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PB-299 015

# Estimating the Gas and Dye Quantities for Modified Tracer Technique Measurements of Stream Reaeration Coefficients

(U.S.) Geological Survey, NSTL Station, MS

Feb 79

PB 299015

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U.S. GEOLOGICAL SURVEY
Water-Resources Investigations 79-27

U.S. DEPARTMENT OF THE INTERIOR
MARCH 3, 1849

**BIBLIOGRAPHIC DATA SHEET**

1. Report No. USGS/WRD/WRI-79/029

2\.

3\. Recipient's Accession No. PB299015

4\. Title and Subtitle

ESTIMATING THE GAS AND DYE QUANTITIES FOR MODIFIED TRACER TECHNIQUE MEASUREMENTS OF STREAM REAERATION COEFFICIENTS

5\. Report Date February 1979

6\.

7\. Author(s) R. E. Rathbun

8\. Performing Organization Rept. No. USGS/WRI 79-27

9\. Performing Organization Name and Address

U.S. Geological Survey, Water Resources Division
Gulf Coast Hydroscience Center
National Space Technology Laboratories
NSTL Station, Mississippi 39529

10\. Project/Task/Work Unit No.

11\. Contract/Grant No.

12\. Sponsoring Organization Name and Address

U.S. Geological Survey, Water Resources Division
Gulf Coast Hydroscience Center
National Space Technology Laboratories
NSTL Station, Mississippi 39529

13\. Type of Report & Period Covered Final

14\.

15\. Supplementary Notes

16\. Abstracts Measuring stream reaeration coefficients with a modified tracer technique has been accomplished by injecting ethylene or ethylene and propane together and a rhodamine-WT dye into the stream. The movement of the tracers through the stream reach is described by a one-dimensional diffusion equation. The peak concentrations of the tracers at the downstream end of the reach depend on the concentrations in the stream at the injection site, the longitudinal dispersion coefficient, the water velocity, the reach length, and the duration of the injection period. The downstream gas concentrations also depend on the gas desorption coefficients. The concentrations of the gases in the stream at the injection site depend on the gas flow rates through the injection diffusers, the efficiency of the absorption process, and the stream discharge. The concentration of dye in the stream at the injection site depends on the dye flow rate, the concentration of the dye solution, and the stream discharge. Equations for estimating the gas flow rates, the quantities of the gases, the dye concentration, and the quantity of dye together with procedures for determining the variables in these equations are presented.

17\. Key Words and Document Analysis. 17a. Descriptors

*Reaeration, *Streams, *Measurement, *Tracers, Dispersion, Mixing

17b. Identifiers/Open-Ended Terms

*Reaeration coefficient, *Non-radioactive tracers, Dye tracing, Hydrocarbon gases, Rhodamine-WT dye, Time of travel

17c. COSATI Field/Group

18\. Availability Statement

**Prepared for NTIS by U.S. Geological Survey, WRD**

No restriction on distribution.

19\. Security Class (This Report) UNCLASSIFIED

20\. Security Class (This Page) UNCLASSIFIED

21\. No. of Pages 52

22\. Price PCA04/A01 /MF

FORM NTIS-35 (REV. 10-73) ENDORSED BY ANSI AND UNESCO. THIS FORM MAY BE REPRODUCED USCOMM-DC 8265-P74

# ESTIMATING THE GAS AND DYE QUANTITIES FOR MODIFIED TRACER TECHNIQUE MEASUREMENTS OF STREAM REAERATION COEFFICIENTS

By R. E. Rathbun

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February 1979

UNITED STATES DEPARTMENT OF THE INTERIOR

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GEOLOGICAL SURVEY

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## LIST OF SYMBOLS

| Symbol | Definition | Units |
|---|---|---|
| B | Width of channel at steady flow | Meter |
| BPS | Basic parameter set | Dimensionless |
| $C$ | Concentration of tracer gas or dye | Microgram/liter |
| $C_B$ | Background concentration of tracer gas or dye in the stream water | Microgram/liter |
| $C_{D_I}$ | Concentration of dye in the solution injected | Microgram/liter |
| $C_{D_M}$ | Peak concentration of dye at the downstream end of the reach | Microgram/liter |
| $C_{D_O}$ | Concentration of dye uniformly mixed in the cross section of the stream at the injection site | Microgram/liter |
| $C_G(x,t)$ | Concentration of tracer gas at longitudinal position $x$ at time $t$ | Microgram/liter |
| $C_{G_M}$ | Peak concentration of tracer gas at the downstream end of the reach | Microgram/liter |
| $C_{G_O}$ | Concentration of tracer gas uniformly mixed in the cross section of the stream at the injection site | Microgram/liter |

| | | |
|---|---|---|
| $C_{G_{O\,BPS}}$ | Concentration of tracer gas uniformly mixed in the cross section of the stream at the injection site for the basic parameter sets | Microgram/liter |
| $C_{WT}$ | Concentration of 20 percent rhodamine-WT dye as supplied by the manufacturer | Microgram/liter |
| $D$ | Longitudinal dispersion coefficient | Square meter/minute |
| $dC_d/dt$ | Rate of change of the tracer gas concentration as a result of desorption | Microgram/liter-minute |
| erf $\Phi$ | Error function of $\Phi$, equal to the value of $(2/\sqrt{\pi})\int_{o}^{\Phi}\exp(-z^2)\,dz$ where $z$ is a dummy variable of integration | Dimensionless |
| $F$ | Froude number, equal to $U/\sqrt{gY}$ | Dimensionless |
| $F_{G_I}$ | Fraction of the gas flowing through the diffusers that is tracer gas | Gram/gram |
| $g$ | Acceleration of gravity | Meter/minute squared |
| $H$ | The function $2\,K_T\,D/U^2$ | Dimensionless |
| $K_T$ | Tracer gas desorption coefficient, natural logarithm base | $\text{Day}^{-1}$ |
| $K_{T_E}$ | Desorption coefficient for ethylene, natural logarithm base | $\text{Day}^{-1}$ |
| $K_{T_P}$ | Desorption coefficient for propane, natural logarithm base | $\text{Day}^{-1}$ |
| $K_{T_{BPS}}$ | Desorption coefficient for the basic parameter sets, natural logarithm base | $\text{Day}^{-1}$ |
| $K_2$ | Reaeration coefficient, natural logarithm base | $\text{Day}^{-1}$ |
| $K_{2_\theta}$ | Reaeration coefficient at stream water temperature $\theta$, natural logarithm base | $\text{Day}^{-1}$ |
| $K_{2_{20}}$ | Reaeration coefficient at 20° Celsius, natural logarithm base | $\text{Day}^{-1}$ |
| $Q$ | Water discharge of the stream | Cubic meter/second |

| | | |
|---|---|---|
| $q_D$ | Rate of injection of dye solution | Milliliter/minute |
| $q_G$ | Flow rate of gas through the diffusers | Gram/minute |
| $q_{G_E}$ | Flow rate of ethylene through the diffuser | Gram/minute |
| $q_{G_P}$ | Flow rate of propane through the diffuser | Gram/minute |
| $S$ | Slope of the stream channel, equal to the slope of the energy gradient for steady uniform flow conditions | Meter/meter |
| $t$ | Time measured from the start of the injection of the tracers | Minute |
| $\bar{t}$ | Time of travel of the centroid of the dye mass | Minute |
| $\bar{t}_d, \bar{t}_u$ | Time of travel of the centroid of the dye mass at the downstream and upstream ends of the reach, respectively | Minute |
| $t_{0.01}$ | Time at which the dye concentration has decreased to 1.0 percent of the peak concentration | Minute |
| $t_M$ | Time of travel of the peak concentration | Minute |
| $t_{M_D}$ | Time of travel of the peak concentration of the dye | Minute |
| $t_{M_E}$ | Time of travel of the peak concentration of the ethylene | Minute |
| $t_{M_P}$ | Time of travel of the peak concentration of the propane | Minute |
| $U$ | Mean water velocity | Meter/minute |
| $V_{air}$ | Volumetric air flow rate | Standard cubic foot/minute |
| $V_D$ | Volume of rhodamine-WT dye | Milliliter |
| $V_E$ | Volumetric ethylene flow rate | Standard cubic foot/minute |
| $V_P$ | Volumetric propane flow rate | Standard cubic foot/minute |
| $V_W$ | Volume of water to be mixed with the dye | Milliliter |

| | | |
|---|---|---|
| $w_E$ | Weight of ethylene | Kilogram |
| $w_P$ | Weight of propane | Kilogram |
| $x$ | Longitudinal position | Meter |
| $Y$ | Mean depth of flow | Meter |
| $\varepsilon$ | Efficiency of the gas absorption process | Gram/gram |
| $\theta$ | Water temperature | Degrees Celsius |
| $\sigma_t^2$ | Variance of the dye concentration-versus-time curve | Square minute |
| $\sigma_{t_d}^2, \sigma_{t_u}^2$ | Variance of the dye concentration-versus-time curve at the downstream and upstream ends of the reach, respectively | Square minute |
| $\tau$ | Duration of the injection period | Minute |
| $\Phi$ | Argument of the error function | Dimensionless |

## CONVERSION TABLE: METRIC UNITS TO INCH-POUND UNITS

| Multiply | By | To Obtain |
|---|---|---|
| micrometer (μm) | $3.937 \times 10^{-5}$ | inch (in.) |
| millimeter (mm) | $3.937 \times 10^{-2}$ | inch (in.) |
| meter (m) | 3.281 | foot (ft) |
| milliliter (mL) | .03381 | fluid ounce (fl oz) |
| meter per second (m/s) | 3.281 | foot per second (ft/s) |
| meter per minute (m/min) | 3.281 | foot per minute (ft/min) |
| square meter per minute ($m^2$/min) | 10.765 | square foot per minute ($ft^2$/min) |
| cubic meter per second ($m^3$/s) | 35.31 | cubic foot per second ($ft^3$/s) |
| liter per minute (L/min) | .03531 | cubic foot per minute ($ft^3$/min) |
| liter per hour (L/h) | .03531 | cubic foot per hour ($ft^3$/h) |
| kilogram (kg) | 2.205 | pound (lb) |
| gram per minute (g/min) | .002205 | pound per minute (lb/min) |
| milligram per liter (mg/L) | $62.44 \times 10^{-6}$ | pound per cubic foot ($lb/ft^3$) |
| microgram per liter (μg/L) | $62.44 \times 10^{-9}$ | pound per cubic foot ($lb/ft^3$) |
| kilopascal (kPa) | .1450 | pound per square inch ($lb/in^2$) |
| degree Celsius (°C) + 17.78 | 1.8 | degree Fahrenheit (°F) |

# ESTIMATING THE GAS AND DYE QUANTITIES FOR MODIFIED TRACER TECHNIQUE MEASUREMENTS OF STREAM REAERATION COEFFICIENTS

By R. E. Rathbun

## ABSTRACT

Measuring the reaeration coefficient of a stream with a modified tracer technique has been accomplished by injecting either ethylene or ethylene and propane together and a rhodamine-WT dye solution into the stream for a period of time. The movement of the tracers through the stream reach after injection is described by a one-dimensional diffusion equation. The peak concentrations of the tracers at the downstream end of the reach depend on the concentrations of the tracers in the stream at the injection site, the longitudinal dispersion coefficient, the mean water velocity, the length of the reach, and the duration of the injection period. The downstream gas concentrations also depend on the gas desorption coefficients of the reach. The concentrations of the tracer gases in the stream at the injection site depend on the flow rates of the gases through the injection diffusers, the efficiency of the gas absorption process, and the stream discharge. The concentration of dye in the stream at the injection site depends on the flow rate of the dye solution, the concentration of the dye solution, and the stream discharge. Equations for estimating the gas flow rates, the quantities of the gases, the dye concentration, and the quantity of dye together with procedures for determining the variables in these equations are presented.

