of the Cache La Poudre River.

Figure 55. A segment of the time-of-travel and total-recovery gaging reach, Hourglass Creek.

Figure 56. A segment of the time-of-travel and total-recovery gaging reach, Little Beaver Creek.

The exposed film strips were analyzed in a laboratory-based fluorometer by the same techniques previously described. The results were records of time-distributed dye-cloud passage in the stream. The centroid of the area under each time-concentration curve was located with the aid of a planimeter. Passage times of these centroids determined time-of-stream-travels.

Time-of-travels were computed from one of two equations:

$$V_r = \frac{L_r}{t_r} \qquad \text{or} \qquad (30)$$

$$V_r = \frac{L_s - L_c}{t_s - (L_c/V_c)} \quad . \qquad (31)$$

where $V_r$ is the travel speed of the stream according to dye movement through the reach,

$L_r$ is the length of the reach,

$t_r$ is travel time of the dye-cloud through the reach length, $L_r$ ,

$L_s$ is the sum of the reach and conduit lengths,

$t_s$ is the travel time of the dye-cloud through the distance, $L_s$ ,

$L_c$ is the length of the conduit,

$V_c$ is the flow velocity through the conduit, which is volumetrically measured when the equipment is installed.

Equation (30) sufficed when film-registered tracer-events were related to stream events by judicious placement of time marks on the film. This practice excluded the registration of tracer travel time through the detection system sampler with its 130 to 210-foot conduit. For all other time-of-travel measurements equation (31) accounted for sampler influence and provided true travel speeds through the stream reach exclusively.

The total-recovery method of stream discharge measurement inherently included information sufficient for time-of-travel determination, provided the gaging distance was known. This "bonus" was exploited during stream gaging necessary to this study. Lengths of all such gaging reaches were determined with a steel tape and applied in the usual way to compute time-of-stream-travels.

Table 10 contains a summary of all stream travel speeds computed from in-situ measurements obtained with the tracer-detection system described herein.

Table 10. Time-of-stream-travel.

| Stream and Date of Measurement | Stream Discharge cfs | Reach Length feet | Travel Speed ft/sec |
|---|---|---|---|
| East Saint Louis Creek | | | |
| June 17, 1968 | 18.1 | 2075 | 2.2 |
| June 22, 1968 | 22.2 | 2875 | 2.1 |
| | 22.7 | 4875 | 2.0 |
| June 28, 1968 | 22.2 | 875 | 1.8 |
| | 22.3 | 1875 | 1.8 |
| | 22.3 | 2875 | 1.9 |
| | 22.3 | 3875 | 1.8 |
| | 22.2 | 4875 | 1.8 |
| July 6, 1968 | 9.6 | 875 | 1.3 |
| | 9.5 | 1875 | 1.6 |
| | 9.5 | 2875 | 1.5 |
| | 9.4 | 3875 | 1.5 |
| | 9.4 | 4875 | 1.6 |
| July 7, 1968 | 8.9 | 875 | 1.1 |
| | 8.8 | 1875 | 1.2 |
| | 8.8 | 2875 | 1.2 |
| | 8.8 | 3875 | 1.2 |
| | 8.8 | 4875 | 1.2 |
| | 8.9 | 875 | 1.1 |
| | 9.0 | 1875 | 1.2 |
| | 9.0 | 2875 | 1.2 |
| | 9.0 | 3875 | 1.2 |
| | 9.0 | 4875 | 1.3 |
| August 9, 1968 | 4.0 | 875 | 0.71 |
| | 4.1 | 1875 | 0.77 |
| | 4.5 | 2875 | 0.79 |
| | 4.8 | 3875 | 0.86 |
| September 6, 1968 | 2.4 | 875 | 0.54 |
| | 2.4 | 1875 | 0.61 |
| | 2.5 | 2875 | 0.61 |
| | 2.5 | 3875 | 0.62 |
| | 2.6 | 4875 | 0.65 |
| Deadhorse Creek | | | |
| June 29, 1968 | 3.0[a] | 276 | 1.3 |
| August 22, 1968 | 0.8 | 106 | 0.4 |

Table 10. (continued)

| Stream and Date of Measurement | Stream Discharge cfs | Reach Length feet | Travel Speed ft/sec |
|---|---|---|---|
| Little South Fork, Cache La Poudre River | | | |
| June 10, 1969 | 100.0 | 259 | 0.8 |
| | 100.0 | 929 | 1.3 |
| | 100.0 | 2010 | 1.4 |
| June 11, 1969 | 77.3 | 2010 | 1.0 |
| Hourglass Creek | | | |
| June 22, 1969 | 33.5 | 1000 | 1.6 |
| | 33.5 | 2000 | 1.7 |
| | 33.5 | 3000 | 1.7 |
| July 5, 1969 | 23.0 | 1000 | 1.2 |
| | 23.0 | 2000 | 1.3 |
| | 23.0 | 3000 | 1.3 |
| | 23.0 | 4000 | 1.4 |
| | 23.0 | 5000 | 1.4 |
| July 20, 1969 | 15.6 | 312 | 1.2 |
| | 15.6 | 2000 | 1.2 |
| | 15.6 | 3000 | 1.2 |
| | 15.6 | 4000 | 1.2 |
| | 15.6 | 5000 | 1.2 |
| Little Beaver Creek | | | |
| July 22, 1969 | 10.8 | 325 | 1.1 |
| | | 14400 | 0.6 |
| July 23, 1969 | 5.2[a] | 250 | 0.9 |
| | 5.2[a] | 1000 | 1.1 |
| | 5.2[a] | 2000 | 1.1 |
| | 5.2[a] | 3000 | 1.0 |
| | 5.2[a] | 4000 | 1.0 |
| | 5.2[a] | 5000 | 0.9 |
| | | 15000 | 0.6 |
| July 24, 1969 | 4.8[a] | 4000 | 1.0 |
| | 4.8[a] | 5000 | 0.9 |

[a] Estimate

# CHAPTER V

# TRACER INFORMATION FLOW

The tracer detection system described in this report is a means of transferring information from the stream to a time-distributed record. This qualifies the system as a communications operation possessing properties of information flow and theory.

## Tracer Signal

Tracer concentration information flows through components of the detection system in the form of a signal, a signal which contains both information and "noise". The information consists of time-related, stream-borne tracer concentrations passing through the system from the intake to the fluorometric record. Noise, which according to Singh (1966), is a vitiation preventing perfect communication, develops from inherent impedance of information flowing through the system. It is the modulation that a signal undergoes passing from the stream to the output record.

## Communications Channel

Noise reduces the operating efficiency of a communications channel and limits its capacity. The time required to transmit a unique

tracer concentration through a channel plagued with noise is greater than if the channel were noiseless. In other words, noise in the tracer detection system decreases the frequency with which the channel can respond to a single-valued concentration transmission.

The modulating effect of noise can be evaluated theoretically. The channel capacity of any communications system depends upon the limit of the signal power and the way the noise is distributed over it. If, for any signal of power, $S$, with a noise of power, $N$, distributed about it in a normal statistical fashion, the frequency with which a channel can transmit any single bit of information depends on the ratio, $S/N$.

The ratio, $S/N$, is derived from a set of principles beginning with Fourier's theorem. His theorem states that any curve, no matter how complicated, consists of an appropriate number of simple harmonic curves. In other words, frequencies of all component waves must be exact multiples. By this theorem, any curve may be reduced into a finite number of harmonics with a limiting frequency of, say, $W$ cycles per minute.

Before any curve can be transmitted over a channel, it must be reduced to a series of discrete and finite measurements. By choice, these finite units can be made to coincide with Fourier's harmonics. Neiquest's sampling theorem is the vehicle by which discrete harmonics are defined. This theorem assures that any curve extending over any duration, $T$, but band-limited in frequency to $W$ cycles per minute,

can be completely specified if its amplitude, or ordinate, is sampled at intervals of $1/(2W)$ minutes. It therefore follows that a sample at $2W$ points every minute or at $2WT$ distinct points in all during the life span, $T$, of the curve will exactly define the curve.

In this manner, the continuous, tracer concentration curve may be defined. Over a span of $T$ minutes, definition of the curve requires $2WT = n$ discrete concentration values with amplitudes of $C_1$, $C_2$, $C_3$ $\cdots$ $C_n$ spaced $1/(2W)$ minutes apart. In n-dimensional Euclidean space, concentrations, $C_1$, $C_2$, $C_3$, $\cdots$ $C_n$, may be represented by a point, $M$, located by the coordinates, $C_1$, $C_2$, $C_3$, $\cdots$ $C_n$. The distance, $OM$, from the origin to the point, $M$, defines a radius, $r$, which, according to the Pythagorean theorem, can be expressed as $r^2 = C_1^2 + C_2^2 + C_3^2 + \cdots C_n^2$.

If the transmission of information over a channel is analogous to the travel of electrical current in a conductor, the power, $P$, driving the signal is given by

$$P = \frac{1}{2WT} (C_1^2 + C_2^2 + C_3^2 + \cdots + C_n^2) \quad , \tag{32}$$

where by substitution

$$P = \frac{r^2}{2WT} \quad . \tag{33}$$

Within the reference of an n-dimensional sphere with a radius, $r$, where the signal point, $M$, is distance, $OM$, from the origin, the

effect of a noise with power, $N$, is to create a fuzzy sphere of uncertainty of radius, $\sqrt{2TWN}$ about the signal point, $M$. After transmission, the point, $M$, may find itself anywhere within a sphere of radius, $\sqrt{2WTN}$. Now, if signals are restricted to an average signal power, $S$, the set of allowable signal points will be contained within a sphere of radius, $\sqrt{2WT(N + S)}$. The volume ratio of the two spheres, the signal plus noise to the noise alone, is a measure of the number, $m$, of distinguishable units of tracer information that can be transmitted through the system at the same time. The spheres are n-dimensional; therefore, their volumes are proportional to the n'th power of their radii. Hence,

$$m = \left[\frac{\sqrt{2WT(N + S)}}{\sqrt{2WTN}}\right]^n \qquad \text{or}$$

$$m = \left(1 + \frac{S}{N}\right)^{\frac{n}{2}} = \left(1 + \frac{S}{N}\right)^{\frac{2WT}{2}} = \left(1 + \frac{S}{N}\right)^{WT} . \tag{34}$$

In binary code, the informational content of this signal is

$$\log_2 m = \log_2 \left(1 + \frac{S}{N}\right)^{WT} = WT \log_2 \left(1 + \frac{S}{N}\right) \text{ bits.}$$

Channel capacity, $Cp$, which can be described as the maximum rate of transmission of tracer information during time interval, $T$, and reckoned in bits per minute, is

$$Cp = \frac{WT}{T} \log_2 \left(1 + \frac{S}{N}\right) = W \log_2 \left(1 + \frac{S}{N}\right) , \qquad (35)$$

and is known as the Shannon-Hartley law (Singh, 1966).

