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**Gas Transfer at Weirs Using the
Hydrocarbon Gas Tracer Method
With Headspace Analysis**

by

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and

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ABSTRACT

Gas transfer at hydraulic structures is an important source or sink of dissolved gas in a river system, even though the water is in contact with the structure for a short period of time. The primary reason is that bubbles are entrained into the flow, greatly increasing the surface area available for transfer. Thus, the same gas transfer that might require several miles of stream can occur at a waterfall or hydraulic structure, such as an overflow weir or a spillway [Thene and Gulliver, 1988].

The gas transfer which occurs at hydraulic structures is the subject of this thesis. Attempts which have been made to predict the reaeration which occurs at the base of a free overfall or weir are reviewed herein.

Because of the uncertainties involved in the prediction and measurement of oxygen transfer at hydraulic structures, a hydrocarbon gas tracer method, previously used for the measurement of open channel reaeration, was adapted to hydraulic structures. Its past use is outlined as a basis for its use at hydraulic structures.

A simple "headspace" gas chromatographic technique was applied to the measurement of two dissolved light hydrocarbon tracer gases: propane, a gas that is nearly biologically inert and commercially available, and naturally occurring methane, which is proposed as a tracer gas for use at hydraulic structures. A detailed uncertainty analysis was performed on the measurement technique.

Laboratory gas transfer measurements were made at a field-scale weir. The results from the injected propane measurement had a low uncertainty and compared favorably with the predictive equations available. The results based on the naturally occurring methane were very imprecise due to a problem with the gas chromatograph column selected. A more appropriate column may rectify these problems.

Finally, the measurements made here and those of others were used to modify some predictive equations from the literature. The results are applicable to weirs and overfalls that do not have sufficient height to burst into droplets.

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Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the view of the National Science Foundation.

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LIST OF SYMBOLS

a	Specific surface area
A	GC area response
b	Width of weir
b	Width of nappe
B_{C_d}	Bias in C_d
$B_{C_{SYR}}$	Bias in C due to a bias in syringe volume
B_{C_u}	Bias in C_u
B_E	Bias in E due to standard gas bias
B_{EH}	Bias in E due to a bias in Henry's law constant
B_{ES}	Bias in E due to a bias in syringe volume
B_{F_D}	Bias in F_D
B_V	Bias in vial volume
$B_{V_{SYR}}$	Bias in syringe volume
C	Concentration of dissolved gas
C_d	Concentration downstream from structure
C_{HS}	Concentration of propane in headspace
C_i	Concentration of gas standard i
\bar{C}_i	Average concentration of n_i samples from vial i
$C_{i,j}$	Concentration of jth sample from vial i
C_s	Saturation concentration of dissolved gas
C_{STD}	Standard gas concentration
C_{SYR}	Concentration of propane in syringe
C_u	Concentration upstream of structure
C_W	Concentration of propane in water
d	Diameter of circular jet
D	Molecular diffusivity
d'	Optimum tailwater depth
E	Transfer efficiency
f	A constant function

F_D	Factor to account for dilution of headspace with sampling
F_J	Jet Froude number
Fr_1	Froude number of jet at nozzle
Fr_i	Froude number of jet at impact
F_W	Conversion factor to convert to C_W from C_H
g	Acceleration due to gravity
h	Fall height of weir
H	Tailwater depth
H_P	Henry's law constant for propane
K	A constant
K_L	Liquid film coefficient
K_2	Reaeration (oxygen) coefficient
K_e	Desorption rate coefficient for ethene
K_m	Desorption rate coefficient for methane
K_P	Desorption rate coefficient for propane
k_5	A constant
LOD	Limit of detection
LOQ	Limit of quantification
M	Molar mass
M_{CAP}	Average mass of open-topped screw cap
M_{EMPTY}	Mass of empty, dry, un-capped vial
M_{FULL}	Mass of capped vial filled with water
M_{HS}	Mass of propane in headspace
M_{INJ}	Mass of standard gas injected into GC
M_m	Molar mass of methane
M_P	Molar mass of propane
M_{SEPTUM}	Average mass of a septum
M_w	Molar mass of water
n	Constant exponent such that $1/2 \leq n \leq 1$
n	Moles of propane
n_d	Number of downstream samples
n_i	Number of concentrations determined from vial i
n_u	Number of upstream samples
P	Pressure
P_{HS}	Partial pressure of propane in headspace
p	Perimeter of jet