## INTRODUCTION

The modified tracer technique (Rathbun and others, 1975) is used to measure the reaeration coefficients of streams, and this technique has been applied (Rathbun and others, 1977) to a number of different types of streams. Application of the technique is accomplished by injecting low molecular weight hydrocarbon gases and a water soluble dye into the stream for a period of time. The technique has been applied using either ethylene or ethylene and propane together and a water solution of rhodamine-WT dye. This report describes procedures for estimating the gas flow rates, the quantities of the tracer gases, the dye concentration, the quantity of dye, and the length of the injection period necessary for measuring the reaeration coefficient of a stream with the modified tracer technique. These procedures are applicable to streams with discharges less than about 8.5 $m^3/s$, primarily because most of the measurements completed thus far have been for streams with discharges of this magnitude or smaller. Some general guidelines are given, however, for modifying the procedures for application to larger flows.

Metric units are used in this report, with one exception. Inch-pound units are used for the volumetric flow rates of the tracer gases because rotameters used for monitoring these flow rates are usually provided with calibrations in inch-pound units. A table of metric-inch-pound conversion factors is included on page VIII of this report.

## THE TRACER TECHNIQUE

Measuring the reaeration coefficient of a stream with the modified tracer technique is accomplished by injecting the tracer gas (or gases) and dye solution into the stream, obtaining samples of the stream water at various points downstream as the gas and dye tracers pass, analyzing the water samples for concentrations of the tracers, computing a desorption coefficient for the tracer gas, and converting the desorption coefficient to the reaeration coefficient with the ratio determined in laboratory studies. Details of these procedures have been described in other reports (Rathbun and others, 1975; Shultz and others, 1976; Rathbun and others, 1977; Rathbun and others, 1978) and will not be repeated here. However, a brief discussion of the injection process will be given in the following paragraphs to serve as a basis for the description of the procedures for estimating the gas flow rates, the quantities of the gases, the dye concentration, the quantity of dye, and the length of the injection period. The dye solution flow rate will usually be determined within limits by the type of equipment used for injection.

The hydrocarbon gas and the dye solution are injected into the stream for a time period sufficient to give concentrations at the downstream end of the reach that can be measured with a precision of about 2 percent. For streams with discharges less than about 8.5 $m^3/s$, it is generally possible to obtain sufficient concentrations of both ethylene and propane in the stream so that these gases can be used simultaneously. Because these gases desorb at different rates, two measurements of the reaeration coefficient are possible in a single experiment with only a little additional effort. For streams with discharges larger than 8.5 $m^3/s$, ethylene alone has been used as the tracer gas.

The ethylene and propane are injected into the stream by bubbling through porous tube diffusers placed on the bottom of the stream in the center of the flow. The diffusers were obtained from the Norton Company[1], Worcester, Mass., and are 0.46 m long, 75 mm in outside diameter, and 19 mm thick. Two diffusers with an approximate average pore size of 6.3 microns are used for propane and one diffuser with an average pore size between 15 and 20 microns is used for ethylene. A larger surface area is used for the propane because one of the variables affecting the rate

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[1] The use of the brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

of solution of the gas in water is the solubility. Propane has a solubility of 62.4 mg/L at 25°C compared with an ethylene solubility of 131 mg/L at 25°C (McAuliffe, 1966). The gases are fed directly from the cylinders in which they are supplied through two-stage regulating valves to the diffusers. Rotameters are used to monitor the flow rates.

The rhodamine-WT dye and water solution is injected into the stream at the same injection site and for the same injection period as is used for the ethylene and propane. This solution is injected using either a Mariotte vessel or a positive displacement metering pump. A Mariotte vessel is a constant head device, and details of the design and operation have been presented by Cobb (1967). It is inexpensive to construct and simple to operate, however, some means of getting the solution from the discharge point of the vessel to the center of the stream must be devised. An alternative dye injector is a battery-powered metering pump, which is simple to operate and has the advantage that the dye solution can be pumped directly to the center of the stream. A pump, however, is more expensive than a Mariotte vessel.

## MATHEMATICAL BASIS

After the tracer gases and the dye are injected into the stream, the transport and the ultimate fate of these substances are determined by the physical processes of dispersion and convection with the tracer gases also being affected by the process of desorption through the surface of the stream. Assuming that the tracers are uniformly mixed in the cross section, the resultant effect of the combination of these processes can be described by the one-dimensional diffusion equation with a desorption term added. This equation has the form

$$\frac{\partial C}{\partial t} + U\frac{\partial C}{\partial x} = D\frac{\partial^2 C}{\partial x^2} - K_T C \qquad (1)$$

where $C$ is the concentration; $t$ is time; $x$ is longitudinal position; $D$ is the longitudinal dispersion coefficient; $U$ is the mean water velocity; and $K_T$ is the tracer gas desorption coefficient. For the dye which is assumed to be conservative, $K_T$ is equal to zero. The one-dimensional diffusion equation has been discussed in detail by Fischer (1966).

Equation 1 assumes that the desorption of the tracer gas through the stream surface is a first order process of the form

$$\frac{dC_d}{dt} = -K_T C \qquad (2)$$

where $dC_d/dt$ is the rate of change of the gas concentration as a result of desorption and the gas concentration in the atmosphere is assumed to be zero relative to the concentration in the water. Such a first order process is commonly assumed for the desorption of slightly soluble gases from water (Rathbun and others, 1978).

Following O'Loughlin and Bowmer (1975) and Rose (1977), the solution of equation 1 for an injection of the gas tracer for a time period $\tau$ is

$$C_G(x,t) = \frac{C_{G_O}}{2} \exp\left(\frac{-K_T x}{U}\right)\left[\operatorname{erf} \frac{x - U(t-\tau)(1+H)}{\sqrt{4D(t-\tau)}} - \operatorname{erf} \frac{x - Ut(1+H)}{\sqrt{4Dt}}\right] \qquad (3)$$

where $C_G(x,t)$ is the concentration of tracer gas in the stream water at longitudinal position $x$ at time $t$; $C_{G_O}$ is the concentration of the tracer gas in the water at the injection site assumed to be uniformly mixed over the cross section; $H$ is the function $2K_T D/U^2$; erf denotes the error function; and time $t$ is measured from the start of the injection of the tracers. Equation 3 also applies to conservative substances if the desorption coefficient, $K_T$, is set equal to zero. (O'Loughlin and Bowmer, 1975).

The injection time, $\tau$, will almost always be small relative to the time of travel so that a peak concentration rather than a plateau concentration will be observed at the downstream end of the reach. Again following O'Loughlin and Bowmer (1975) and Rose (1977), it can be shown that the time of travel, $t_M$, of this peak concentration at longitudinal position $x$ is given by

$$t_M = \frac{x + \frac{U\tau}{2}(1+H)}{U(1+H)} \qquad (4)$$

Writing equation 3 in terms of $t_M$ gives

$$C_{G_M} = \frac{C_{G_O}}{2} \exp\left(-\frac{K_T x}{U}\right)\left[\operatorname{erf} \frac{x - U(t_M-\tau)(1+H)}{\sqrt{4D(t_M-\tau)}} - \operatorname{erf} \frac{x - Ut_M(1+H)}{\sqrt{4Dt_M}}\right] \qquad (5)$$

where $C_{G_M}$ is the peak concentration at longitudinal position $x$. Thus, this peak concentration depends on the concentration of the gas in the stream water at the upstream end of the reach, the tracer gas desorption coefficient, and the duration of the injection period.

The concentration of the gas obtained in the water at the upstream end of the reach depends on the flow rate of the gas through the diffusers, the efficiency of the absorption process, and the stream discharge. From a mass balance, it follows that

$$QC_B + \varepsilon q_G F_{G_I} = QC_{G_O} \quad (6)$$

where $Q$ is the stream discharge; $C_B$ is the background concentration of the gas in the water; $\varepsilon$ is the efficiency of the absorption process; $q_G$ is the flow rate of the gas through the diffusers; and $F_{G_I}$ is the fraction of the gas flowing through the diffusers that is tracer gas. Equation 6 assumes that the dissolving of the gas in the water is an instantaneous process, that is, any gas not immediately dissolved is desorbed through the stream surface to the atmosphere. In most streams, the background concentration will be negligible relative to the concentration of gas injected, thus $C_B = 0$. Also the gas injected will be virtually all tracer gas, thus $F_{G_I} = 1.0$. With these simplifications, equation 6 reduces to

$$C_{G_O} = \frac{\varepsilon q_G}{Q} \quad (7)$$

Equation 6 also applies to the injection of the dye solution except that the absorption efficiency will be 100 percent and the concentration of the solution injected will not be 1.0. Thus, for the dye solution, equation 6 reduces to

$$C_{D_O} = \frac{q_D C_{D_I}}{Q} \quad (8)$$

where $C_{D_O}$ is the concentration of dye assumed to be uniformly mixed in the cross section of the stream at the injection site; $q_D$ is the injection rate of the dye solution which is small relative to the stream discharge; and $C_{D_I}$ is the concentration of dye in the solution injected.

The objective of estimating the gas and dye quantities is to insure that the gas and dye concentrations observed at the downstream end of the reach will be large enough to be measured with good precision. A gas chromatographic technique (Shultz and others, 1976) is used to measure the concentrations of the tracer gas, and a concentration of about 1 μg/L can be measured with a precision of about 2 percent. Fluorometric techniques (Cobb and Bailey, written commun., 1965; Wilson, 1968; and Kilpatrick, Martens, and Wilson, written commun., 1970) are used to measure the concentrations of the dye, and concentrations in the range from about 3 to 5 μg/L can be measured with a precision of at least 2 percent. Therefore, these concentrations are used as the peak concentrations at the downstream end of the reach in the estimation procedures.

## ESTIMATING THE GAS QUANTITIES

Estimating the quantity of tracer gas required for a modified technique measurement of the reaeration coefficient of a stream requires the use of equations 5, 7, and 4. In equation 5 the variables $x$, $U$, $D$, $K_T$, and $H$ can be estimated from the hydraulic and geometric properties of the stream, and $C_{G_M}$ is arbitrarily set at 1.0 µg/L as discussed previously. The remaining variables are $C_{G_O}$, $\tau$, and $t_M$ which is a function of $\tau$ as given by equation 4. Because equation 5 cannot be solved explicitly for $\tau$, the procedure adopted has been to set the value of $\tau$ based on the stream discharge and then to compute $C_{G_O}$ from equations 5 and 4. This value of $C_{G_O}$ is used in equation 7 with the stream discharge and the estimated efficiency of the absorption process to compute the required flow rate of the tracer gas through the diffusers. Finally, the product of this flow rate and the duration of the injection period gives the quantity of gas required.

It is immediately apparent that the objective of the experiment, the tracer gas desorption coefficient, must actually be estimated before the experiment to permit a calculation of the quantity of tracer gas required. Procedures for estimating this coefficient are available, however. Also equation 5 is a one-dimensional equation and thus $C_{G_O}$ computed from this equation is the concentration at the upstream end of the reach uniformly mixed over the width of the stream. The tracer gas is injected, however, only over a part of the width and thus the actual concentration in the stream at the injection point is larger than it would be, if the tracer gas were uniformly distributed over the channel width. This results in a somewhat larger desorption rate initially because the driving force for desorption is the concentration difference between the water and the air. However, in small streams, lateral dispersion is relatively rapid, and thus it is expected that this larger initial desorption rate would have relatively little effect on the tracer gas concentration that is ultimately attained in the stream water.

Procedures for estimating the various variables in equations 5 and 7 are given in the following paragraphs. These estimated variables, however, are subject to error, and it is necessary to have some indication of the effect of these errors on the computed values. The gas flow rate computed from equation 7 is directly proportional to the discharge and the gas concentration at the injection site, and inversely proportional to the efficiency of the absorption process. Thus, errors in these variables directly or inversely affect the computed gas flow rate, and a special error analysis is not necessary. With equation 5, however, the effect of errors in the variables on the computed tracer gas concentration at the injection site is not readily apparent. Therefore, an analysis of the effect of errors in the estimated variables in equation 5 is presented in the following paragraphs also.