This law can be used to define the channel capacity of the tracer detection system. To begin with, the band limit, $W$, is assumed to equal 0.5 cycles per minute. During stream gaging trials reported in Chapter IV, the system was found to be accurate within $\pm$ 3%. If this is valid, the $S/N$ ratio for the detection system is about 100/3. Substitution of the above values into equation (35) results in an estimated channel capacity, $Cp$, for the system of 2.5 bits of tracer concentration information per minute.

## Tracer Information Flow Sequence

The diagram in Figure 57 charts the flow sequence of time-distributed, tracer information through the detection system. Each rectangle represents a functional unit capable of altering the information passing through it. In a sense, each unit is a subordinate communications channel complete with channel capacity and signal impedance.

Processes relating to units 1 through 7 of Figure 57 have been discussed in Chapter III. A brief analysis of the remaining units follows:

Film storage, unit 8, over 13 months, apparently does not alter tracer information bound in the gelatin matrix. Evidence is presented in Chapter VI.

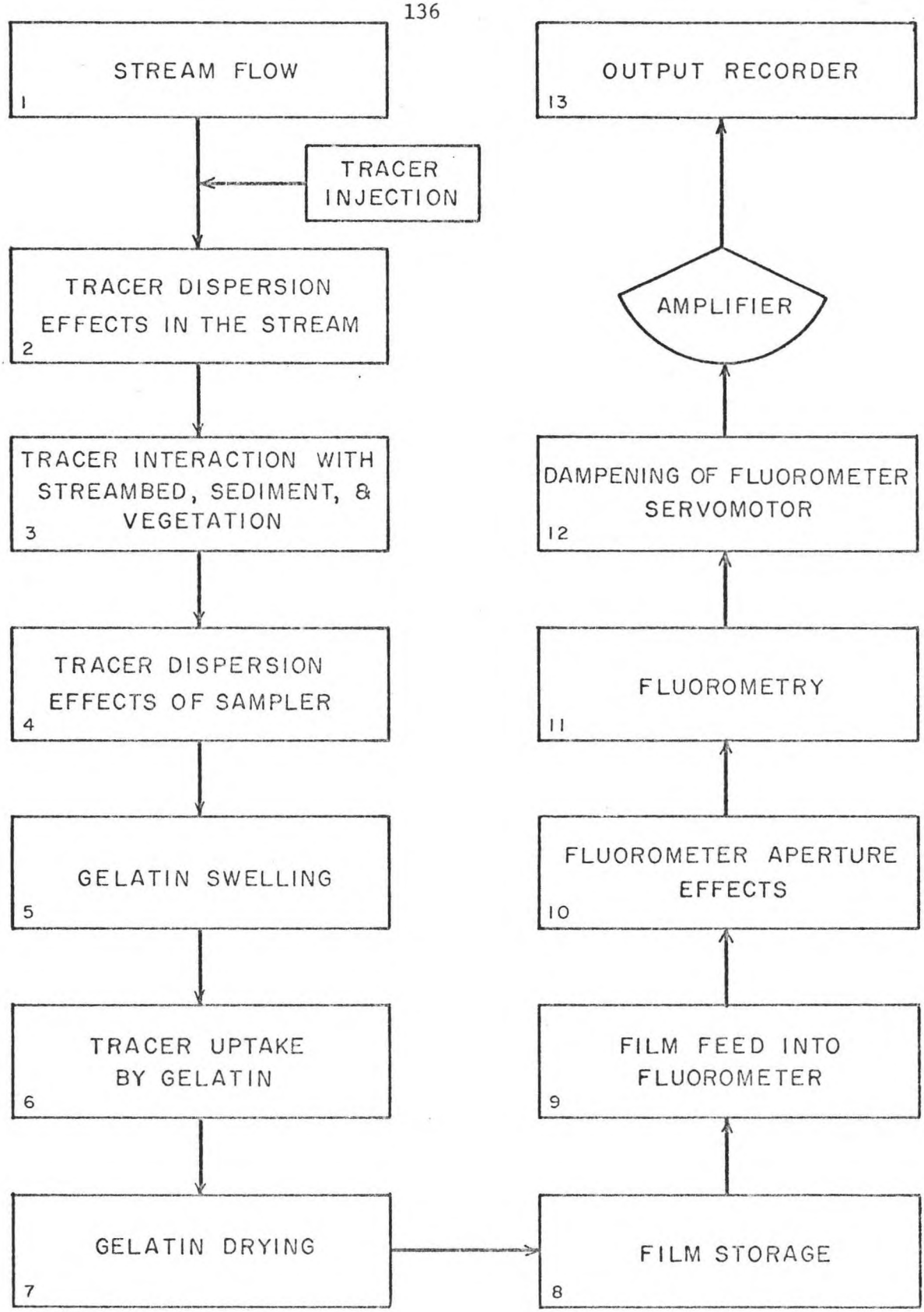


Figure 57. Diagram of information flow through the detection system.

Units 9 and 10, film feed into fluorometer and aperture effects, provide a combined effect on signal modification. Fluorometer aperture refers to a constant-sized opening placed between the source radiation and the moving gelatin-coated film. The aperture confines the scanned area of the film to approximately 3.4 $cm^2$ and excludes the perforation-lined edges of the film. By design, however, only a 1.0-cm length of film is scanned at any given instant. With a film speed of 4.5 inches (11.43 cm) per minute, the time that a given tracer molecule is irradiated amounts to 5.2 seconds.

Fluorometry was discussed previously and is probably a very rapid process. Its modulating effect on signals is probably very minimal.

The output signal from the fluorometer is controlled by activation of the servomotor. Reaction speeds of this motor are regulated by an electronic dampening circuit (Turner and Associates, 1964). Figure 58 is a plot of the reaction time necessary to transmit a square-wave function through the fluorometer. The ordinate is scaled in relative fluorescence standardized by presenting values as ratios based on the maximum fluorescence value. The abscissa is scaled in time units which reflect effects on stream-tracer events registered on gelatin-coated film in the usual manner. Therefore, although dampening effects of the fluorometer occur within seconds, they modulate tracer information registered on film which is time-scaled in minutes. Data for Figure 58 were obtained by passing through the fluorometer a

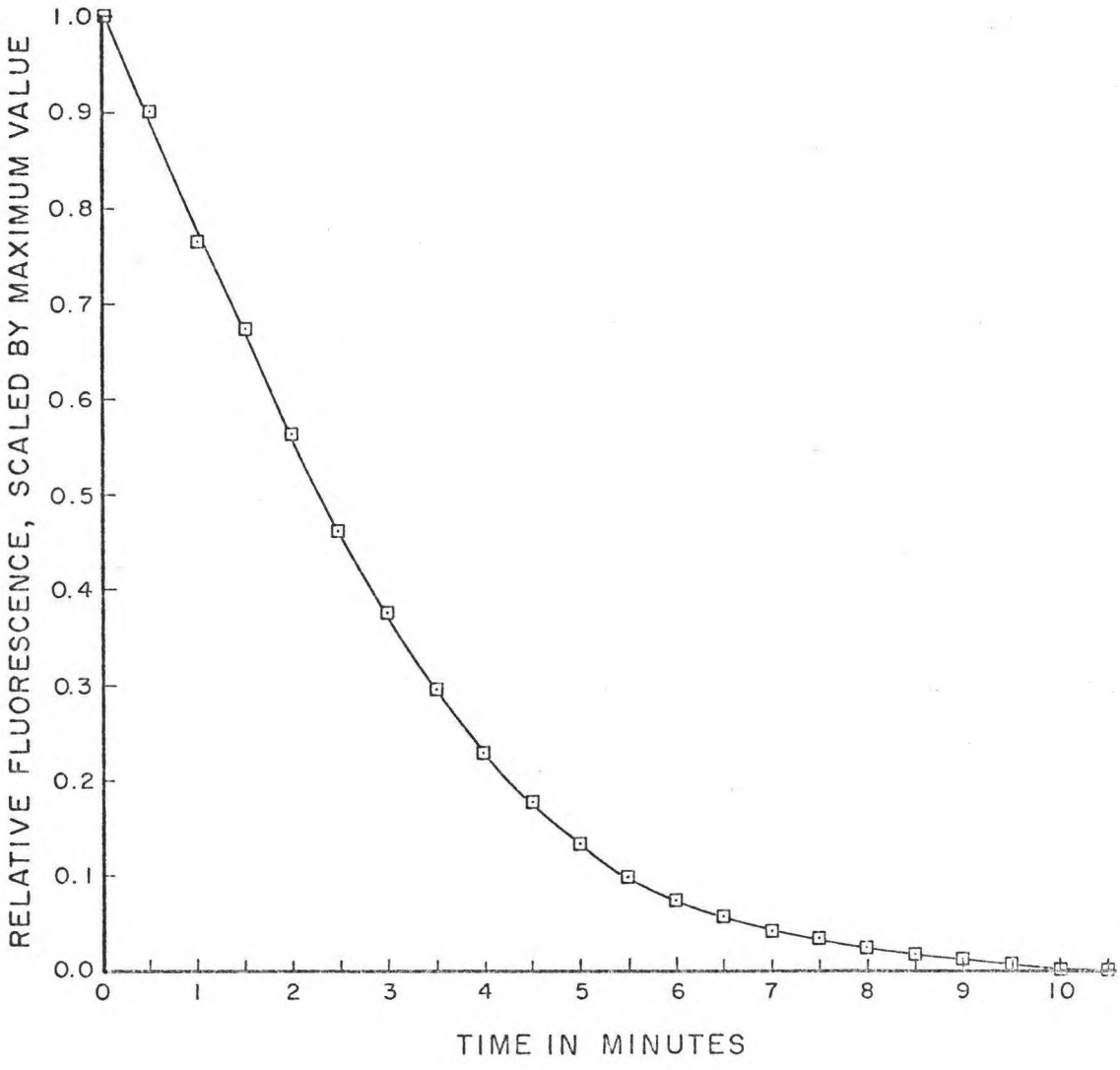


Figure 58. Response curve (recession limb) resulting from a square-wave input to the fluorometer; abscissa scaled in stream event time.

strip of film containing a sudden decrease in the number of tracer molecules registered in its matrix. Consequently, the resulting curve represents the combined modulation of a square-wave signal by the fluorometer and the strip-chart recorder that is, functional units 9 through 13 listed on the flow chart. Apparently, the long tail of the curve was induced by the dampening effect of the fluorometer.