q	Specific discharge
q _a	Specific discharge of air
q _i	Discharge/nappe width
q _J	Jet discharge per unit jet perimeter at impact
q _w	Specific discharge of water
Q _a	Air flow rate
Q _w	Water flow rate
r	Deficit ratio
r _T	Deficit ratio for oxygen at temperature T
r ₁₅	Deficit ratio for oxygen at 15° C
r ₂₀	Deficit ratio for oxygen at 20° C
R	Reynolds number: q_J/ν
R _h	Hydraulic radius
R _e	Ratio between K ₂ and K _e
R _m	Ratio between K ₂ and K _m
R _p	Ratio between K ₂ and K _p
R _V	Ratio of volumes, V_{HS}/V_W
R _u	Universal gas constant
s	Slope of calibration line
s	Standard (rms) error in C
t	Time
t	Thickness of jet at impact
t _c	Time of contact
t _r	Hydraulic retention time
T	Temperature
U _E	Total uncertainty in E
v	Velocity of jet at impact
v ₀	Minimum velocity for air entrainment
V _a	Volume of air entrained

I. INTRODUCTION

Efforts to predict the transfer of gases at hydraulic structures have not been highly successful to date. The data and equations are generally restricted to one type of structure and cannot be used reliably for another structure. Because of the wide variety of structures and the inability to predict gas transfer from the hydraulic parameters of a given structure, measurement of gas transfer is preferred for associated water quality problems.

Most gas transfer studies deal with reaeration or the adsorption of oxygen from the atmosphere. It therefore seems natural to use oxygen for measurement. There are, however, problems associated with the use of oxygen. One is that the oxygen levels are often already near saturation and that, coupled with the uncertainty involved in the measured concentrations and saturation concentration, gives a large if not prohibitive uncertainty in the gas transfer measurement. A further complication is that of reservoir stratification. When a reservoir has layers stratified by oxygen, it is very difficult to predict which portion of the flow over the structure comes from each layer to the precision required of gas transfer measurements.

Accurate oxygen transfer data have been taken [Rindels and Gulliver, 1986] during the winter when upstream ice cover causes low oxygen levels and low temperatures cause high saturation concentrations. The results are quite good, but can only be obtained for the low flows which typically occur in winter. Furthermore, these measurements can only be made in regions where rivers freeze over, and then at only about half of the structures.

Other methods of measuring oxygen transfer include taking advantage of diurnal fluctuations in dissolved oxygen (D.O.) by sampling during periods of high photosynthesis and supersaturation or after a period without photosynthesis (night or overcast conditions) and low dissolved oxygen. Few sites may actually have the photosynthetic and respiratory rates required to make these techniques feasible.

The use of tracers for reaeration measurement has been further developed over the past two decades. Originally used to measure open channel reaeration, the technique involves injecting a tracer gas into a river and measuring the desorption rate of that gas. The desorption rate of the tracer gas is then converted to a reaeration (oxygen transfer) rate by using the results from concurrent laboratory measurements of the two transfer rates.

Tsivoglou et al. [1965] originally used the radioactive krypton-85 gas as a tracer. Although quite accurate, the krypton technique involved highly qualified personnel and an extensive permitting process. Rathbun et al. [1978] modified the technique to use the light hydrocarbons propane and

ethylene as biologically inert tracers. The hydrocarbon tracer method has gained widespread use and acceptance since that time.

The use of tracers has the obvious advantage that tracers can be chosen which have no atmospheric component and therefore have zero saturation concentrations. Because of this, tracer measurements can be made independent of the ambient conditions. Propane injection is a viable technique to measure gas transfer across structures in small streams and laboratory flumes, but is difficult and expensive for typical river structures. However, injected tracers have not been widely utilized to measure gas transfer at hydraulic structures because of the need for uniform injection across wide structures. Naturally occurring methane does not require injection, and should not have the sharp transverse concentration gradients of an injected tracer gas. Future investigations will therefore focus on the use of naturally occurring methane as a tracer gas at hydraulic structures.

The purpose of this work is to measure a parameter to characterize the gas transfer at weirs. Traditionally the transfer has been given as a ratio of transfer potentials. For oxygen and other atmospheric gases, it is given as the deficit ratio, r :

$$r = \frac{C_s - C_u}{C_s - C_d} \quad (I-1)$$

where C_s is the saturation concentration, C_u is the upstream concentration and C_d is the downstream concentration, which are typically given as mg/L or $\mu\text{g/L}$.