Four BPS (basic parameter sets) were designed for use in the error analysis. Values were arbitrarily assumed for the tracer gas desorption coefficient, the dispersion coefficient, and the mean velocity that would approximately cover the range of these parameters that might be encountered in streams with discharges less than 8.5 $m^3/s$. No attempt was made to fit these assumed values to predictive equations for the reaeration coefficient, primarily because other variables such as the depth of flow required by these equations are not necessary in the present analysis. Use was made, however, of the fact that the various predictive equations (Bennett and Rathbun, 1972) suggest that the reaeration coefficient, and consequently, the tracer gas desorption coefficient, increases as the longitudinal dispersion coefficient and the mean velocity increase. Thus, combinations of large desorption coefficients and small longitudinal dispersion coefficients and small mean velocities were not considered. Reach lengths and injection periods were those that would commonly be used in a modified technique measurement of the reaeration coefficient. Short reaches were used for the large desorption coefficients to insure that sufficient tracer gas remained for measurement at the downstream end of the reach. A short reach was also used for the small velocity experiment to permit completion of the study within a reasonable time period. A downstream peak concentration of the tracer gas of 1.0 μg/L was used, and the tracer gas concentration at the injection site was computed from equation 5. The algorithm presented by Carslaw and Jaeger (1959) for small values of the argument of the error function was used in evaluating these functions. The BPS are presented in table 1.

Table 1.--Basic parameter sets used in the error analysis of equation 5

| BPS no. | $K_T$ [days$^{-1}$] | $D$ [$m^2$/min] | $U$ [m/min] | $x$ [m] | $\tau$ [min] | $C_{G_O}$ [μg/L] |
|---|---|---|---|---|---|---|
| 1 | 30 | 2,500 | 30 | 4,000 | 90 | 17.0 |
| 2 | 10 | 1,000 | 15 | 5,000 | 90 | 15.9 |
| 3 | 3.0 | 400 | 7.5 | 6,000 | 90 | 15.5 |
| 4 | 1.0 | 200 | 4 | 3,000 | 90 | 6.37 |

## Tracer Gas Desorption Coefficient, $K_T$

Numerous predictive equations (Rathbun, 1977) can be used to estimate the reaeration coefficient of a stream, and this reaeration coefficient can then be converted to desorption coefficients for ethylene and propane using equations presented by Rathbun and others (1978). Most of these predictive equations require the mean velocity and mean depth of flow, although a few also require the slope. These equations give a large range of predicted coefficients for a specific set of hydraulic conditions. Rathbun and Grant (1978) found that reaeration coefficients predicted with 19 equations for two reaches each of two Wisconsin streams had ranges varying from about 600 percent for one reach to almost 1100 percent for another reach. Some of this variation can be reduced by using an equation developed from data on a stream with hydraulic characteristics similar to the reach for which the reaeration coefficient is being measured. However, large variations in predicted coefficients should still be expected.

If velocity and depth data are not available, there are two predictive equations requiring only the slope, and this usually can be determined from a topographic map. It will be assumed in this report that steady uniform flow conditions exist so that the channel slope and the slope of the energy gradient are equal. The equation of Foree (1976) has the form

$$K_2 = 0.27 + 4940\, S^{1.2} \tag{9}$$

and the equation of Tsivoglou and Neal (1976) has the form

$$K_2 = 3130\, S \tag{10}$$

where $K_2$ is the reaeration coefficient on a natural logarithm base in days$^{-1}$ at 20°C and $S$ is the channel slope in meters per meter. The Tsivoglou and Neal equation (1976) is valid for discharges between 0.57 and 86 $m^3/s$. Reaeration coefficients predicted by these equations are plotted in figure 1 as a function of the channel slope. These equations are probably less accurate than equations containing two or three variables describing the hydraulics of the stream, however, they do provide a means of estimating the reaeration coefficient if hydraulic data are not available.

The estimated reaeration coefficient is corrected from 20°C to the average stream water temperature using the equation

$$K_{2_\theta} = K_{2_{20}} (1.0241)^{\theta - 20} \tag{11}$$

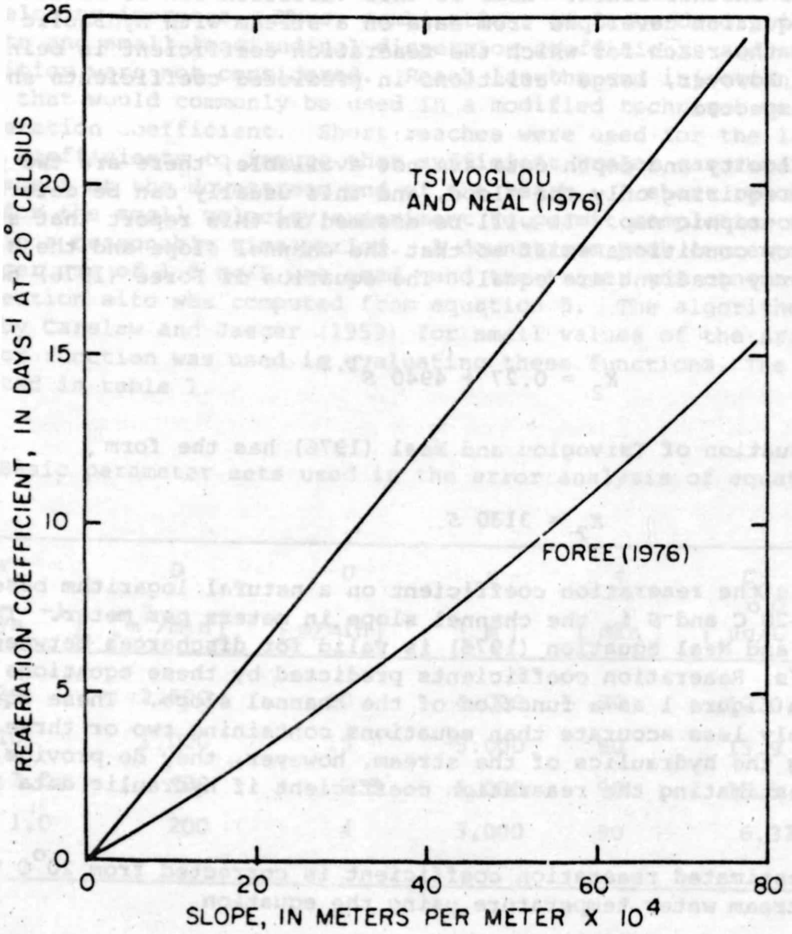

Figure 1.--Reaeration coefficients predicted with the equation of Tsivoglou and Neal (1976) and of Foree (1976) as a function of channel slope.

where $K_{2_\theta}$ is the reaeration coefficient at the stream water temperature θ, $K_{2_{20}}$ is the reaeration coefficient at 20°C, θ is the water temperature in degrees Celsius, and the 1.0241 factor was determined by Elmore and West (1961).

The tracer gas desorption coefficients are determined from the equations (Rathbun and others, 1978)

$$K_{T_E} = K_{2_\theta}/1.15 \tag{12}$$

and

$$K_{T_P} = K_{2_\theta}/1.39 \tag{13}$$

where $K_{T_E}$ and $K_{T_P}$ are the desorption coefficients for ethylene and propane, respectively.

These estimated values of the tracer gas desorption coefficients can easily be in error by several hundred percent because the reaeration coefficient cannot be estimated accurately, as discussed previously. In actuality, the need for the tracer measurement technique exists because reaeration coefficients of streams cannot be predicted with confidence. To illustrate the effect of errors in $K_T$ on $C_{G_O}$, values of $C_{G_O}$ were computed from equation 5 for the BPS presented in table 1 with the value of $K_T$ varied over a range of plus or minus 100 percent of the BPS value. The results are presented in figure 2 where the percentage error in the upstream gas concentration, $C_{G_O}$, is plotted as a function of the percentage error in the gas desorption coefficient. The percentage error in the upstream gas concentration is defined as

$$\text{percentage error} = \frac{C_{G_O} - C_{G_{O\,\text{BPS}}}}{C_{G_{O\,\text{BPS}}}} \times 100 \tag{14}$$

and the percentage error in the gas desorption coefficient is defined as

$$\text{percentage error} = \frac{K_T - K_{T\,\text{BPS}}}{K_{T\,\text{BPS}}} \times 100 \tag{15}$$

Figure 2 shows that the percentage error in the upstream gas concentration increases as the percentage error in the gas desorption coefficient increases, with the rate of increase considerably larger for overestimates of the desorption coefficient. Thus, overestimating the desorption coefficient results in overestimating the upstream gas concentration and consequently overestimating the quantity of gas to be injected. The effect of errors

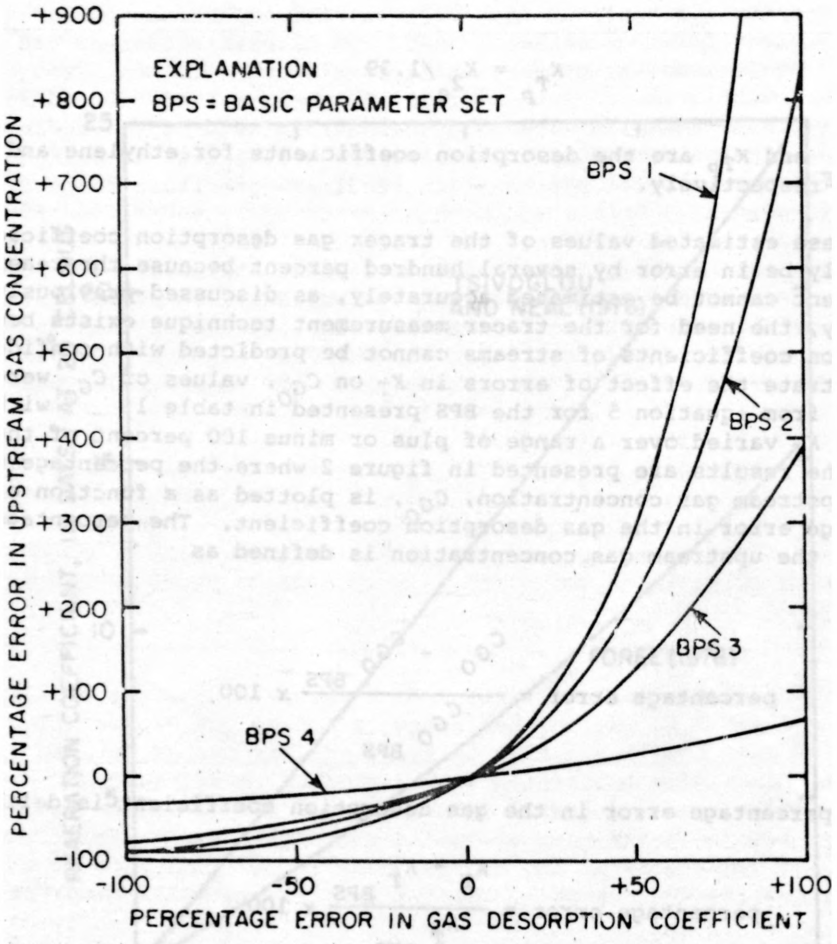

Figure 2.--Percentage error in the upstream tracer gas concentration as a function of the percentage error in the gas desorption coefficient.

in the desorption coefficient is largest for the BPS with the largest desorption coefficients. The definition of the percentage error, equation 14, requires that the percentage error in the upstream gas concentration have a limiting value of -100 percent for underestimations of the desorption coefficient because negative values of $C_{G_O}$ are impossible. In general, it is better from an experimental point of view to overestimate the desorption coefficient because this results in conservatively high values of the gas concentration in the stream. This procedure requires extra quantities of the tracer gases; however, the cost of the extra gas is insignificant compared with the cost of repeating the experiment, should an insufficient quantity of gas be injected into the stream.