The above conclusion assumes that signal modulations by the fluorometer amplifier and output recorder are minor. Support for this assumption comes from observations of the ink pen movement across the strip-chart. The movement was always rapid and in direct response to fluorescent magnitudes read directly from the fluorometer. It remains to determine the extent that each functional unit affects the flow of tracer information through it.

## Signal Modulation

A tracer concentration signal flowing through components of the detection system undergoes a modulation which diminishes its frequency, increases its wave length, and reduces its amplitude. To determine the extent of signal modification by each component, the time-distribution of a square-wave tracer signal was determined at four points along the informational flow path. The four points and the functional units through which the signal had flowed to arrive at each point are:

| Point | Units that signal flowed through |
|---|---|
| I. Tracer Injector | 0 |
| II. Aliquot Intake | 1, 2, 3 |
| III. Registration Reservoir | 1, 2, 3, 4 |
| IV. Fluorometer Output | 1 through 13 |

The square wave was propagated at the tracer injector by suddenly and completely shunting what had been a steady injection of a Rhodamine WT solution into the stream. Downstream at the intake vessel, liquid samples were taken from the stream at known intervals while the wave passed and subsequently analyzed fluorometrically. Liquid samples were also taken from the registration reservoir located 130 feet from the aliquot intake. The final signal determination was read from the fluorometer output as recorded on a strip-chart. Data from these four monitoring points were plotted in Figure 59 as a function of time and each fitted with a curve. To facilitate comparisons of these curves, relative fluorescences were divided by maximum fluorescent values for each curve, thereby standardizing ordinates.

From data presented in Figure 59, the greatest modulation appears to have occurred between points II and III. Its cause rests with the tracer dispersion effects of the stream sampling component. To verify this conclusion and to make further comparisons, the logarithms of relative fluorescence (tracer concentrations) from all these data were plotted as functions of time in Figure 60. In addition, the square-wave fluorometer response, shown in Figure 58, was plotted

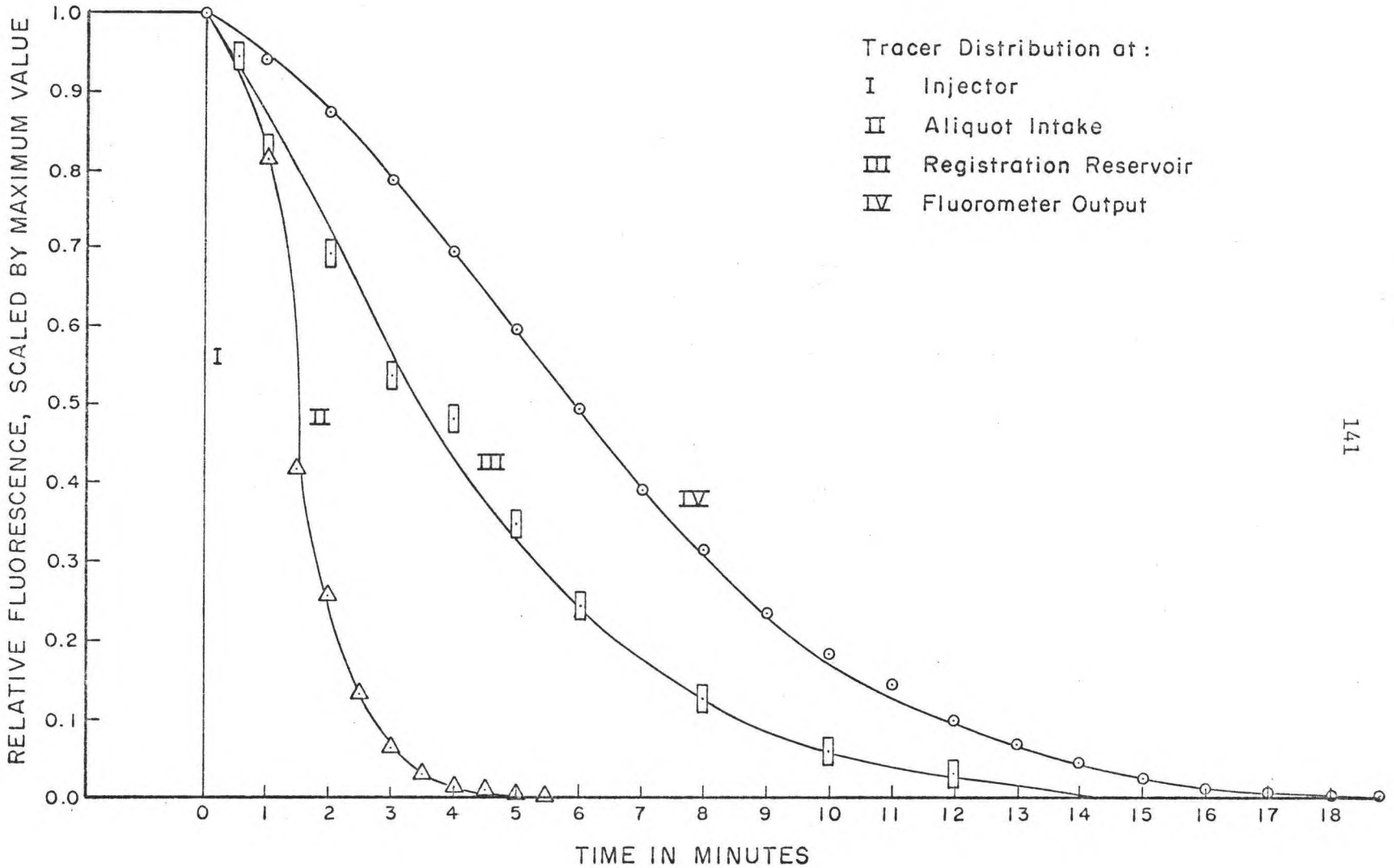


Figure 59. Modulation of a square-wave input passing through the tracer detection system.

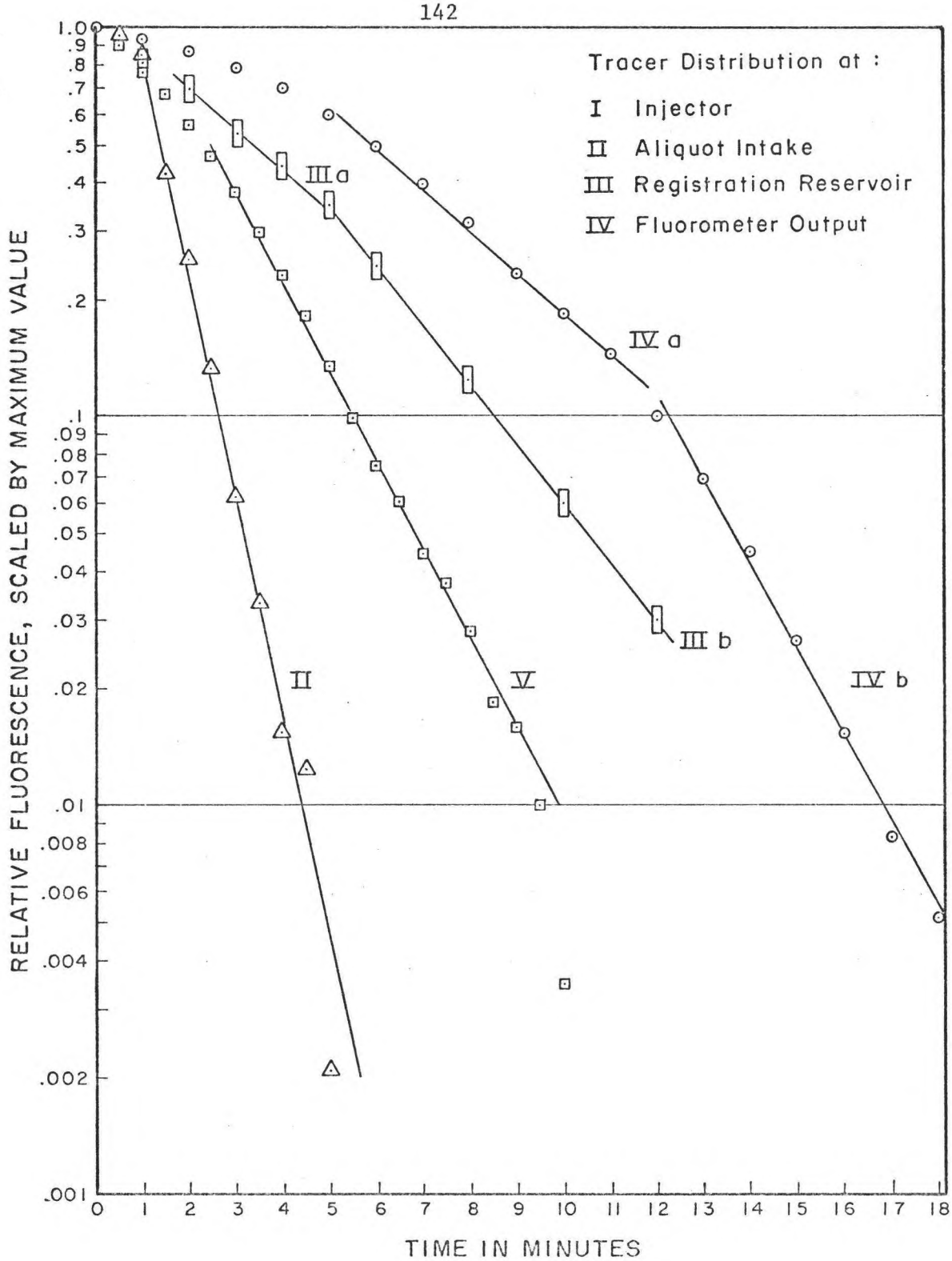


Figure 60. Modulation in semi-logarithmic form of a square-wave input passing through the tracer detection system.

(curve V) in semi-logarithmic form. The comparative slopes of curves fitted to these data were determined. For curves and curve segments, slopes are -0.563 for II; -0.230 for V; -0.104 for IIIa; -0.152 for IIIb; -0.107 for IVa; and -0.219 for IVb, respectively. The strength of these slopes indicates the degree of modulation the signal had undergone up to that point -- the less the slope, the greater the modulation. These slope data support the contention that signal modulation is most pronounced through the aliquot sampling component.

Curves III and IV each possess a flexure point separating legs a and b. No explanation is set forth for the flexure in curve III. However, the flexure in curve IV occurs at about the 11-minute value. From here, curve IV follows a slope, -0.219, approximately equal to the slope, -0.230, of curve V, which represents the signal modulation through the fluorometer alone. Perhaps the change to a steeper slope in curve IV at the 11-minute mark occurred because the functional units between points III and IV only minutely modulated the tail of the signal. Consequently, when at this time, the fluorometer suddenly sensed a reduced tracer concentration, the only limiting modulation of the signal resulted from the dampening circuit of the fluorometer.