## Longitudinal Dispersion Coefficient, *D*

The peak concentrations of the tracers are reduced by the effects of longitudinal dispersion as the tracer masses move downstream, and these effects are quantified by the longitudinal dispersion coefficient. This coefficient can be predicted by the method of Fischer (1968); however, this method requires considerable information. An equation requiring only the stream discharge, the slope of the energy gradient, and the channel width was presented by McQuivey and Keefer (1974). This equation which has a standard error of estimate of approximately 30 percent has the form

$$D \simeq 3.5 \frac{Q}{SB} \tag{16}$$

where $D$ is the longitudinal dispersion coefficient in $m^2$/min; $Q$ is the discharge at steady flow in $m^3$/s; $S$ is the slope of the energy gradient at steady flow in m/m; and $B$ is the channel width in meters at steady flow. Equation 16 is valid for Froude numbers less than 0.5, and this will be true for most streams at low flow conditions. The Froude number, $F$, is given by

$$F = \frac{U}{\sqrt{gY}} \tag{17}$$

where $g$ is the acceleration of gravity and $Y$ is the mean depth of flow. Other procedures for estimating the longitudinal dispersion coefficient that are applicable over the entire Froude number range include those of Jain (1976) and Liu (1977). Both are based on the development of Fischer (1967). Jain's analysis is based on the definition of an idealized cross section and Liu's analysis is based on the definition of a dimensionless lateral dispersion coefficient that is independent of stream size.

The dispersion coefficient can be measured by injecting a dye into the stream and determining the complete concentration-versus-time curves at the upstream and downstream ends of the stream reach. The dye should be injected as a line source, or the injection point should be far enough upstream of the first measurement cross section so that the dye is uniformly mixed in the cross section. It is suggested that samples be obtained at each cross section until the concentration has decreased to at least 10 percent of the peak concentration and that the experimental data then be extrapolated to a concentration equal to 1 percent of the peak concentration by assuming that the concentration decreases exponentially with time. The dispersion coefficient is then calculated according to the method of moments given by (Fischer, 1968)

$$D = \frac{u^2}{2} \, \frac{\sigma_{t_d}^2 - \sigma_{t_u}^2}{\bar{t}_d - \bar{t}_u} \tag{18}$$

where $\sigma_t^2$ is the variance of the concentration-versus-time curve; $\bar{t}$ is the time of travel of the centroid; and the $d$ and $u$ subscripts indicate the downstream and upstream ends of the reach, respectively. These quantities are defined by the equations

$$\sigma_t^2 = \frac{\int_o^{t_{0.01}} Ct^2 \, dt}{\int_o^{t_{0.01}} C \, dt} - (\bar{t})^2 \tag{19}$$

and

$$\bar{t} = \frac{\int_o^{t_{0.01}} Ct \, dt}{\int_o^{t_{0.01}} C \, dt} \tag{20}$$

where $C$ is the concentration of dye and $t_{0.01}$ is the time at which the concentration has decreased to 1 percent of the peak concentration. These integrals can be numerically evaluated by using the trapezoid rule.

To illustrate the effect of errors in the estimation of the longitudinal dispersion coefficient on the upstream gas concentration, values of $C_{G_O}$ were computed from equation 5 for the BPS presented in table 1 with the value of $D$ varied over a range of plus or minus 100 percent of the BPS value. The results are presented in figure 3 where the percentage error in the upstream gas concentration is plotted as a function of the percentage error in the longitudinal dispersion coefficient. The percentage error in the dispersion coefficient is defined analogously to equation 15.

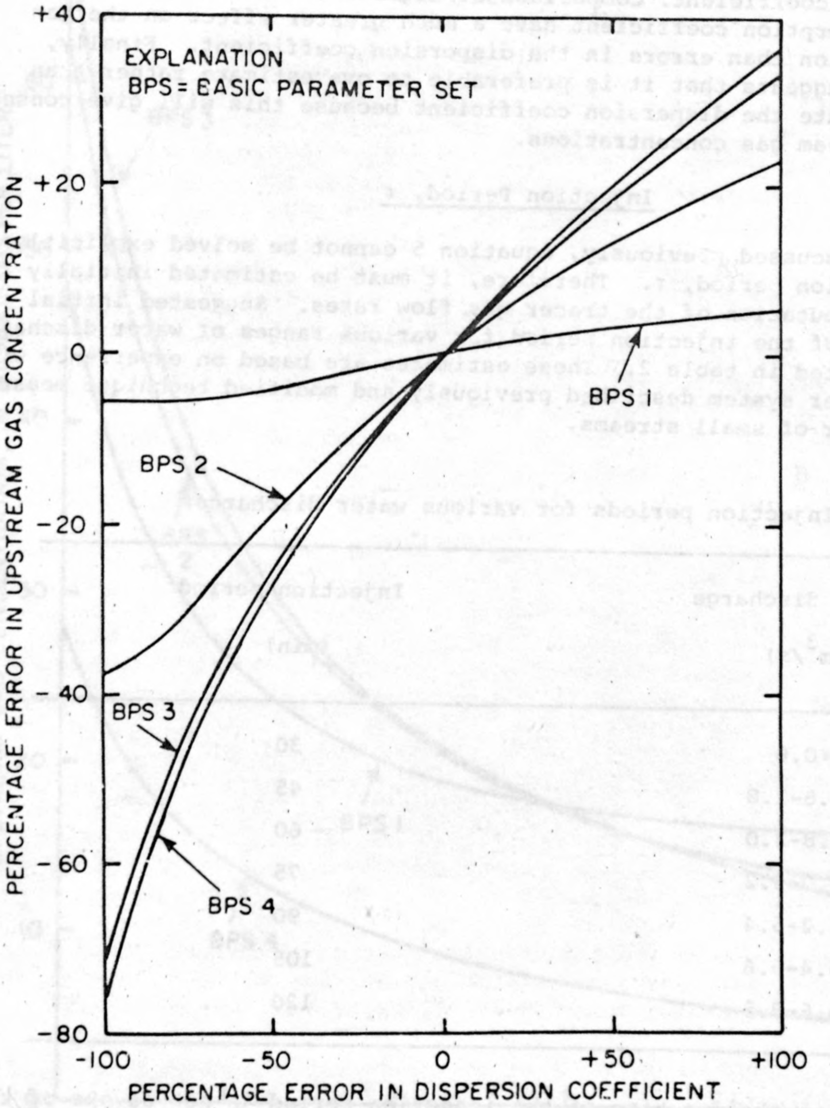

Figure 3.--Percentage error in the upstream tracer gas concentration as a function of the percentage error in the longitudinal dispersion coefficient.

Figure 3 shows that the percentage error in the upstream gas concentration increases as the percentage error in the longitudinal dispersion coefficient increases, with the rate of increase larger for underestimates of the dispersion coefficient. The effect of errors in the dispersion coefficient is largest for the BPS with the smallest dispersion coefficient. Comparison of figures 2 and 3 shows that errors in the desorption coefficient have a much greater effect on the gas concentration than errors in the dispersion coefficient. Finally, figure 3 suggests that it is preferable to overestimate rather than underestimate the dispersion coefficient because this will give conservatively high upstream gas concentrations.

## Injection Period, $\tau$

As discussed previously, equation 5 cannot be solved explicitly for the injection period, $\tau$. Therefore, it must be estimated initially to permit computation of the tracer gas flow rates. Suggested initial estimates of the injection period for various ranges of water discharges are presented in table 2. These estimates are based on experience with the diffuser system described previously and modified technique measurements on a number of small streams.

Table 2.--Injection periods for various water discharges

| Water discharge ($m^3/s$) | Injection period (min) |
|---|---|
| <0.6 | 30 |
| 0.6-1.8 | 45 |
| 1.8-3.0 | 60 |
| 3.0-4.2 | 75 |
| 4.2-5.4 | 90 |
| 5.4-6.6 | 105 |
| 6.6-8.5 | 120 |

Because the duration of the injection period is set as one of the conditions of the experiment, it will be subject to virtually no error, and an error analysis is not necessary. However, values of the upstream gas concentration were calculated for the BPS given in table 1 to illustrate the effect of varying the duration of the injection period. The results are presented in figure 4 where the upstream gas concentration is plotted as a function of the injection period. These upstream gas concentrations

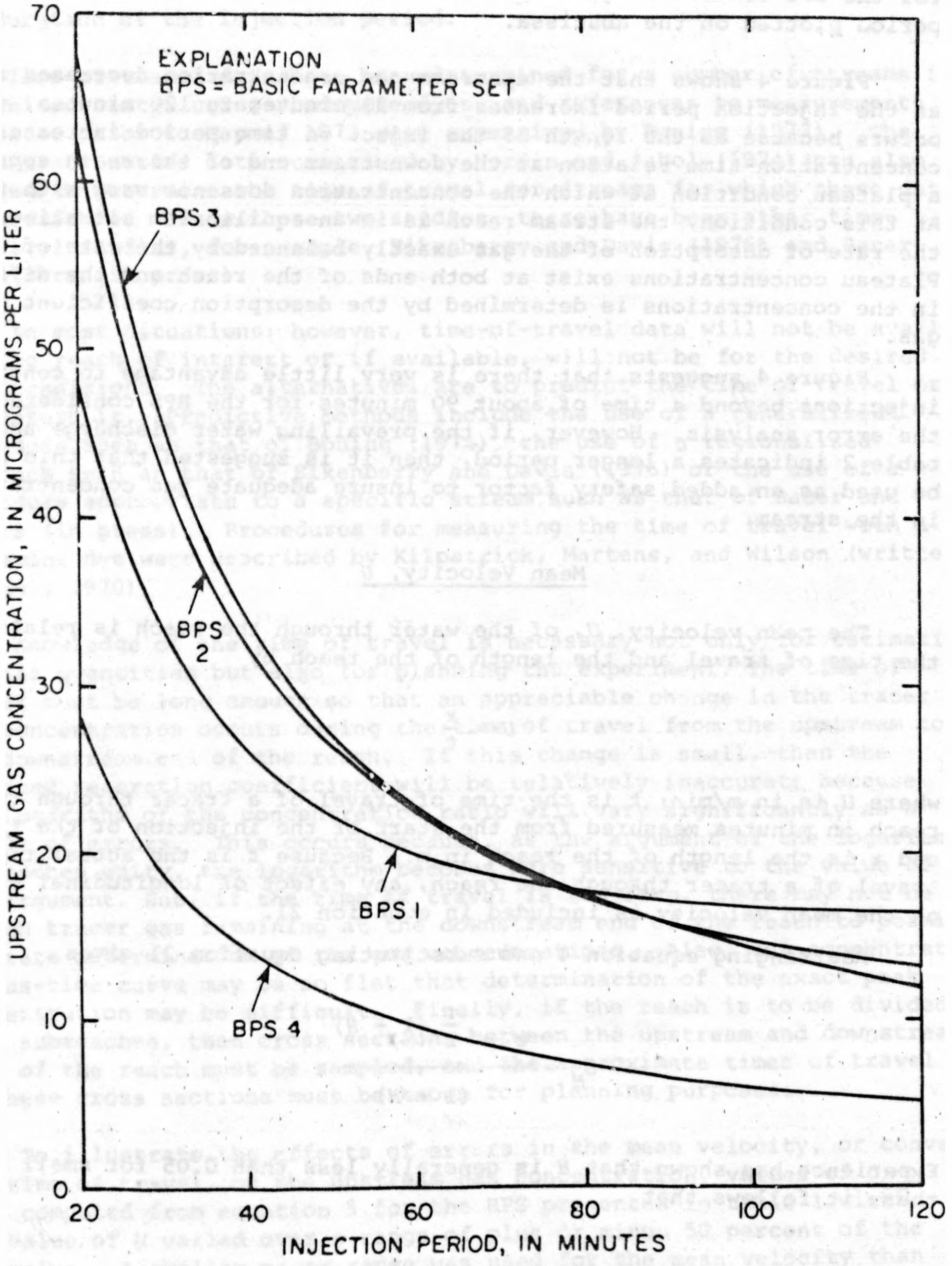

Figure 4.--Upstream tracer gas concentration as a function of the injection period.

are those necessary to give a downstream peak concentration of 1.0 µg/L for the BPS conditions given in table 1 and the corresponding injection period plotted on the abscissa.