Equations of the curves shown in Figure 60 were determined and are of the form

$$F = A\, e^{-t/j} \quad , \qquad (36)$$

where F denotes relative fluorescence, e the base of the natural logarithm, A and j two constants, and t time duration in minutes. For the curves, the A constants were: 3.00 for II; 1.83 for V; 1.98 for IIIb; 2.09 for IVa; and 48.7 for IVb, while the j constants were: -0.77 for II; -1.89 for V; -2.85 for IIIb; -4.05 for IVa; and -1.98 for IVb, respectively. The addition and subtraction of these equations would yield empirically-derived functional relationships for the extent of signal modification ascribable to information flow routes between points I and II, II and III, III and IV for the case of a square-wave input. They would not describe functions for the general case and, therefore, they were not determined.

# CHAPTER VI

## PRECISION

Precision associated with the tracer detection system varies with conditions of the instruments, length of record, strength of the tracer to be detected, climatic fluctuation, character of the stream, etc. Consequently, precision inherent to the system is difficult to entirely evaluate. However, based on the system's performance in laboratory tests and in application on mountain streams, some judgement of its overall precision can be expressed. With all components functioning properly, expected precision of the system under normal field application will range within $\pm$ 5%.

Precision specific to this system is manifested in two dimensions. During operation, the system measures the relative concentration of the fluorescent tracer flowing in a stream and the specific time the event occurred. Laboratory test results shown in Figure 19, indicate the capability of the system to measure with good precision relative tracer concentration without regard to time. Field operation adds the dimension of time and an increased potential for mechanical failure. As previously described, the difficulty in measuring the occurence time of a tracer event with any precision stems from modulation of tracer signals as the information flows through the system. The extent of this modulation depends on the degree of change in tracer

concentration. Large changes in concentration cause the most distortion with a concomitant decrease in precision.

The factors affecting precision of the system are numerous. For convenience they are outlined below with respect to the dimension they affect most; the concentration, the timing, or both.

## Factors Affecting Concentration

### Tracer diffusion and dispersion

Diffusion and dispersion of the tracer cloud as it moves through the system tend to lower its peak concentration and amplify its subordinate values. For a given stream-side installation this modification of peak and trough concentrations turned out to be constant and relatively minor during field trials.

In the stream the processes of diffusion and dispersion cause the mixing of tracer with water which is so desirable in stream gaging. The extent of tracer mixing was occasionally checked during periods of continuous gaging. Samples of tracer concentration from stream sections below mixing reaches typically indicated lateral mixing to be at least 97% complete.

### Flow rate of the stream aliquot

At the sampling section a small aliquot of the stream is diverted through an intake, a hose conduit, and a constant-head tank. Then,

the sample flow is divided to give a smaller aliquot. It is this second aliquot which flows through the registration reservoir and contacts the immersed gelatin-coated film. The flow rate of this second aliquot must be completely stablized to insure adequate precision in tracer registration.

The effect of a decreasing flow rate for the registration aliquot was tested during field operations in 1968. The flow rate over 19 hours decreased gradually from 0.58 to 0.30 liters per minute, a 48% deviation. The resulting tracer record showed a gradual reduction of 36%. Additional checks of the same phenomenon indicated a similar relation:

| Change in Aliquot Flow Rate | Change in Tracer Registration |
|---|---|
| 16% | 6% |
| 30 | 14 |
| 45 | 18 |
| 21 | 26 |

Except for the last check, the registration effect of changing flow rates is less than one to one.

Furthermore, the change in effect appeared to diminish as the actual flow rate increased. Comparisons at flow rates of 0.2, 0.6, 1.0, 1.2 and 1.6 liters per minute showed that magnitudes of tracer registration were constant at flow rates greater than 1.0 liter per min, but decreased with rates below that amount. Liquid samples of the aliquot were obtained at the entrance and exit of the registration

reservoir at the same time as above flow rate data were taken. Under the low flow rates of 0.2 and 0.6 liters per min, tracer concentrations in the aliquot leaving the reservoir were less than those entering. These differences were probably related to the uptake of tracer by the gelatin-coated film. Although these differences were not drastic, they might infer a significant effect on tracer uptake.

Reducing flow rates through the reservoir also reduces turbulence, which lowers the tracer concentration gradient, $dc/dx$, adjacent to gelatin surfaces. This limits the amount of tracer uptake, because uptake is directly proportional to $dc/dx$.

Another possible cause for the depression of tracer registration with less aliquot flow involves the storage potential of the reservoir. Despite a large outlet, the quantity of liquid impounded in the reservoir increases with an increase in flow rate. The increased storage raises the liquid level in the reservoir, flooding a greater length of immersed gelatin-coated film, extending contact time between tracer solution and the film, and augmenting the opportunity for tracer sorption.

To evaluate this storage effect, aliquot flow rates were varied from 0.7 to 2.5 liters per min and the resulting film immersion length measured. This effort suggested that a 300% increase in flow rate caused only a 5.5% increase in film-tracer contact time.

Film exposure

The uptake of Rhodamine WT by a gelatin-coated film follows an exponential function of contact time. This was observed in all tests of this phenomenon including those whose results are exhibited in Figure 21. In another test the removal of tracer solutes from aqueous solutions by the film proceeded such that little took place beyond 60 minutes and 60% of the 60-minute quantity was accomplished in 19 minutes. On this evidence a 19-minute interval was chosen as a nominal exposure time during field gaging trials.

Film type

Of the two types of gelatin-coated films that were tried during development of the detection system, the double-coated film proved inferior to the single-coated variety. The latter film was less susceptible to contamination and more adaptable to carriage through the fluorometer.

Two advantages to fluorometry are associated with single-coated film. The first is mechanical. The routing, pulling, and spooling of the film to pass it over the sensing area of the fluorometer is facilitated by a single gelatin coat. The second is fluorometric and was discovered by comparing the background fluorescence of the two types of film as each of their two surfaces were scanned. Background fluorescence includes gelatin fluorescence and surface reflectance of source radiation. Relative fluorescence values between these surfaces amounted to: 26.0 for double-coated film, thick gelatin

side oriented toward radiation source; 23.5 for double-coated, thin side toward radiation source; 22.5 for single-coated, gelatin side toward radiation source; 19.5 for single-coated, support side toward radiation source. This latter fluorometric arrangement was followed, thereby taking advantage of reduced fluorescence background.

Perhaps the greatest advantage of the single-coated film is exhibited when applied to streamflows carrying sediment. During stream gaging on East Saint Louis Creek two summer rain events of about the same magnitude caused flows each of which suspended about 200 parts per million (ppm) sediment. Each flow event was monitored by a different film type. Sediment particles adhered to the double-coated film, causing erroneous fluorometric readings. The single-coated film remained free of sediment and registered fluorescence values with no apparent error.

The different behavior of each film when subjected to sediment stemmed from the presence or absence of the second gelatin layer and the method of film immersion. In both cases the immersed loop of film was placed in the liquid reservoir so that the thick gelatin layer faced downward. Thus, the upper film surface consisted in one case of a sticky, swelling surface of gelatin and a smooth, polyethylene surface in the other case. Sediment adhered to the double-coated film, but was shed from the single-coated variety.

Spatial variation in the thickness of either the gelatin layer or its support may influence the precision of tracer concentration

detection. If the quantity of gelatin varies along the length of film, the variation will be reflected in the tracer registration and output record. The result is a loss in measurement sensitivity. Fortunately, this error source is minor. The manufacturer[1/] of the film reported the average production tolerance for each spool of the product to be within ± 1.0% for the support film thickness and ± 0.3% for the 0.8-mil gelatin layer.

Stream sediment

Suspended sediment in streams presents no greater problems to tracer detection by this system than by analysis of liquid samples. The film-based detection system was tested for its reaction to a known quantity of suspended sediment in the stream. A 12 ppb Rhodamine WT solution, containing 2600 ppm of sediment consisting of 76% clay, 19% silt, and 5% fine sand, was maintained in the constant-head tank for two hours. On routing this agitated mix through the tracer registration device installed on East Saint Louis Creek, the quantity of tracer taken up was only 2.5% less than from a comparable solution free of suspended sediment. Single-coated film was used exclusively. Replogle et al. (1966) tested the sorptive potential of similar sediment for the same tracer. Using a tracer strength of 10 ppb, a suspended sediment concentration of 1000 ppm and measuring the fluorescence of liquid samples, they found a 6% tracer loss by sorption.

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1/ Personal Communication with E. G. Tirk of Eastman Kodak Company, Rochester, New York.

Dissolved solids and pH

In general, the effect of solids dissolved in the stream on tracer uptake by gelatin is of concern because of the wide range of natural salinities encountered in streamflow. No tests were conducted to determine this effect, because the streams of immediate concern contain few dissolved solids.

Existence of high purity was verified in other studies. During the summer of 1965, Stottlemyer and Ralston (1967) monitored ion contents of streams in the Fraser Experimental Forest. They measured average cation concentrations for Deadhorse and East Louis Creeks of 15 and 5 ppm, respectively. In the Cache La Poudre River Basin dissolved solids concentrations of streams were measured in 1964 and 1965 by Kunkle and Meiman (1967). They recorded mean July values of: 50 ppm for the Little South Fork; 40 ppm for Hourglass Creek; and 70 ppm for Little Beaver Creek.

Changes in stream-borne hydrogen ion concentration expressed as pH, can cause error by inducing differential swelling of the gelatin (Chapter III) and by altering fluorescent properties of the tracer. The effect of differential swelling is potentially major only in those cases where the tracer solution remains in contact with the film for very short periods, such as in time-of-travel measurements.

The effect of pH on the tracer, Rhodamine WT, was studied by Siverts. He concluded that within the pH range of 5.5 to 11 no effect need be expected.

A pH of 8.2 for both Deadhorse and East Saint Louis Creeks was obtained with a Beckman pH meter in September of 1969. Kunkle and Meiman (1967) reported 1965 pH measurements of a similar magnitude for the Little South Fork, Hourglass and Little Beaver Creeks.

Stream temperature

The effects of stream temperature on tracer uptake by gelatin-coated film proved to be difficult to evaluate. Initial tests in 1967 with a tracer registration device under a cold-room environment indicated that neither stream nor air temperatures affected uptake. During these tests, temperature effects may have been masked by the small but steady loss of tracer from its solution onto the gelatin-coated film. The test period covered three days during which time the same tracer solution was continuously circulated through the registration device losing tracer molecules at each pass, and thereby gradually becoming a weaker solution.

Even field testing of the detection system failed to suggest that any tracer uptake variation was caused by temperature changes. This may have been because weekly temperature fluctuations of all test streams were small. Spot thermometer readings from all test streams coupled with automatic thermographs on Hourglass and Little Beaver Creeks indicated an average weekly range of about 3°C.

Temperature effects on tracer uptake were again investigated during the sorption test of October 1969. Here gelatin strips were immersed in a 4-ppb Rhodamine WT solution at selected temperatures.

Although not pronounced, the results suggested a positive relation between solution temperature and tracer uptake; that is, uptake increased slightly with increasing temperatures.

The most recent temperature test was initiated in March 1970 and was conducted under more controlled conditions. A tracer solution at various temperatures was routed through the tracer registration device. Exposed film strips were analyzed in a temperature-stabilized fluorometer. The results, previously graphed in Figure 20, support the premise that stream temperature indeed affects tracer uptake by the film. Furthermore, the relation is inverse; a one degree Celsius increase in temperature caused a 1.9% reduction in tracer uptake.

Given the somewhat conflicting evidence on temperature effects gathered during this research, one cannot definitely report that tracer uptake by the gelatin layer follows an inverse function of solution temperature. However, such a conclusion would support the adsorption theory of solute uptake by gelatin presented in Chapter III.

The effects of stream temperature outlined above are detrimental only when the system is applied to continuous stream gaging. Even here the problem is not overwhelming, for if an inverse relation between stream temperature and tracer uptake is accepted, two ameliorations are possible. Recorded stream temperatures and a laboratory-determined correction coefficient can be used to adjust the uptake record, or the length of the unit period of record may be reduced.

Film drying

Drying of the gelatin-coated film causes moisture gradients along its surface. No evidence of tracer migration induced by this gradient was found during this study. Apparently, once sorbed on gelatin substrates, tracer molecules do not migrate within the liquid phase of the gelatin gel.

Film storage

Film storage effects on tracer detection could originate either before or after film contact with the tracer solution. According to the film's manufacturer, pre-tracer storage should not be deleterious. They claim that their product remains useful after indefinate periods of dry storage (Eastman Kodak Co., 1966). During this study the film was stored in a cool, dry facility until needed.

After immersion in a tracer solution followed by drying, the film can go into storage for later scrutiny. Although immediate analysis was the rule during this research, one film strip from gaging trials on East Saint Louis Creek, which had been exposed to Rhodamine WT concentrations approaching 7 ppb, was stored one month in a refrigerator maintained at 5 to 10°C before analysis. The stream hydrograph produced from this film strip deviated from the weir-based hydrograph by 2.3%. This deviation is comparable to the average absolute deviation of 1.8% obtained from hydrograph comparisons from the entire 640 hours of film strip record compiled in Table 8. Normally, "exposed" film strips were analyzed within a few days of removal from stream sites.

Thirteen months later this same film strip was again fluorometrically analyzed. Comparisons of tracer registration recorded before and after 13 months of storage are shown in Figure 61. Absolute concentrations in the after-storage trace are much lower than those recorded 13 months earlier. However, the shape of both curves are similar and can be made congruent by a 30% magnification of the after-storage record. The congruency of this adjusted after-storage trace with the before-storage track is exhibited in Figure 61. Deviations between these traces are 4.4% for the maximum, 1.8% for the average absolute, and +0.9% for the average algebraic. These two records could not be expected to coincide exactly, for each film analysis is subject to varying influences. These include mechanical erosion of the gelatin surface while it is moving in the fluorometer, temperature variations of the fluorometer and film sample, and minute distortions of the gelatin surface which causes variability in the reflectance of source radiation off of the film surface.

The investigations described above lead to the conclusion that tracer concentration information can be stored on gelatin-coated film for months, but at the loss of record resolution. Records from stored film can still be calibrated by the techniques described in Chapter IV.

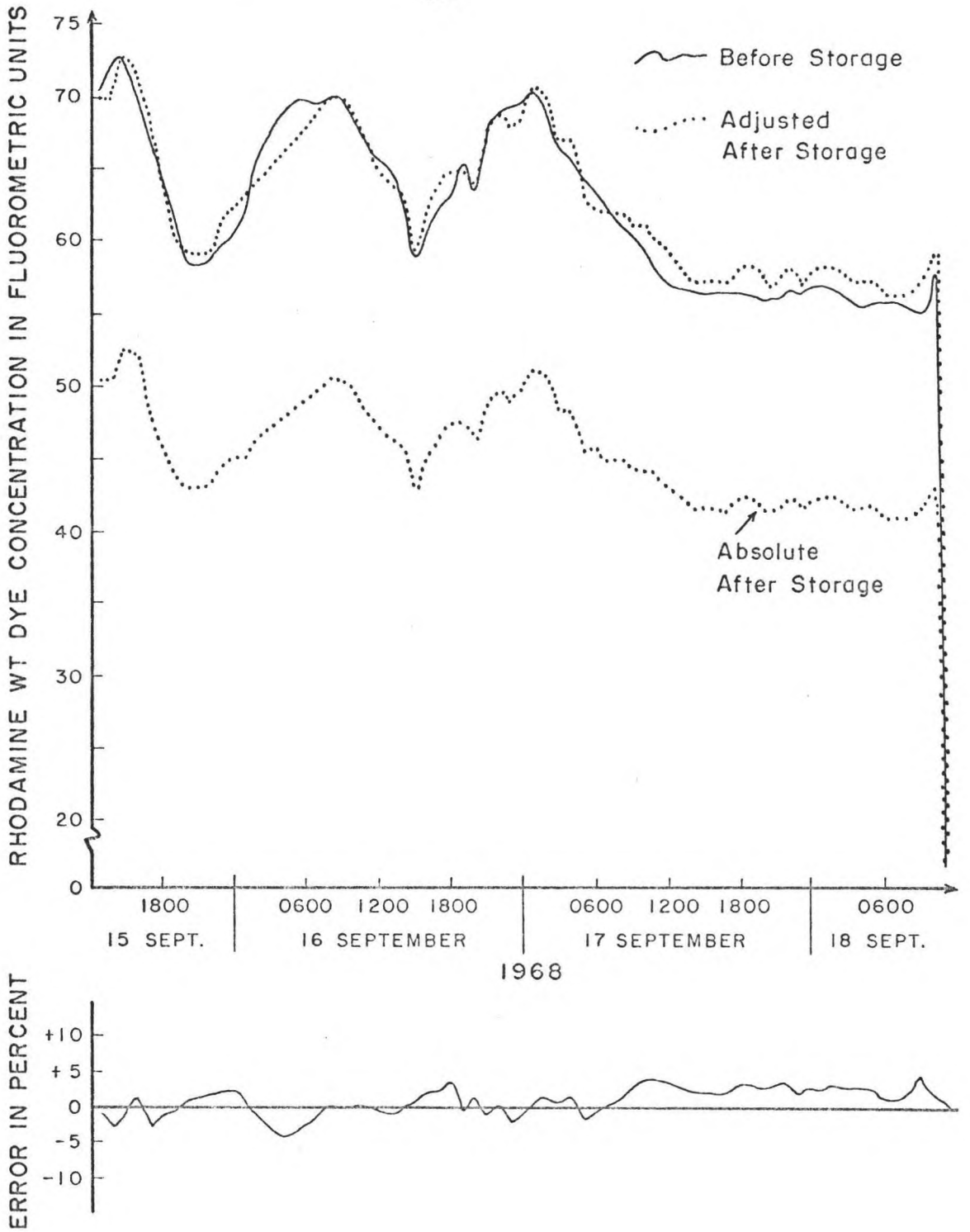


Figure 61. Comparison of tracer concentration on gelatin-coated film before and after 13 months storage.

Fluorometer temperature

The effect of sample temperature on fluorescence of a liquid rhodamine solution is well known and has been reported by Cobb and Bailey (1965), Dunn and Vaupel (1965), Butts (1969), and others. The effect is apparently similar for Rhodamine WT contained within gelatin. That is, lowering sample temperature tends to amplify fluorescence. This fact was advantageously exploited by providing a water cooling system for the reflective surface with which the film is in contact during analysis. Not only was temperature stablized by this addition, but fluorescence was magnified by about 35%. Care was taken not to lower sample temperatures below the dew point during analyses, and thereby cause vapor condensation. A small supply of desiccant was kept in the fluorometer chamber to further insure against condensation.

The effect of fluorometer chamber temperature on the tracer record was investigated. Dunn and Vaupel (1965) reported that fluorescence increased proportionally with chamber temperature, but they gave no explanation. They placed liquid samples at room temperature in the fluorometer chamber and observed fluorescence as sample temperature approached equilibrium with chamber temperature. In this study a gelatin-coated film strip was kept stationary in the fluorometer while ambient temperatures of the room were varied and recorded. At the same time chamber temperatures were measured by a copper-constantan thermocouple and automatically recorded. These data, along with concurrent sample fluorescence were collected over a three-hour period.

Figure 62 presents the experimental relation between fluorescence and chamber temperature. Obviously, the relationship is not simple. The small figures adjacent to certain data points refer to the measured ambient temperature at that time. As the upper arrow indicates, ambient temperatures were first decreased from 44 to 11°C. Chamber temperature, though lagging, followed suit. But, contrary to the findings of Dunn and Vaupel, fluorescence increased. When the trend of ambient temperature reversed, rising from 11 to 44°C, chamber temperature again did likewise and fluorescence decreased, but with a strength different than in the rising limb. The result was the hysteresis of Figure 62.

Explanation for the above temperature phenomenon rests on the relationships depicted in Figure 63. Here, chamber temperatures during the three-hour experiment are plotted as a function of ambient temperatures. Again, hysteresis is evident. The equations describing the major segments of both the increasing and decreasing legs are of the form,

$$T_{ch} = B + m\,T_{ab} \quad , \qquad (37)$$

where $T_{ch}$ and $T_{ab}$ are chamber and ambient temperatures, respectively; the slope, $m$, equals 1.0 and the constant, $B$, is negative on the increasing leg and positive on the decreasing leg.