Figure 4 shows that the upstream gas concentration decreases rapidly as the injection period increases from 20 minutes to 120 minutes. This occurs because as the length of the injection time period increases, the concentration-time relation at the downstream end of the reach approaches a plateau condition at which the concentration does not vary with time. At this condition, the stream reach is in an equilibrium situation with the rate of desorption of the gas exactly balanced by the rate of injection. Plateau concentrations exist at both ends of the reach and the difference in the concentrations is determined by the desorption coefficient of the gas.

Figure 4 suggests that there is very little advantage to continuing injections beyond a time of about 90 minutes for the BPS considered in the error analysis. However, if the prevailing water discharge and table 2 indicates a longer period, then it is suggested that this period be used as an added safety factor to insure adequate gas concentrations in the stream.

## Mean Velocity, $U$

The mean velocity, $U$, of the water through the reach is related to the time of travel and the length of the reach by

$$U = \frac{x}{t} \tag{21}$$

where $U$ is in m/min; $t$ is the time of travel of a tracer through the reach in minutes measured from the start of the injection of the tracer; and $x$ is the length of the reach in m. Because $t$ is the actual time of travel of a tracer through the reach, any effect of longitudinal dispersion on the mean velocity is included in equation 21.

Rearranging equation 4 and substituting equation 21 gives

$$t_M = \frac{t + \frac{\tau}{2}(1 + H)}{(1 + H)} \tag{22}$$

Experience has shown that $H$ is generally less than 0.05 for small streams; thus, it follows that

$$t_M \approx t + \frac{\tau}{2} \tag{23}$$

Equation 23 shows that the time of travel to the downstream end of the reach of the peak concentration of a tracer injected for $\tau$ minutes is approximately equal to the time of travel through the reach plus half the duration of the injection period.

Time-of-travel data have been determined for a number of streams in the United States using rhodamine dyes, and references to measurements completed prior to May of 1973 were summarized by Boning (1973). The concentration-time data summarized by Nordin and Sabol (1974) can also be used to determine the time of travel for streams for which these data are available. Since these two studies, there have been other time-of-travel studies, for example, Eikenberry and Davis (1976) and Bauer and others (in press).

In most situations, however, time-of-travel data will not be available for the reach of interest or if available, will not be for the desired flow conditions. The alternatives are to predict the time of travel or to measure it. Predictive methods include the use of a generalized procedure such as that of Boning (1974), the use of a regionalized approach such as that of Eikenberry and Davis (1976) or the use of a procedure appropriate to a specific stream such as that of Bauer and others (in press). Procedures for measuring the time of travel with a rhodamine dye were described by Kilpatrick, Martens, and Wilson (written commun., 1970).

Knowledge of the time of travel is necessary not only for estimating the gas quantities but also for planning the experiment. The time of travel must be long enough so that an appreciable change in the tracer gas concentration occurs during the time of travel from the upstream to the downstream end of the reach. If this change is small, then the computed reaeration coefficient will be relatively inaccurate because the logarithm of the concentration ratio will vary significantly as a result of errors. This occurs because, as the argument of the logarithm approaches unity, the logarithm becomes more sensitive to the value of the argument. But, if the time of travel is too long, there may not be enough tracer gas remaining at the downstream end of the reach to permit accurate determination of the gas concentrations. Also, the concentration-versus-time curve may be so flat that determination of the exact peak concentration may be difficult. Finally, if the reach is to be divided into subreaches, then cross sections between the upstream and downstream ends of the reach must be sampled, and the approximate times of travel to these cross sections must be known for planning purposes.

To illustrate the effects of errors in the mean velocity, or conversely the time of travel, on the upstream gas concentration, values of $C_G^O$ were computed from equation 5 for the BPS presented in table 1 with the value of $U$ varied over a range of plus or minus 50 percent of the BPS value. A smaller error range was used for the mean velocity than for the gas desorption coefficient and the longitudinal dispersion coefficient because the mean velocity will generally be known more accurately than the desorption and dispersion coefficients. The length of the reach, $x$, is assumed to be accurately known, thus errors in the mean velocity and the time of travel will in general have inverse effects on the upstream tracer gas concentration.

The results are presented in figure 5 where the percentage error in the upstream gas concentration is plotted as a function of the percentage error in the mean velocity. The percentage error in the velocity is defined analogously to equation 15.

Figure 5 shows that the percentage error in the upstream gas concentration decreases as the percentage error in the mean velocity increases, with the rate of decrease considerably larger for underestimates of the velocity. The effect of errors in the velocity is largest for the BPS with the largest desorption coefficients. Comparison of figures 2 and 5 shows that errors in the velocity produce errors in the upstream gas concentration considerably larger than errors in the desorption coefficient produce. Figure 5 suggests that if there is any doubt about the values of the velocity, it is preferable to underestimate the mean velocity because this will give conservatively high values of the upstream gas concentration in the stream.

## Absorption Efficiency, $\varepsilon$

The efficiency of the absorption process, $\varepsilon$, is defined as the ratio of the quantity of gas that actually dissolves in the stream water to the quantity of gas passing through the diffusers. The value of $\varepsilon$ depends on a combination of variables including the depth and velocity of flow at the injection point, the water temperature, and the flow rate of the gas through the diffuser. The porosity of the diffusers is also important. However, because this report is based only on the diffuser system described previously, porosity will not be considered as a variable. No attempt has been made to optimize the absorption process because the tracer gases are inexpensive, and only small amounts are needed. Therefore, only approximate values of $\varepsilon$ for ethylene and propane are available. Guidelines for estimating these efficiencies are given in the following paragraphs.

Table 3 lists the four variables which affect the efficiency of the absorption process and assigns a positive, average, or negative effect to each for a range of the variable. The positive values represent conditions for which the absorption is better than average, and the negative values represent conditions for which the absorption is worse than average. These are qualitative estimates based on experience with the technique and the diffuser system described previously. The desired quantity, the tracer gas flow rate, must actually be estimated beforehand to provide one of the variables, $\varepsilon$, needed in computing the gas flow rate. Therefore, it is suggested that the middle range of flow rates be used for this purpose because the actual values used will be within this range for most experiments. Table 3 shows that the slower the gas flows through the diffuser, the more efficient is the absorption process. But despite the improved absorption efficiency, the quantity of gas obtained in solution may be too small if the flow rate is too small. There must be a balance between these factors.

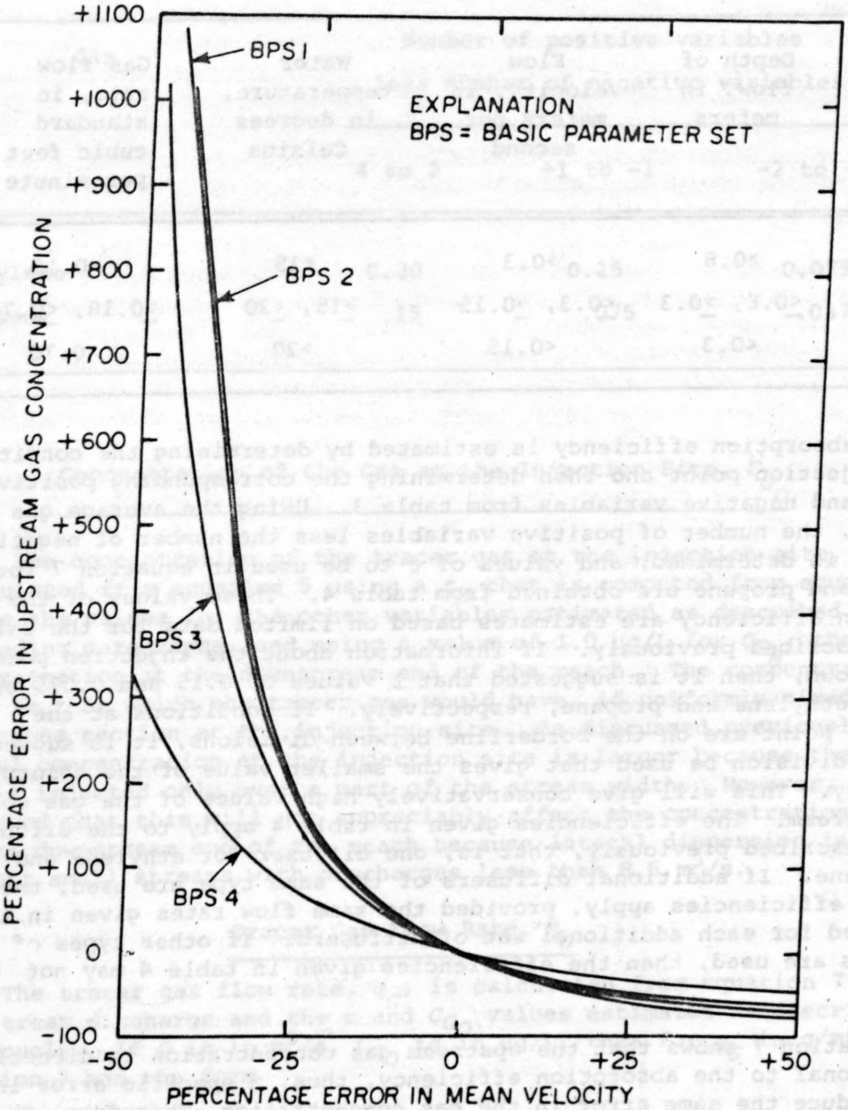

Figure 5.--Percentage error in the upstream tracer gas concentration as a function of the percentage error in the mean velocity.

Table 3.--Variables and ranges of the variables having positive, average, and negative effects on the efficiency of the absorption process

| Effect on absorption efficiency | Depth of flow, in meters | Flow velocity, in meters per second | Water temperature, in degrees Celsius | Gas flow rate, in standard cubic feet per minute |
|---|---|---|---|---|
| Positive | >0.8 | >0.3 | <15 | <0.18 |
| Average | ≤0.8, ≥0.3 | ≤0.3, ≥0.15 | ≥15, ≤20 | ≥0.18, ≤0.70 |
| Negative | <0.3 | <0.15 | >20 | >0.70 |

The absorption efficiency is estimated by determining the conditions at the injection point and then determining the corresponding positive, average, and negative variables from table 3. Using the average gas flow rate, the number of positive variables less the number of negative variables is determined, and values of ε to be used in equation 7 for ethylene and propane are obtained from table 4. These values of the absorption efficiency are estimates based on limited data for the diffuser system described previously. If information about the injection point is not known, then it is suggested that ε values of 0.15 and 0.075 be used for ethylene and propane, respectively. If conditions at the injection point are on the borderline between divisions, it is suggested that the division be used that gives the smaller value of the absorption efficiency. This will give conservatively high values of the gas concentrations in the stream. The efficiencies given in table 4 apply to the diffuser system described previously, that is, one diffuser for ethylene and two for propane. If additional diffusers of the same type are used, then the same efficiencies apply, provided the same flow rates given in table 3 are used for each additional set of diffusers. If other types of diffusers are used, then the efficiencies given in table 4 may not apply.

Equation 7 shows that the upstream gas concentration is directly proportional to the absorption efficiency, thus, a specific error in ε will produce the same error in the gas concentration. Therefore, no special error analysis is presented for ε.

Table 4.--Absorption efficiencies for the injection of ethylene and propane

| Gas | Absorption efficiency<br>Number of positive variables<br>less number of negative variables<br>4 to 2 | <br><br><br>+1 to -1 | <br><br><br>-2 to -4 |
|---|---|---|---|
| Ethylene | 0.30 | 0.15 | 0.075 |
| Propane | .15 | .075 | .0375 |

## Concentration of the Gas at the Injection Site, $C_{G_O}$

The concentration of the tracer gas at the injection site, $C_{G_O}$, is calculated from equation 5 using a $t_M$ that is computed from equation 4, using the values for the other variables estimated as described in preceding paragraphs, and using a value of 1.0 μg/L for $C_{G_M}$, the peak concentration at the downstream end of the reach. The concentration, $C_{G_O}$, is that which the tracer gas would have, if uniformly mixed over the cross section at the injection site. As discussed previously, the actual concentration at the injection site is larger because the tracer gas is injected only over a part of the stream width. However, it is believed that this will not appreciably affect the concentrations obtained at the downstream end of the reach because lateral dispersion is rapid in most small streams with discharges less than 8.5 $m^3/s$.