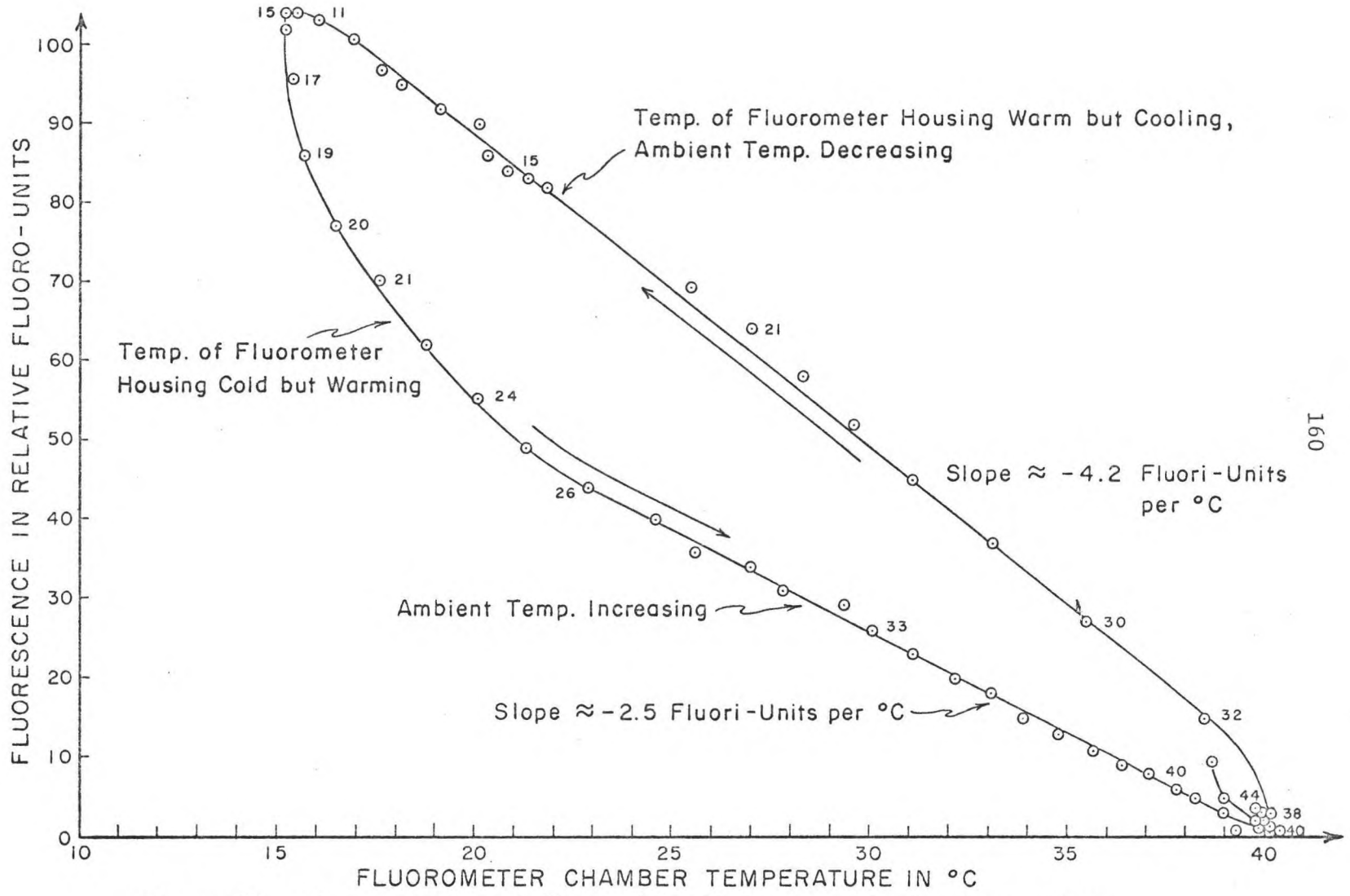


Figure 62. Fluorescence as influenced by fluorometer chamber temperature; figures adjacent data points indicate ambient temperature.

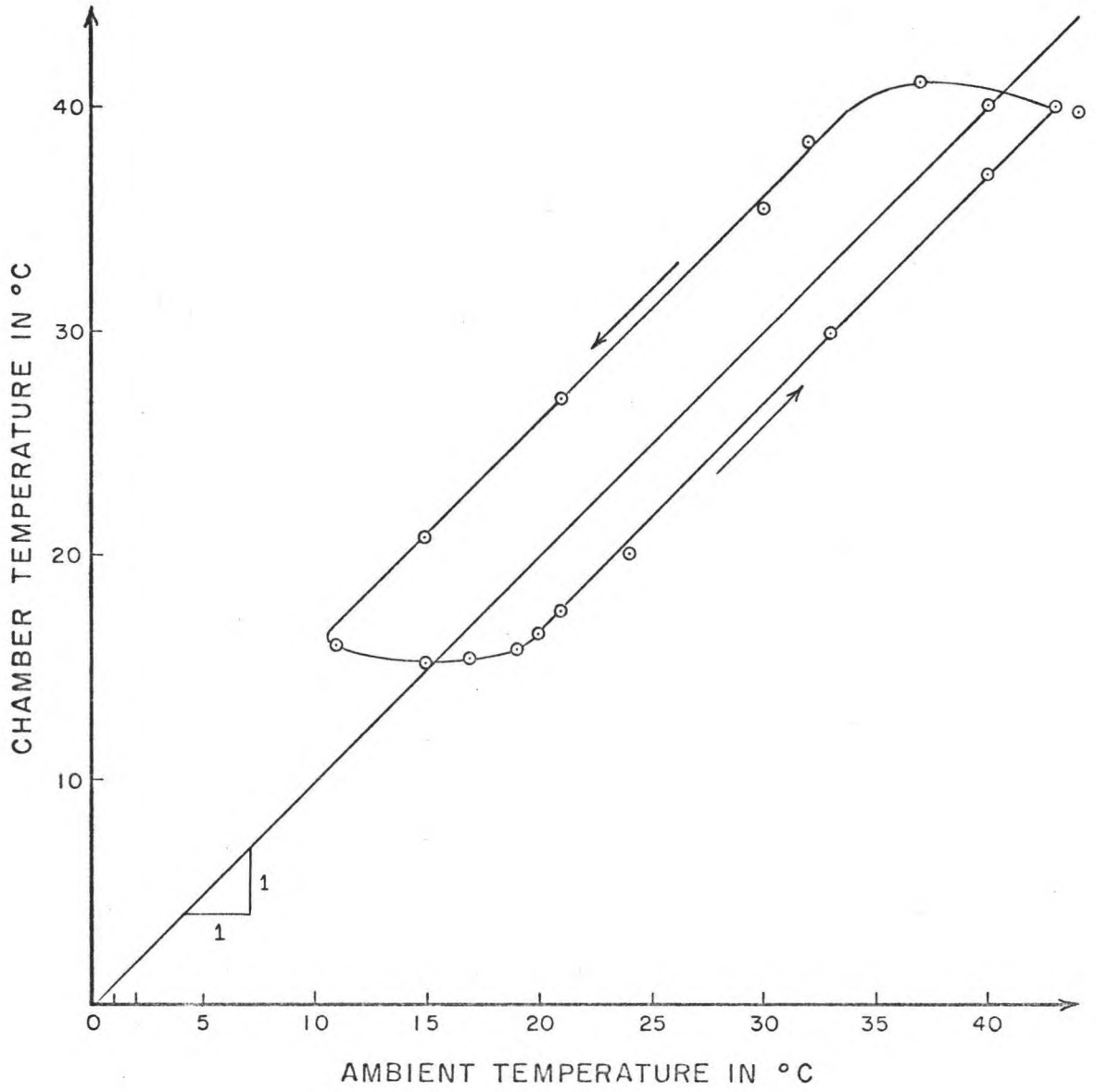


Figure 63. Fluorometer chamber temperature as a function of ambient temperature.

Ficks law, equation (2), is often used to describe heat flow and may apply to the heat flux between the ambient air and the fluorometer chamber. The rate of heat flux, $dQ/dt$, depends on the temperature gradient designated $\partial u/\partial x$ in Fick's equation. When increasing ambient temperatures force chamber temperatures upward, they do so under $\partial u/\partial x$ bolstered by electronic and radiative heat germane to the fluorometer. This results in a negative value for the constant, $B$, in equation (37). But, when decreasing ambient temperatures force chamber temperatures downward, they must do so under a greater $|\partial u/\partial x|$, because heat from the fluorometer itself must be dissipated. In this case $B$ is positive and of a larger absolute value, because temperature differences between ambient air and chamber are greater.

The positive relation between chamber temperature and fluorescence observed by Dunn and Vaupel probably developed from heat sources in the fluorometer. The electronic and servo-motor systems undoubtedly function more efficiently in a warm environment. But, their effect is noticeable only when liquid samples with high specific heats negate the effects of chamber temperatures on sample temperatures. The gelatin-coated film, having a much lower specific heat than aqueous solutions, significantly reflects the temperature influence of the fluorometer chamber. Consequently, temperature stabilization is important to accurate analysis of gelatin-coated films. This concern is multiplied when long film strips are analyzed which may require up to three hours for completion.

## Factors Affecting Timing

### Time marks

The modulation of a drastic stream-tracer event, imposed by suddenly denying the stream a tracer source, was described in Chapter V. Similar modulations probably accompany any time mark register by suddenly altering the tracer concentration of the stream aliquot. Modulation causes the undesirable temporal expansion of time marks on the final record; a two-minute change in the quantity of tracer released into the stream is recorded as a 20-minute event on the fluorometric output. Consequently, any mistake in applying and understanding time marks may cause wide descrepancies in time scale of the record.

### Stream sampling component

The suggested practice of placing time marks on the film by changing tracer concentrations in the stream harbors a potential error in timing. Time marks placed in this manner depend on a constant travel time for the tracer in the aliquot between the intake and the constant-head tank. Tracer movement approximately equals the flow rate of the aliquot, which in a gravity system varies with the hydrostatic head derived from streamflow over the intake vessel.