## Tracer Gas Flow Rate, $q_G$

The tracer gas flow rate, $q_G$, is calculated from equation 7 with the stream discharge and the ε and $C_{G_O}$ values estimated as described previously. If $Q$ is in $m^3/s$, $C_{G_O}$ is in μg/L, then for $q_G$ in g/min, equation 7 has the form

$$q_G = \frac{0.0600\ C_{G_O}\ Q}{\varepsilon} \qquad (24)$$

The calculation of $C_{G_O}$ and $q_G$ is done for both ethylene and propane, if the two tracer gases are to be used simultaneously.

The tracer gas flow rates calculated from equation 24 are in grams/minute and most rotameters presently available are calibrated in terms of standard cubic feet per minute (std. $ft^3$/min), or standard cubic feet per hour (std. $ft^3$/h) of air where standard conditions are 1 atmosphere and 70°F (21°C). A flow rate of ethylene measured with a rotameter calibrated in terms of air can be taken directly as the ethylene flow rate because the molecular weights of ethylene and air are virtually the same. With propane, however, a correction equal to the square root of the ratio of the molecular weights, or 0.81 for air-propane (Hall, 1951) must be applied. Thus, a flow rate of propane measured with a rotameter calibrated in terms of air must be multiplied by 0.81 to obtain the propane flow rate.

These procedures assume that the ethylene and propane are metered at standard conditions of 70°F and 1 atmosphere. The pressure drop through the diffusers, tubing, and rotameters is small, therefore, the pressure at which the gases are metered needs to be only slightly larger than atmospheric. A gauge pressure of 138 kPa which is equal to 20 $lb/in^2$ is suggested. The temperature at which the gases are metered is undoubtedly considerably less than 70°F because of the cooling effect of the expanding gas. Consideration of a nomograph presented in the Fischer and Porter Catalog No. 10A 1000-73 (1963) shows that a temperature change from 70°F to 30°F (21°C to -1°C) has an insignificant effect on the flow rates, and a temperature change from 70°F to -60°F (21°C to -51°C) increases the flow rates about 10 percent relative to the rates at 70°F. Because the effect is small and because the exact temperature at which the gases are metered is not known, it is suggested that the rates at standard conditions of 70°F and 1 atmosphere be used without correction. This is a conservative procedure because the actual gas flow rates at the lower temperatures are larger than predicted.

The mass flow rates computed from equation 24 are converted to volumetric flow rates using properties of perfect gases. For ethylene, the volumetric flow rate, $V_E$, in standard $ft^3$/min at 70°F and 1 atmosphere is given by

$$V_E = 0.0304\, q_{G_E} \tag{25}$$

where $q_{G_E}$ is the ethylene flow rate in grams/minute, and for propane,

$$V_p = 0.0193\, q_{G_P} \tag{26}$$

where $q_{G_P}$ is the propane flow rate in grams/minute. Thus, in an experiment, the ethylene flow rate is set at an air equivalent rate equal to the rate computed from equation 25, and the propane flow rate is set for an air equivalent rate equal to the rate computed from equation 26 divided by 0.81. Equations 25 and 26 are given in terms of standard $ft^3$/min rather than metric units because commercially available rotameters are usually supplied with standard $ft^3$/min calibrations. If calibrations in terms of liters/minute are provided, then the constants in equations 25 and 26 are 0.861 and 0.547, respectively.

In theory, any ethylene and propane flow rate can be used. In practice, however, it has been found that the propane rate must be limited or freezing may occur in the system with a resultant reduction in the flow rate. This condition depends on a combination of the gas flow rate, the length of the injection period, and to some extent, the ambient air temperature. Thus, it is not possible to specify one maximum flow rate, however, flow rates higher than about 0.6 std ft$^3$/min of propane for injection periods longer than 60 minutes should be used with caution. If higher flow rates are needed, then it is suggested that a dual cylinder-regulating value arrangement be used so that a switch can be made quickly to the second cylinder if problems occur. This freezing problem seems to occur more readily with the small-size cylinders and also when the cylinders are nearly empty.

No difficulties have been experienced with the injection of the ethylene, although during long injections, the regulating valve frequently becomes coated with frost. Maximum flow rates used have been about 0.5 std ft$^3$/min. If the computations suggest flow rates more than twice this value, then the computations should be repeated with a longer injection time.

There is one additional problem in the use of the propane. Because propane is supplied as a liquefied gas, the pressure in the cylinder is the vapor pressure of the liquid for the prevailing temperature, regardless of the quantity of propane in the cylinder. Thus, the regulating valve pressure gage provides no indication of how much propane is used during an experiment or how much remains in the cylinder. This can be determined, however, by weighing the cylinder before and after each experiment.

The quantities of ethylene and propane required for an experiment can be determined from the tracer gas flow rates calculated from equation 24 and the injection time period. Thus

$$w_E = q_{G_E} \tau/1000 \tag{27}$$

and

$$w_P = q_{G_P} \tau/1000 \tag{28}$$

where $w_E$ and $w_P$ are the weights required in kilograms of ethylene and propane, respectively. Technical grade ethylene is generally used, and it is commonly supplied in 13.6-kg amounts in a cylinder having a gross weight of 68.0 kg. This size of cylinder can usually be handled conveniently, and it contains sufficient ethylene for a number of measurements. If the injection point is some distance from the nearest road, then a smaller cylinder such as the one containing 2 kg would be more convenient. This cylinder will contain sufficient ethylene for only one or two measurements. Natural or CP grade propane is generally used, and it is commonly supplied in 45.4-kg amounts in a cylinder having a gross weight of about 80 kg. If a smaller cylinder is desired for ease in handling, then cylinders containing 15.9, 6.4, 4.1, and 2.3 kg are available from various suppliers. If small cylinders are used, then the problem with freezing discussed previously should be noted. Other sizes of cylinders may be available from some gas suppliers.

Finally, a word of caution regarding the use of ethylene and propane is necessary. These gases are flammable and explosive, and smoking and open flames should be avoided in the area of the injection apparatus and at the point in the stream above the diffusers where unabsorbed gases leave the water and enter the atmosphere. The gases have odors and therefore, leaks in the system are readily detected and corrected. Once the gases are absorbed in the water and mixed in the stream, there is no hazard because the concentrations are so small. Also, the usual precautions in handling high pressure gas cylinders should be observed. These include tying down the cylinders securely when they are in use and replacing the cylinder caps whenever moving the cylinders.

### Water Discharge, $Q$

The final variable that must be determined is the discharge of the stream. This is the quantity of water into which the tracers are mixed to give the concentrations at the injection site. The water discharge can vary over the length of a stream reach as a result of two types of change. First, the discharge can increase in the downstream direction as a result of tributary inflow or flow accrual as a result of surface runoff or ground-water inflow. All these changes would reduce the concentrations of the tracers because of the dilution effect. Second, the discharge can decrease in the downstream direction as a result of a flow diversion or flow loss as a result of seepage. Neither of these changes would affect the concentrations of the tracers, provided the tracers were uniformly mixed in the flow before the diversion or seepage loss. It follows, however, that for either type of reach the maximum water discharge should be used in estimating the gas quantities to insure that the desired concentration of tracer gas is attained in the stream water. In the first situation, this is the discharge at the downstream end of the reach and in the second situation, this is the discharge at the upstream end of the reach before the flow losses occur.

Equation 7 shows that the upstream gas concentration is inversely proportional to the water discharge. Thus, the effect on the upstream gas concentration of an error in $Q$ is easily determined.

## ESTIMATING THE DYE QUANTITIES

A rhodamine-WT dye and water solution is injected into the stream for the same time period that the tracer gases are injected. Therefore, the variables describing the dye injection must be estimated also.

The concentration of the dye solution to be injected can be calculated from equation 8. Rearranging this equation and adding a constant to correct the units gives

$$C_{D_I} = \frac{60.0 \times 10^6\, C_{D_O}\, Q}{q_D} \qquad (29)$$

where $C_{D_I}$ and $C_{D_O}$ are in µg/L; $Q$ is in $m^3/s$; and $q_D$ is in mL/min. A mass balance requires that the volume, $V_D$, in mL of rhodamine-WT dye injected during a time period $\tau$ be given by

$$V_D = \frac{q_D\, \tau\, C_{D_I}}{C_{WT}} \qquad (30)$$

where $\tau$ is in minutes and $C_{WT}$ is the concentration in µg/L of 20 percent by weight rhodamine-WT dye as supplied by the manufacturer. Combining equations 29 and 30 gives

$$V_D = \frac{60.0 \times 10^6\, C_{D_O}\, Q\tau}{C_{WT}} \qquad (31)$$

This equation was obtained previously by Cobb and Bailey (written commun., 1965) for determining the quantity of dye required to make a discharge measurement by the dye-dilution procedure. In this procedure, the dye injection is continued long enough to give a plateau concentration at the measurement cross section. Thus, assuming no losses of the dye, the concentration of dye in the stream at the injection cross section, $C_{D_O}$, and the concentration at the measurement cross section are the same. Cobb and Bailey (written commun., 1965) suggest using 10 µg/L for $C_{D_O}$, and $C_{WT}$ is taken as 23.8 x $10^7$ µg/L.

Equation 31 with a value of 10 µg/L for $C_{D_O}$ has been used to estimate the quantity of dye needed for modified technique measurements of the reaeration coefficient. This has resulted in smaller peak concentrations at the downstream end of the reach because the injection of dye has never been continued long enough to give a plateau concentration at this cross section. For most of the injection times and times of travel encountered in modified technique measurements, the downstream peak dye concentrations have ranged from about 3 to 7 µg/L. These concentrations can be accurately and conveniently measured with fluorometric techniques referenced earlier. In applying equation 31, the water discharge used should be the largest observed in the reach of interest, for the same reasons discussed previously in estimating the gas quantities.

An alternative to simply specifying the value of $C_{D_O}$ in equation 31 is to compute from equations 4 and 5 the value of $C_{D_O}$ required to give a particular peak concentration of dye at the downstream end of the reach, as was done for the tracer gases. For dye, the desorption coefficient and $H$ are zero, assuming that the dye is conservative. Some dye loss does occur, however, the loss is generally small relative to the loss of gas. Thus, equation 5 becomes

$$C_{D_M} = \frac{C_{D_O}}{2}\left[\operatorname{erf}\frac{x - U(t_M - \tau)}{\sqrt{4D(t_M - \tau)}} - \operatorname{erf}\frac{x - Ut_M}{\sqrt{4Dt_M}}\right] \tag{32}$$

where $C_{D_M}$ is the peak concentration of dye in µg/L at the downstream end of the reach and $C_{D_O}$ is the concentration of dye in µg/L at the injection site. It is suggested that a value of 4 µg/L be used for $C_{D_M}$. The value of $C_{D_O}$ computed from equation 32 is used in equation 31 to compute the volume of dye required.

The procedure of using equation 31 with an arbitrary value for $C_{D_O}$ is easier to apply, however, this procedure does not consider the effects of longitudinal dispersion. The use of equation 32 to compute $C_{D_O}$ is more exact and should be used when estimates of the dispersion coefficient and time of travel are available. If these estimates are not available, then equation 31 can be used.

The volume of water, $V_W$, to be mixed with the volume of the dye estimated from equation 31 is calculated from the length of the injection period, $\tau$, and the flow rate of the device used to inject the dye-water solution. If $q_D$ is the injection rate of the dye-water solution in mL/min, then

$$V_W = q_D\tau - V_D \tag{33}$$

where $V_W$ is the volume of water in mL.

An excess of the dye-water solution should be prepared. If a metering pump is used to inject the solution, then the excess has to be large enough only to provide a small sample of the solution for analysis at a later time. If a Mariotte vessel is used to inject the solution, a larger excess must be prepared because the solution below the tip of the air-vent tube cannot be injected without a change in the flow rate. The volume of this excess will depend on the design of the particular Mariotte vessel in use. Details of the design and operation of Mariotte vessels were presented by Cobb (1967). A small allowance should also be made for the fact that a dye loss of about 10 to 20 percent will probably occur in the stream during the measurement.

## EXAMPLE

To demonstrate the use of the equations, an example is presented in which data from a measurement of the reaeration coefficient are used to compute the injection quantities. The computed quantities are then compared with those actually used in the measurement. Data are from a measurement on a reach of Black Earth Creek near Mazomanie, Wisconsin, and this measurement was described by Rathbun and Grant (1978). Mean properties of the overall reach are as follows:

$$
\begin{aligned}
x &= 8300 \text{ m} \\
U &= 19.2 \text{ m/min} \\
S &= 0.000788 \text{ m/m} \\
Q &= 1.12 \text{ m}^3\text{/sec} \\
B &= 7.6 \text{ m} \\
K_2 &= 9.14 \text{ days}^{-1} \text{ at } 20^{\circ}\text{C} \\
\theta &= 22.4^{\circ}\text{C} \\
Y &= 0.29 \text{ m}
\end{aligned}
$$

where the variables have been defined previously. Steps in the procedure are as follows:

(1) Estimate the reaeration coefficient using one or more of the predictive equations from the literature. For the data of the example, reaeration coefficients predicted with the 19 equations evaluated by Rathbun (1977) ranged from 3.42 to 26.3 days$^{-1}$ at 20°C, and coefficients predicted with equations 9 and 10 were 1.20 and 2.47 days$^{-1}$ at 20°C, respectively. For the example, the measured value of 9.14 days$^{-1}$ at 20°C will be used, and the consequence of using the predicted values will be discussed later.

(2) Correct the reaeration coefficient to the expected mean water temperature using equation 11.

$$K_{2_{22.4}} = (9.14)(1.0241)^{22.4 - 20}$$

$$= 9.68 \text{ days}^{-1}$$

(3) Compute the desorption coefficients for ethylene and propane from equations 12 and 13.

$$K_{T_E} = 9.68/1.15 = 8.42 \text{ days}^{-1}$$

$$K_{T_P} = 9.68/1.39 = 6.96 \text{ days}^{-1}$$

(4) Estimate the dispersion coefficient from equation 16.

$$D = (3.5)(1.12)/(0.000788)(7.6)$$

$$= 655 \text{ m}^2\text{/min}$$

Estimate the Froude number from equation 17.

$$F = 19.2/\sqrt{(35,300)(0.29)}$$

$$= 0.190$$

where 35,300 is the acceleration of gravity in $m/min^2$. Because the Froude number is less than 0.5, the use of equation 16 is valid.

(5) Estimate the length of the injection period from the water discharge and table 2.

$$\text{For } Q = 1.12\ m^3/s,\ \tau = 45\ \text{min}$$

The actual injection period used was 55 min to be conservative, therefore, use this value in the calculations.

(6) Compute the time of travel of the peak concentrations of the tracer gases and the dye to the downstream end of the reach from equations 21 and 22.

$$\text{For ethylene, } H = (2)(8.42)(655)/(19.2)^2(1440) = 0.0208$$

$$\text{For propane, } H = (2)(6.96)(655)/(19.2)^2(1440) = 0.0172$$

where 1440 is the factor converting days to minutes.

$$\text{For ethylene, } t_{M_E} = \frac{(8300/19.2) + (55/2)(1.0208)}{1.0208}$$

$$= 451\ \text{min}$$

$$\text{For propane, } t_{M_P} = \frac{(8300/19.2) + (55/2)(1.0172)}{1.0172}$$

$$= 452\ \text{min}$$

$$\text{For dye, } t_{M_D} = (8300/19.2) + (55/2)$$

$$= 460\ \text{min}$$

(7) Compute $C_{G_M}/C_{G_O}$ for ethylene and propane from equation 5. Similarly, compute $C_{D_M}/C_{D_O}$ for the dye from equation 32. A table of the error function values from Carslaw and Jaeger (1959) is presented in table 5. Note also that $\text{erf}(-\Phi) = -\text{erf}(\Phi)$.

$$C_{C_M}/C_{G_O} = 1/2 \exp\left[\frac{(-8.42)(8300)}{(1440)(19.2)}\right]\left[\operatorname{erf}\frac{8300 - (19.2)(451 - 55)(1.0208)}{\sqrt{(4)(655)(451 - 55)}}\right.$$

$$\left.\operatorname{erf}\frac{8300 - (19.2)(451)(1.0208)}{\sqrt{(4)(655)(451)}}\right]$$

$$= (0.0399)\ [\operatorname{erf}\ (0.529) - \operatorname{erf}\ (-0.496)]$$

$$= (0.0399)\ [\operatorname{erf}\ (0.529) + \operatorname{erf}\ (0.496)]$$

Determining the erf terms from table 5 by linear interpolation gives

$$C_{G_M}/C_{G_O} = 0.0399\ [0.545 + 0.517]$$
$$= 0.0424$$

Similarly, for propane

$$C_{G_M}/C_{G_O} = 0.0655$$

and for dye,

$$C_{D_M}/C_{D_O} = 0.518$$

(8) For downstream peak gas concentrations of 1.00 µg/L and a downstream peak dye concentration of 7.00 µg/L, compute the concentrations at the injection site.

For ethylene, $C_{G_O} = 1.00/0.0424 = 23.6$ µg/L

For propane, $C_{G_O} = 1.00/0.0655 = 15.3$ µg/L

For dye, $C_{D_O} = 7.00/0.518 = 13.5$ µg/L

(9) Assume that the average depth of flow and the average velocity at the injection point are 0.6 m and 0.4 m/s, respectively. Assume also that the gas injection rates will be between 0.18 std ft$^3$/min and 0.70 std ft$^3$/min. The water temperature was 22.4°C; thus, from table 3, the ratings are average, positive, negative, and average and the sum of the number of positive variables less the sum of the number of negative variables is zero. From table 4, the corresponding estimated efficiencies are 0.15 and 0.075 for ethylene and propane, respectively.

Table 5.--Values of the error function from Carslaw and Jaeger (1959)

| $\phi$ | erf $\phi$ | $\phi$ | erf $\phi$ |
|---|---|---|---|
| 0 | 0 | 1.0 | 0.842701 |
| 0.05 | 0.056372 | 1.1 | .880205 |
| .1 | .112463 | 1.2 | .910314 |
| .15 | .167996 | 1.3 | .934008 |
| .2 | .222703 | 1.4 | .952285 |
| .25 | .276326 | 1.5 | .966105 |
| .3 | .328627 | 1.6 | .976348 |
| .35 | .379382 | 1.7 | .983790 |
| .4 | .428392 | 1.8 | .989091 |
| .45 | .475482 | 1.9 | .992790 |
| .5 | .520500 | 2.0 | .995322 |
| .55 | .563323 | 2.1 | .997021 |
| .6 | .603856 | 2.2 | .998137 |
| .65 | .642029 | 2.3 | .998857 |
| .7 | .677801 | 2.4 | .999311 |
| .75 | .711156 | 2.5 | .999593 |
| .8 | .742101 | 2.6 | .999764 |
| .85 | .770668 | 2.7 | .999866 |
| .9 | .796908 | 2.8 | .999925 |
| .95 | .820891 | 2.9 | .999959 |
|  |  | 3.0 | .999978 |

(10) Compute the tracer gas flow rates from equation 24.

$$q_{G_E} = \frac{(0.0600)(23.6)(1.12)}{(0.15)} = 10.6 \text{ g/min}$$

$$q_{G_P} = \frac{(0.0600)(15.3)(1.12)}{(0.075)} = 13.7 \text{ g/min}$$

(11) Compute the volumetric flow rates from equations 25 and 26.

$$V_E = (0.0304)(10.6) = 0.322 \text{ std ft}^3\text{/min}$$

$$V_P = (0.0193)(13.7) = 0.264 \text{ std ft}^3\text{/min}$$

(12) Convert the volumetric flow rates to air flow rates such as would be measured with commercially available rotameters.

For ethylene, no conversion is necessary.

For propane, the corresponding air flow rate is

$$V_{AIR} = \frac{V_P}{0.81} = \frac{0.264}{0.81} = 0.326 \text{ std ft}^3\text{/min}$$

(13) Compute the quantities of gas needed from equations 27 and 28.

$$w_E = (10.6)(55)/1000 = 0.583 \text{ kg}$$

$$w_P = (13.7)(55)/1000 = 0.754 \text{ kg}$$

(14) Compute the volume of dye needed from equation 31.

$$V_D = \frac{(60.0 \times 10^6)(55)(13.5)(1.12)}{23.8 \times 10^7}$$

$$= 210 \text{ mL}$$

(15) Assume that the Mariotte vessel used for injecting the dye-water solution has a flow rate of 70 mL/min and that 85 percent of the solution in the vessel is injected. Also assume that only 85 percent of the dye injected is actually measured because of

dye losses in the reach. Thus, the quantity of dye needed becomes

$$V_D = (210/0.85)/(0.85)$$

$$= 291 \text{ mL}$$

(16) Compute the volume of water needed from equation 33.

$$V_W = (70)(55) - 291$$

$$= 3560 \text{ mL}$$

and correcting for the fact that only 85 percent of the mixture is injected gives

$$V_W = (3560)/(0.85)$$

$$= 4190 \text{ mL}$$

The computed and actual experimental quantities are summarized in table 6. The actual observed downstream ethylene peak concentration was 1.75 µg/L compared with the value of 1.00 µg/L used in the computations. The computed ethylene flow rate was 0.322 std $ft^3$/min, and multiplying by the ratio 1.75/1.00 to correct for the difference in downstream peak concentrations gives a rate of 0.564 std $ft^3$/min, in fair agreement with the actual rate used in the experiment. The fact that a peak ethylene concentration of 1.75 µg/L was obtained with a flow rate of 0.422 std $ft^3$/min compared with the corrected computed value of 0.564 std $ft^3$/min suggests that the ethylene absorption process was somewhat more efficient than that indicated by the 0.15 factor used in Step (10). The actual observed downstream propane peak concentration was 1.86 µg/L compared with the value of 1.00 µg/L used in the computations. The computed propane flow rate was 0.264 std $ft^3$/min and multiplying by the ratio 1.86/1.00 to correct as before for the difference in downstream peak concentrations gives a rate of 0.491 std $ft^3$/min, in fair agreement with the actual rate used. The fact that a peak concentration of 1.86 µg/L was obtained with a flow rate of 0.563 std $ft^3$/min compared with the corrected computed rate of 0.491 std $ft^3$/min suggests that the propane absorption process was somewhat less efficient than that indicated by the 0.075 factor used in Step (10). Some of the differences between the computed and experimental flow rates could also be the result of an error in the estimated value of the longitudinal dispersion coefficient.

A downstream peak dye concentration of 7.00 µg/L was used in Step (8) compared with the actual observed peak concentration of 6.86 µg/L. The computed volume of dye was 291 mL compared with the actual volume of 300 mL, and the computed volume of water was 4190 mL compared with the actual volume of 4800 mL. This agreement shows that the mathematical basis presented previously is a good model of the actual stream situation.

Table 6.--Computed and experimental parameters for the Black Earth Creek measurement

| Gas | Parameter<br>Downstream concentration (µg/L) | <br>Flow rate (std ft$^3$/min) |
|---|---|---|
| Ethylene | | |
| Computed | 1.00 | 0.322 |
| Experimental | 1.75 | .422 |
| Propane | | |
| Computed | 1.00 | .264 |
| Experimental | 1.86 | .563 |

The effect of using the minimum and maximum predicted reaeration coefficients (Step (1)) was also investigated. First, the minimum predicted coefficient of 1.20 days$^{-1}$ was used to estimate the required gas quantities, then these gas quantities were used to compute what the downstream peak gas concentrations would be for these gas quantities, the same absorption efficiencies, and the actual observed reaeration coefficient. The computed peak concentrations were 0.114 and 0.166 µg/L for ethylene and propane, respectively. These concentrations are considerably smaller than the 1.00 µg/L value used as a standard for downstream sections, however, they can be accurately measured. For example, a set of 20 samples containing mean ethylene and propane concentrations of 0.145 and 0.258 µg/L, respectively, were measured with relative standard deviations of 2.28 and 2.06 percent for ethylene and propane, respectively. (D. Y. Tai, written commun., 1975). However, these concentrations are approaching the lower limit of concentrations that can be measured without special precautions in the analytical technique, and higher concentrations are desirable.