The magnitude of this time variance for a given change in streamflow depth can be evaluated using Figure 64 and Bernoullii's energy equation,

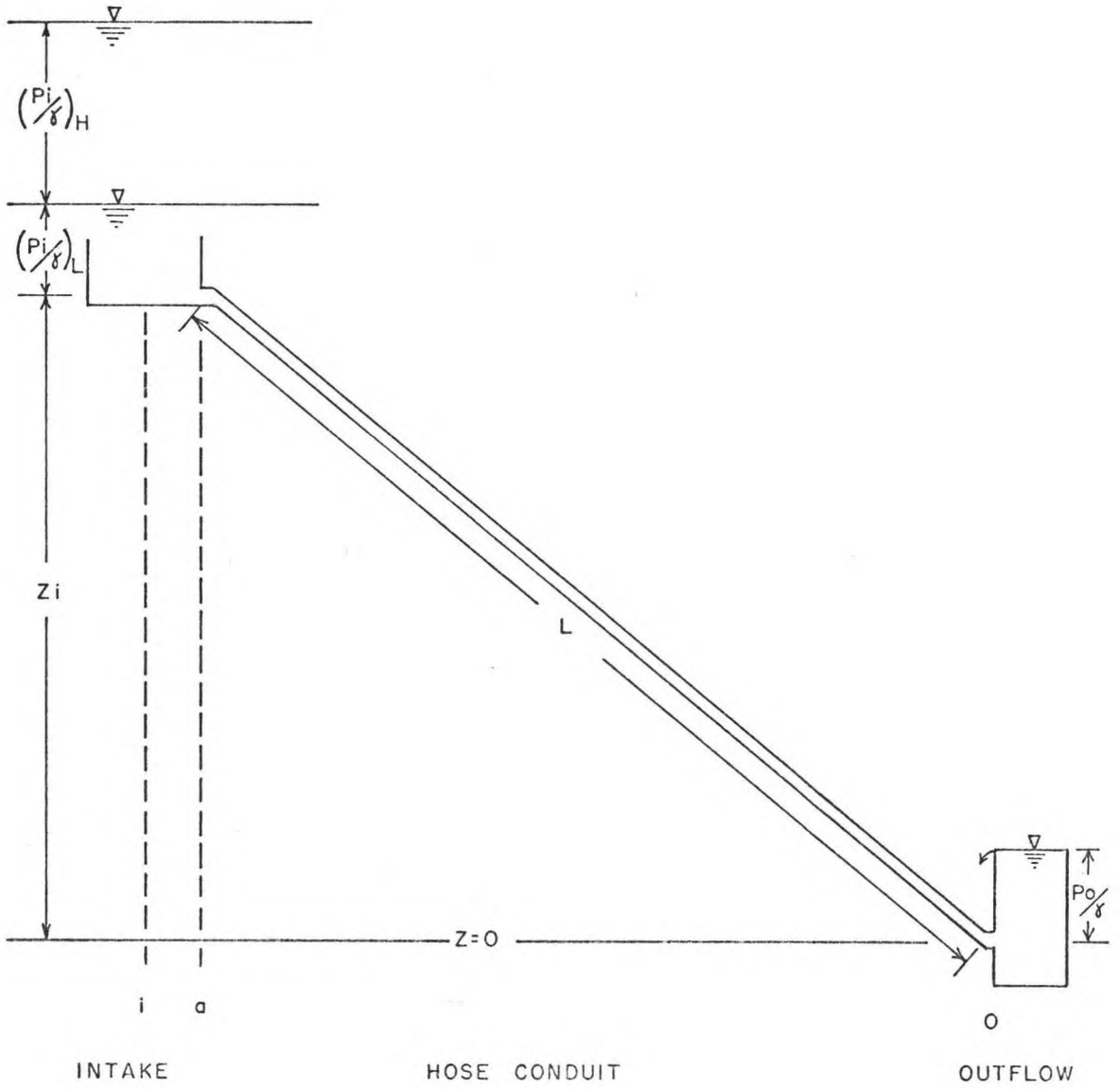


Figure 64. Hydraulic head diagram of the gravity stream sampling unit.

$$\frac{V_i^2}{2g} + \frac{P_i}{\gamma} + Z_i = \frac{V_o^2}{2g} + \frac{P_o}{\gamma} + Z_o + H \qquad (38)$$

where $V$ designates flow velocity, $g$ the gravitational constant (32.2 ft/sec$^2$), $P$ the hydrostatic pressure, $Z$ elevation above datum, $\gamma$ the specific weight, $H$ the head loss, and the subscripts $i$ and $o$ indicate the evaluation of these parameters at the center of the intake vessel and the outflow into the constant-head tank, respectively. Head loss is the sum of energy losses caused by shear drag, $h_s$, and form drag, $h_f$, and can be estimated by

$$H = h_f + h_s \qquad \text{or}$$

$$H = C_a \frac{V_a^2}{2g} + \frac{fLV_a^2}{2Dg} \qquad (39)$$

where $V_a$ is the velocity through the conduit at $a$,

$C_a$ is an entrance coefficient (approx. 0.5),

$L$ is the length of conduit (200 ft.),

$D$ is the inside diameter of the conduit (0.0624 ft), and

$f$ is a friction factor (approx. 0.012 from a Moody resistance diagram for uniform flow in a smooth conduit, as given in Albertson, Barton and Simons, 1960).

Equation (39) evaluated for H between i and o is

$$H = 0.5 \frac{V_a^2}{2g} + \frac{(0.012)(200)\, V_a^2}{(0.0624)\ 2g} \qquad \text{or}$$

where by continuity $V_a = V_o$ ,

$$H = 39.0 \frac{V_o^2}{2g} \quad .$$

This expression for H is substituted into equation (38) and used to evaluate $V_o$ first when the pressure head, $P_i/\gamma$ , equals 1.0 ft., and again when it equals 3.0 ft., their difference representing a two-foot rise in stream stage. In this example the head difference which remains constant is

$$\frac{V_i^2}{2g} + Z_i - \frac{P_o}{\gamma} - Z_o = 0 + 7 - 1 - 0 = 6 \text{ ft.}$$

At the low stage, $V_o = 3.36$ ft/sec; at the high stage, $V_o = 3.81$ ft/sec.

Travel time, t , for each condition is derived from the expression,

$$t = \frac{L}{V} \quad .$$

For velocities of 3.81 and 3.36 ft/sec, t is 52.5 and 59.5 seconds respectively, yielding a travel time difference of seven seconds for a two-foot rise in stream stage.

A difference of seven seconds represents a very small time shift along the tracer record even during time-of-travel measurements. If, however, this problem is of concern, the sampling system can be instrumented to ameliorate this effect of varying stream depth. Installation of a pump system would shorten the conduit and decrease travel time between intake and constant-head tank. Or, still keeping a gravity system, one may place a small intermediary constant-head tank near the intake vessel, thereby forcing a constant flow throughout most of the conduit.

Film stretching

Variations in the time scale of the gelatin-coated film might develop, if, while in the registration device, the film were lengthened.

To test this, a three inch length of film under various tensions of up to 12 pounds was soaked with tap water for six hours. During this interval the film stretched by about 0.7%. Conditions of this test were far more severe than those encountered during tracer registration. Therefore, the effect of film stretching was discounted.

Film exposure

During stream gaging, each length of gelatin-coated film was exposed to the tracer aliquot for 19 minutes. At first one might

suppose that the resulting tracer registration in a unit volume of gelatin represents the integration of tracer concentrations over 19 minutes. This is not so, because gelatin does not immediately swell to its maximum and because a concentration equilibrium develops between the tracer solution and the gelatin. Consequently, tracer molecules taken up by a unit volume of gelatin will only represent integrated concentrations caused by time delays in the processes of tracer diffusion into the gelatin gel and sorption onto substrate surfaces. This means that any tracer concentration ordinate recorded on the fluorometer output will represent integrated tracer uptake extended over periods less than 19 minutes. This exposure time still represents a significant delay in the continuous function of the tracer detection system and perhaps modulates apparent extremes of tracer concentration.

## Factors Affecting Both Concentration and Timing

### Mechanical operation

The tracer detection system is mechanically simple. Precision, never-the-less, strongly depends on smooth mechanical operation. If battery power is adequate, metal parts are kept lightly oiled, and film trains are maintained under uniform tension, smooth operation can be assured.

Sensitivity of the output record

The precision with which an output record from the fluorometer can be read depends on the range in tracer concentration that can be recorded. Records with narrow ranges are more sensitive to concentration changes than records with wide ranges. In other words, resolution of the record is better when concentration changes cause a large change in fluorescence amplitude. Record sensitivity varies with many factors including fluorometer, output recorder, and tracer sampling technique. Never-the-less, changes in tracer concentration recorded from film analyses during field trials were always of satisfactory resolution.

Injection system

Although classed as a separate system and not under study in this research, the injection of tracer into the stream vitally affects precision of the tracer detection system. During continuous stream gaging the concentration of the tracer solution and the rate at which it is injected into the stream must remain constant.

Table 11 contains comparisons between changes in tracer injection rates and the amounts of tracer registrated on gelatin-coated film as determined by fluorometry. The agreement between values in rows IV and V support the interdependancy of tracer uptake by the film with tracer concentration in the stream. These results also verify the premise, previously postulated, that tracer uptake follows a linear function of stream-tracer concentration.

Table 11. Changes in tracer injection rates and their registration on gelatin-coated film.

| | | Change Event | | | | |
|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | |
| I | Time interval over which the change occurred | 3.0 | 2.5 | 1.5 | 1.0 | hour |
| II | Change in stream discharge | 1.5 | -3.5 | 0 | 0 | % |
| III | Change in tracer injection rate | 32.3 | 18.1 | 25.0 | -100 | % |
| IV | Combined effect of change in discharge and injection rate | 30.8 | 21.6 | 25.0 | -100 | % |
| V | Change in tracer concentration registered on the film | 32.0 | 21.2 | 25.0 | -100 | % |

# CHAPTER VII

# CONCLUSIONS AND SUGGESTIONS FOR IMPROVEMENT

The basic objective of this study was to develop an inexpensive, field-operative system for detecting fluorescent tracers in streamflow. Achievement of this objective required determination of the most advantageous kind of system, fabrication of instruments and support equipment necessary to the system, explanation of the processes involved, and application of the system to field studies.

## The System

The use of fluorescent dyes as tracers in natural waters spread with the development and application of ultra-sensitive fluorometers to hydrometry. The system researched in this study adds a third element, a sensitive, gelatin-coated film. Here, the fluorometer is not confined to analyzing tracers dissolved in a liquid medium; streamflow tracers can be taken up by the film in a predictable manner, stored if necessary, and quantified by analysis in a modified ultra-sensitive fluorometer. Freeing the fluorometer from its singular dependency on liquid sample analyses in order to detect tracers in streamflow, adds new dimensions to tracer techniques in hydrometry.

## Advantages

Registration of tracer molecules on to gelatin-coated films prior to fluorometry retains all the advantages characteristic of liquid sampling and adds some of its own. The system's major advantage rests in its ability to monitor stream-borne tracer concentrations continuously without requiring the fluorometer to be located at the stream site. This eliminates concern for exposure of an expensive, temperature-sensitive instrument to an outdoor environment and possible vandalism; a 110-volt power source is not required and the entire analytic utility of the fluorometer is not confined to one site. In comparison to systems utilizing automatic samplers which integrate discretely apportioned liquid samples, this system reduces dependency of the record on a single integrated tracer concentration sample.

The system also forms an excellent complement to tracer detection by the collection of liquid in containers. Supported by a time-scaled distribution of stream-borne tracer concentrations registered on gelatin-coated film, one knows the relation of his liquid sample to events in the stream. He will know, for example, whether streamflow rose or declined and, most importantly, whether tracer concentration reached an equilibrium or not.

## Disadvantages

The primary disadvantage of the detection system developed here is its lack of a visible concentration record at the stream site. In this sense, the system is like exposing photographic film to light and being required to develop the image in a laboratory dark room. Field operation under this disadvantage forced this worker to observe the stream more carefully, noting closely its stage, periodicity, and character.