Finally, the maximum predicted coefficient of 26.3 days$^{-1}$ was used to estimate the required gas quantities, then these gas quantities were used to compute what the downstream peak gas concentrations would be for these gas quantities, the same absorption efficiencies, and the actual observed reaeration coefficient. The computed peak concentrations were

109 and 48.6 µg/L for ethylene and propane, respectively. These concentrations are much larger than necessary for precise measurement. Also, such large concentrations at the downstream end of the reach require concentrations of 2,570 and 741 µg/L of ethylene and propane, respectively, at the upstream end of the reach and concentrations this large are not attainable unless a very large number of diffusers is used. However, computation of the quantities of the gases required demonstrates an important point. These quantities are presented in table 7 for the examples of the experimental reaeration coefficient and the minimum and maximum predicted reaeration coefficients. The costs are computed from 1978 Matheson prices for technical grade ethylene in a 13.61-kg cylinder and natural grade propane in a 15.88-kg cylinder. The results presented in table 7 show that the difference in costs for a wide range of gas quantities is insignificant relative to the total cost of a reaeration coefficient measurement. This supports the point made previously that it is much better to overestimate the reaeration coefficient and thus insure adequate gas concentrations in the stream than it is to underestimate the coefficient. On the other hand, the flexibility of the analytical technique permits the analysis of a wide range of gas concentrations.

Table 7.--Quantities and costs of the tracer gases for experiments with the experimental and the minimum and maximum predicted reaeration coefficients

| | $K_2$ (days$^{-1}$) | $w_E$ (kg) | Cost (dollars) | $w_P$ (kg) | Cost (dollars) |
|---|---|---|---|---|---|
| (Experimental) | 9.14 | 0.583 | 1.50 | 0.754 | 1.18 |
| (Minimum) | 1.20 | .066 | .17 | .125 | .20 |
| (Maximum) | 26.3 | 63.3 | 162.68 | 36.5 | 57.31 |

The preceding paragraphs have outlined the variables that should be estimated and the quantities that should be computed in planning a measurement of the reaeration coefficient with the modified tracer technique. Considerable information is necessary, and in some situations, time and (or) budget limitations may preclude completing this entire analysis. In this situation, it is possible to plan a measurement on the basis of previous experience with the technique and using estimates of the water discharge and the general reaeration characteristics of the stream. The first step is to measure or estimate the water discharge and then to qualitatively estimate whether the reaeration coefficient is very large, large, intermediate, or small. These general classifications correspond qualitatively to BPS numbers 1, 2, 3, and 4, respectively, given in table 1. Streams having very large and large reaeration coefficients are characterized by many riffle sections, high velocities, and shallow flow; whereas streams having small reaeration coefficients are characterized by many pools, low velocities, and deep flow. The second step is to estimate from table 2 the length of the injection period for the estimated water discharge. It is suggested that the injection period be arbitrarily lengthened 50 percent as a safety factor for streams expected to have very large and large reaeration coefficients. The third step is to estimate the quantities of ethylene and propane required using equations 25, 26, 27, and 28 and flow rates of 0.50 and 0.58 std ft$^3$/min for ethylene and propane, respectively. Experience has shown that these rates with the diffuser system described previously and injection periods from table 2 give adequate gas concentrations for streams with discharges less than 8.5 m$^3$/s. The fourth step is to estimate the volume of dye required from equation 31, using a value of 10 µg/L for $C_{D_O}$. The final step is to estimate the length of reach in terms of time of travel that can be measured in an experiment. This will be determined somewhat by the availability of access points to the stream, but also must be limited to insure that adequate concentrations of the tracer gases remain at the downstream end of the reach. Therefore, as a general guideline, it is suggested that measurements on streams with very large and large reaeration coefficients be limited to traveltimes of about 3 and 6 hours, respectively. Measurements on streams with intermediate and small reaeration coefficients should be limited to traveltimes of 24 hours or less to facilitate accurate determination of the peak concentrations.

The procedures presented in the preceding paragraphs have the objective of obtaining certain minimum peak concentrations of the gas and dye tracers at the downstream end of the reach, namely 1.00 µg/L for the gas tracers and 4.00 µg/L for the dye tracer. These concentrations were selected because the analytical techniques used for the gases and dye permit determination of these concentrations with good precision. However, both techniques have the capability of analyzing smaller and larger concentrations, although the larger concentrations are determined more easily and with better precision. As an example, downstream peak concentrations in measurements with the modified tracer technique have ranged from an ethylene concentration of 34.0 µg/L in the Bonner Branch, Wisconsin measurement (R. S. Grant, written commun., 1977) to a propane concentration of 0.035 µg/L in one of the Yampa River, Colorado measurements (Bauer and others, in press). The downstream peak dye concentrations vary considerably less because the absorption efficiency is 100 percent, and therefore it is possible to control much more exactly the concentrations obtained in the stream. Thus, the concentrations of 1.00 µg/L for the gas and 4.00 µg/L for the dye are guidelines only; however, every effort should be made in the injection process to obtain at least these concentrations so as to obtain an accurate measurement of the reaeration coefficient.

## ESTIMATING THE QUANTITIES FOR LARGE FLOWS

Experience with the modified tracer technique on flows larger than 8.5 m$^3$/s has been limited, however, it is possible to give several general guidelines for estimating the gas and dye quantities. The mathematical basis is the same, however, the larger volume of water will require larger gas flow rates and larger dye concentrations. Therefore, several modifications to the injection process are necessary.

First, it is suggested that only one tracer gas be used and that the injection effort be concentrated on obtaining enough of this one gas in the stream for accurate measurement. Ethylene is preferred for this purpose because its solubility is about twice that of propane.

Second, the number of diffusers will have to be increased. The larger discharges will require larger ethylene flow rates, and to obtain reasonable absorption, this gas must be injected through a greater surface area. The maximum ethylene flow rates and injection periods used thus far with the single diffuser system described previously have been 0.45 std $ft^3$/min for 121 minutes and 0.51 std $ft^3$/min for 85 minutes, and no difficulties were experienced with these rates. Thus, dividing the flow rate computed as described previously by 0.51 std $ft^3$/min can be used as a first approximation of the number of diffusers required. For example, if the computations discussed previously suggest an ethylene flow rate of 2.0 std $ft^3$/min, then 2.0/0.51 or 4 diffusers would be needed. An alternative would be to use a larger gas flow rate and a smaller number of diffusers, although the absorption efficiency would probably be less for a larger gas flow rate. Ruane and others (1977) showed that the efficiency of oxygen absorption decreased for several types of diffusers as the oxygen flow rate through the diffusers increased, and the same general effect is expected for ethylene. A second alternative would be to use two or more supply cylinders and thus have several injection systems. The number of diffusers and the complexity of the injection system will depend basically on how large the discharge of the stream is.

Third, the concentration of the dye injected will have to be increased and the dye injection rate can also be increased. Limiting factors are the concentration of the 20 percent rhodamine-WT dye as supplied by the manufacturer and the maximum flow rate of the device used for injecting the dye. If injection of 20 percent rhodamine-WT dye at the maximum flow rate of the injection device is not sufficient, then a dual injection system will be necessary.

Fourth, the problem of lateral mixing becomes much more significant for large streams, and in deep, sluggish streams such as those that are tidally affected, the problem of vertical mixing may also be significant. In small streams, vertical mixing is very rapid and lateral mixing is relatively rapid. Thus, the minimum of 0.75-hour time of travel allowed between the injection site and the first measurement cross section is probably adequate to insure that the gas and dye tracers are mixed to about the same proportion in the cross section of the stream. This can be verified by obtaining several samples in the cross section of the stream. In large streams, however, complete lateral mixing will require too long a time period for practical purposes, and therefore, greater care must be exercised to insure that the gas and dye tracers are injected over the same width of the channel. One of the basic assumptions of the tracer technique is that the gas and dye tracers undergo exactly the same longitudinal, lateral, and vertical mixing. In fact, the purpose of the dye tracer is to correct the gas concentrations for the effects of mixing. Therefore, in large streams where a number of gas diffusers may be used, the dye injection should be split into multiple injections so as to cover the same width of the stream as covered by the diffusers. This may be done by splitting the output of a single dye pump or by using several pumps. If vertical mixing is expected to be a problem, then the dye should be injected below the surface of the water at the level of the diffusers. A more sophisticated injection device that would permit injecting the tracer gas and the dye together in exactly the same proportion through each diffuser would be a definite advantage. Such a device would not require any mixing zone and the tracers could be sampled at any point downstream from the injection site.

Finally, figure 4 shows for the four sets of example data used in this report that there is little advantage in continuing an injection beyond about 90 minutes. This is true for BPS 4 which has a small desorption coefficient characteristic of large streams and rivers. However, until more experiments are completed on streams with discharges larger than 8.5 $m^3/s$, it is suggested that an injection period of 120 minutes be used.

The use of the modified tracer technique on large streams and rivers requires the injection of larger quantities of the tracers. However, this is partly compensated for by two circumstances. First, the efficiency of the absorption process will probably be improved because the depth of flow will be greater, and second, the desorption coefficient, and thus loss of gas through the stream surface, will generally be considerably smaller for large streams than for small streams.

## SUMMARY AND CONCLUSIONS

The reaeration coefficient of a stream can be measured with the modified tracer technique without the use of radioactive tracers. Application of this technique is accomplished by injecting a tracer gas and a rhodamine-WT dye solution into the stream for a period of time. For streams with discharges less than about 8.5 $m^3/s$, ethylene and propane are used as tracer gases. Use of the two gases with different desorption characteristics permits two measurements of the reaeration coefficient in a single experiment with only a little additional effort. For larger streams, it is suggested that ethylene alone be used as the tracer gas.

The movement of the gas and dye tracers through the stream reach can be described by a one-dimensional diffusion equation. The peak concentrations of the tracers at the downstream end of the reach depend on the concentrations of the tracers in the water at the injection site, the longitudinal dispersion coefficient of the reach, the mean water velocity, the length of the reach, and the duration of the injection period; and the downstream peak gas concentrations also depend on the desorption coefficients of the stream reach. The concentrations of the tracer gases in the water at the injection site depend on the flow rates of the gases through the diffusers used for injecting the gases, the efficiency of the absorption process, and the discharge of the stream. The concentration of the dye in the water at the injection site depends on the flow rate of the dye solution, the concentration of the dye solution, and the discharge of the stream.

All the different variables, with the exception of the absorption efficiency, necessary for estimating the gas flow rates and the dye concentration can be approximated from the hydraulic properties and geometric characteristics of the reach. A sensitivity analysis of the effect of possible errors in these variables on the computed gas concentrations at the upstream end of the reach showed that errors in the mean velocity were most important, followed by errors in the desorption coefficient and the dispersion coefficient. An analysis of the effect of increasing the duration of the injection period on the upstream gas concentration showed, for the parameter sets considered, that there was little advantage to using injection periods longer than 90 minutes.

If a detailed analysis of the stream reach prior to the measurement is not possible, then injection rates of 0.50 and 0.58 std $ft^3$/min should be used for ethylene and propane, respectively, with the diffuser system described previously. The duration of the injection period should be according to the stream discharge and the values given in table 2. If flows larger than 8.5 $m^3$/s are to be measured, then ethylene alone should be used as the tracer gas and the number of diffusers should be increased proportionately to the flow. An injection period of 120 minutes should be used.

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