Another disadvantage of the system, as it is now instrumented, is the necessity of installing equipment directly into, or adjacent to the stream. During bankfull or flood stages, this task may not only be difficult, but also dangerous. During 1969, application of the system to a mountain stream flowing 100 cfs proved possible, but only after considerable attention to stabilization of the in-stream components.

The system depends heavily on the maintenance of gravity-regulated hydrostatic water levels. The water level of the aliquot reservoir in the stream-side, tracer registration device is particularly sensitive. If stream-side components of the system were mounted on a mobile platform subject to rapid pitch and yaw, such as on a boat, successful gaging would be impossible. Instrumentation might be devised to circumvent this problem, but the task was not attempted during this study.

A final disadvantage stems from the greater tracer modulation associated with this system than with liquid sampling. Intermediary components cause additional impedances through which tracer signals must pass. Modulation primarily causes a distortion of the time scale. This distortion, though registered in minutes, does not pose a serious limitation to measurement of the usual hydrographic parameters.

## Applications

Under the test conditions of a few mountain streams during summer operation, the system performed well when applied to continuous stream gaging, time-of-travel measurements, and instantaneous gaging by the total recovery of a slug-released tracer. Hydrographs from 640 hours of stream gaging compared favorably with those obtained from closely located weirs. Maximum deviation between hydrographs reached 10%, while average absolute and algebraic departures equaled 1.8% and +0.3%, respectively. Regression analysis based on 916 pairs of streamflow values taken from these hydrographs resulted in an $R^2$ agreement of 99.9% with an error mean square of 0.006 cfs.

Continuous gaging of turbulent mountain streams by this system offers an option where the measurement of stage is difficult or the stage-discharge relation is complex.

In general, however, it is not expected that the system will supplant gaging by means of control sections where the requirements are

for highly accurate, long-term records, and full details of stream fluctuations. Envisioned is particular utility in water resource inventory where each one of a core of conventional, permanent gaging stations, is complemented by a number of roving or "satellite" stations of the type described here.

The advantage of this time-based detection system for determination of stream travel times is obvious. Not only is the arrival time of the tracer cloud determined automatically, but its entire time-distribution is recorded as well. These records are obtained without requiring the fluorometer to be stationed at the stream site.

Wilson and Forrest (1965) described the efforts involved in measuring time-of-travel in the Potomac River from Cumberland, Maryland, to Washington, D. C. The river was divided into six sub-reaches and a total of six injection sites selected. A total of 23 sampling sites were chosen and five fluorometers were used. The week-long efforts of 35 people were involved, day and night, as sampling continued around the clock. With an endeavor of such a magnitude, the use of automatic sampling equipment would have eased logistics and perhaps increased the accuracy of such a measurement.

The same authors were also interested in deriving the most benefit from instrumentation available to them. In this regard they stated,

> "For time-of-travel studies, grab sampling is generally preferred over continuous flow sampling, because samples from several sites can be tested on one instrument."

Buchanan (1964) held a similar opinion when he wrote,

> "The continuous flow sampling method is not commonly used because information at many points is usually desired during a time-of-travel run. One instrument can be used to measure the concentration of grab samples taken at many different points."

Use of the detection system would ameliorate the difficulty the above investigators referred to. With it, they would be able to obtain automatically a continuous record of the passing tracer cloud from many different points without expending the entire utility of their fluorometer at one sampling site.

Application of this system to the gaging of streams by the total-recovery method was not conclusive. Only three such measurements were performed sufficiently close to weirs to allow critical comparison. In these instances, deviations between the two measurement techniques were all within 3%. Although the tracer cloud was satisfactorly registered on the gelatin-coated film, difficulty in obtaining a suitable concentration value for the injected tracer solution presented a drawback to this application. It should be added that stream gaging by total-recovery has been less satisfactory than constant-rate injection no matter what the sampling technique.

## Factors Affecting Precision

The major factors affecting precision of the detection system are stream temperature changes and contact time between the gelatin-coated film and the tracer solution. The latter factor was adequately

controlled by stabilizing the tracer exposure time for a given length of film. However, the temperature range of a stream is a hydrologic property, which must be known and, if excessive, accounted for to assure adequate precision.

## Suggestions for Improvement

The tracer detection system reported herein performed well during experimental trials on mountain streams. The utility of the basic concepts seems well established. Further trials and refinements should be made to optimize convenience and reliability, to minimize tracer requirements, and to determine the system's adaptability to other types of streams. For ephemeral streams, programmed intermittent operation may be feasible.

During this research, only one tracer dye, Rhodamine WT, was tested. Other dyes, including the often used sodium dichromate (for colorimetry), should be investigated to see if they respond similarly.

The phase of this detection system requiring the most urgent research deals with the inscription of time marks onto the gelatin-coated film. Any faulty time-marking procedure or any non-uniform response by the system to a time mark will render time measurement by the system unreliable. Difficulties with time marks encountered during this study were eased by familiarity with the stream acquired by

frequent visits to the sampling site. The time-marking procedures that can be suggested at this time are:

(1) register the time mark by suddenly altering the tracer concentration at the intake vessel;

(2) make the smallest concentration alteration over the shortest time interval that is possible, yet still register a distinguishable time mark on the output record; and

(3) correlate the time of the alteration with the major initial point of ordinate change recorded on the output.

A number of suggestions to improve instrumentation can be noted. These concern mainly the aliquot sampler, the registration reservoir, and the fluorometer.

Adaptation of a pump-driven sampling component would lessen many difficulties in timing, tracer signal modulating, and stream site installation. Perhaps a change in size of the conduit and the constant-head tank would reduce the difficulties and still allow the retention of a gravity sampler.

Utilization of a liquid reservoir to allow contact of the stream aliquot with gelatin-coated film is, in general, adequate, but might advantageously be superceded by another technique. Regulation of the stream-film contact by using a small, steady liquid jet impinging directly on the film has been suggested, but not attempted.

In reference to stream-side instruments, the possibility exists of providing multiple sampling channels. Perhaps a tracer registration device could be constructed containing a number of registration reservoirs in echelon, each supplied with a stream aliquot taken from different positions along the sampling section of the stream. Multiple channels would have utility on larger streams and rivers.

Improvement efforts with the fluorometer can be aimed toward two objectives, increasing fluorescence sensitivity recorded from the film and modifying the dampening effect of the servomotor. The latter may be difficult to accomplish. Dampening is necessary, because the fluorometer is so balanced that noise from its electronics is relatively large and must be averaged over a long period of time (Turner and Associates, 1964). Fluorometer sensitivity to film-borne fluorescent tracers can be improved by finding a better combination of source radiation, light pipes, reflecting surfaces, and fluorescent energy detection. Specifically, fluorescence from tracer-laden, gelatin-coated film should be attempted using the red-sensitive photomultiplier tube (fluorescent energy detector) which recently became available.[1/]

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1/ Supplied by G. K. Turner, Associates, Palo Alto, California.

# CHAPTER VIII

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# CHAPTER IX

# APPENDICES

Appendix A: Mechanical drawings of instruments and equipment germane to the tracer detection system; outlined below, but included under separate cover.

1 - Intake vessel

2 - Constant-head Tank

3 - Tracer Registration Device

- Base plate
- Base plate assembly
- Registration reservoir
- Supply spool assembly
- Take up spool and drive assembly cover

4 - Film — Acceptable Fluorometer Door

- Film drive mounting plates
- Film drive assembly
- Film mounting assembly
- Light shield
- Film track assembly
- Door assembly

Appendix B: Improvements related to the tracer injection system used in this study.

Three improvements to the injection system developed by Goodell et al. (1967) and Siverts (1967) are reported here.

The first improvement concerns vibration of the orifice appurtenance required to assure a constant release of tracer solution from the injector vessel. During stream gaging trials, it was discovered that the attachment of a long stiff rod to the orifice appurtenance and extended into the turbulent current of the stream,

proved satisfactory for a bank-mounted installation. Stream turbulence vibrated the rod sufficiently to provide the required agitation of the orifice.

The second improvement concerns filtering of the vessel-stored tracer solution before it is injected into the stream. The original filter consisted of a standpipe positioned over the orifice and extended upward above the liquid level in the vessel. Ports drilled through the wall of the standpipe were covered with a 400 mesh stainless steel screen (nominal openings of 37 microns). Large particulate matter was filtered from the solution as it passed into the standpipe. Filtering during this study was accomplished by inserting a stainless steel bushing between the valve and the orifice of the appurtenance assembly. The inside diameter of the bushing was fitted with a 400 mesh screen, which served as a filter. The standpipe filter was eliminated. This simpler filtering arrangement functioned quite satisfactory.

The third improvement deals with charging the injection vessel with a Rhodamine WT supply for long-term, constant tracer-injection. A set of suggested steps are outlined below:

1. As a precaution, do not let Rhodamine WT (20% solution) freeze.

2. When storing Rhodamine WT 20%, occasionally stir or agitate the solution. This retards precipitation.

3. To recharge injector, draw desired amount of Rhodamine WT

20% in a container large enough to allow the addition of an equal volume or more of methanol ($CH_3OH$).

4. Add at least an equal volume of methanol to the drawn dye.

5. Before the mixture is filtered into the injector, vigorously agitate the dye-methanol mixture. Do not excessively agitate the mixture if it cannot be added to the injector within four hours. Let the mixture stand undisturbed for at least two hours before adding to the injector.

6. At the gaging site the first step in charging the injection vessel is to add sufficient stream water to fill the injector half full. Filter this water through two thicknesses of "shark skin" filter paper in the funnel leading into the injector vessel.

7. Replace filter paper with two, clean, fresh, wetted sheets in such a way that they fit in the funnel smooth, flush, and wrinkle-free.

8. Apply vacuum to the injection vessel (three solid strokes with hand pump).

9. Quickly begin adding a constant flow of stream water to the funnel leading to the injector. Then immediately begin strong vacuum pumping and continue until a vacuum of about one-fourth atmosphere is assured.

10. Stop adding stream water to the funnel. Add one or two liters of the dye-methanol mixture when only approximately 5mm of water cover the filter paper.

11. Return to vacuum pumping.

12. If a crystal-appearing filtrate is left on the filter paper, add water to dissolve it. Filter this solution through and continue same until all of the filtrate has been re-dissolved and filtered into the injector.

13. Check the dye-methanol container for large amounts of this crystal precipitate. If found, add stream water to the container and shake moderately.

14. Repeat steps 7 through 13.

15. When the correct amount of dye-methanol has been added to injector, fill the vessel with filtered stream water and prepare injector for operation.

Appendix C: A sample of the actual gelatin-coated film (single-coated) used in the tracer detection system.

Dry Bimat Transfer Film, Type 2436-A; Product of Eastman Kodak Company, Rochester, New York.