For dissolved gases like propane which are not present at significant concentrations in the atmosphere, C_s is essentially zero. Then r becomes:

$$r = \frac{C_u}{C_d} \quad (I-2)$$

In both cases, the deficit ratio varies from unity (no transfer) to infinity (complete transfer). Here we will define E , the transfer efficiency, as a new master variable for gas transfer at hydraulic structures:

$$E = 1 - \frac{1}{r} = \frac{C_u - C_d}{C_s - C_u} \quad (I-3)$$

For gases such as propane E is:

$$E = \frac{C_u - C_d}{C_u} \quad (I-4)$$

The variable E varies from zero for no transfer to unity for complete transfer, hence the name transfer efficiency. Transfer efficiency can be seen as the ratio of the transfer realized to the maximum possible transfer. It will be the result measured in this work and will be used to compare measured data with predictive equations.

Measurement of dissolved light hydrocarbons for the tracer technique has previously been accomplished through a purge and trap gas chromatographic technique. It requires fairly specialized apparatus [Shultz et al., 1976] and, therefore, most gas chromatography labs are not able to perform it without significant preparation. This study, therefore, tested and utilized a simpler "headspace" gas chromatographic method. The method utilizes the sampling of a vapor phase in equilibrium with the dissolved gas and requires only equipment found in most laboratories. The development, testing, and documentation of the headspace technique, and its application to weirs, are the topics of this thesis. Literature equations to predict weir gas transfer are also tested against the data and data from literature. Slight modifications improved the predictive capability of these equations.

The objectives of this study were:

- 1) To test the use of headspace gas chromatographic analysis of dissolved propane for use with the propane gas tracer technique.
- 2) Establish the use of tracers as a useful technique for the measurement and study of gas transfer at hydraulic structures.
- 3) Study reaeration at weirs and free overfalls and attempt to gain insight into the effect of tailwater depth on reaeration.
- 4) Introduce the idea of a methane gas tracer technique for hydraulic structures.

II. REVIEW

A. PREDICTIVE THEORIES

Generally the transfer of gases across a vapor-liquid interface is described by:

$$\frac{dC}{dt} = K_L a (C_s - C) \quad (\text{II-1})$$

where C is the dissolved gas concentration in water (mg/L), C_s is the saturation concentration of the gas in water (mg/L), K_L is the liquid film coefficient (m/s), and a is the specific surface area, or the area available for transfer divided by the control volume of the liquid (m^{-1}). By assuming $K_L a$ is a constant, this equation can be solved for a control volume passing over a hydraulic structure such as a spillway or weir to yield:

$$r = \frac{C_s - C_u}{C_s - C_d} = \exp(K_L a \cdot t_c) \quad (\text{II-2})$$

where r is the deficit ratio, C_u is the upstream dissolved gas concentration, C_d the downstream dissolved gas concentration, and t_c is the time of contact.

A significant transfer of gas can occur at a hydraulic structure because bubbles are entrained into the flow of water. The large surface area associated with these bubbles and the turbulent mixing are responsible for the transfer. This is the type of transfer which occurs when the jet of a weir or overfall impinges on the surface of its tailwater. Bubbles are entrained around the perimeter of the jet and are mixed into the flow. The transfer of gases at weirs is described by a deficit ratio.

Early efforts to describe the transfer of gases at weirs resulted in equations containing only the fall height, h . These equations gave widely varying predictions of deficit ratio and the work leading to them proved to be largely inconclusive [Avery and Novak, 1978]. In reviewing the available predictive equations Avery and Novak [1978] concluded that none of the equations would be adequate because they did not include the effects of discharge or jet shape.

In 1978, Avery and Novak reported the conclusions of several laboratory experiments they had performed on the reaeration due to solid jets. They had studied the effects of fall height, discharge, jet shape and tailwater depth. They used rectangular notch weirs with widths of 100, 220, and 300 mm. The jets fell into a pool 1 meter wide and 1.5 meters long.

To account for the effect of jet shape, they introduced the concept of a jet Froude number. It was defined as

$$F_J = \left[\frac{gh^3}{2q_J} \right]^{0.25} \quad (\text{II-3})$$

where $q_J = R\sqrt{2gh}$ is the jet discharge per unit jet perimeter at the point of impact, and R is the hydraulic radius, or the cross-sectional area of the jet divided by the perimeter. For a long thin jet, the jet Froude number can be expressed as $F_J = \sqrt{h/t}$ where t is the thickness of the jet at impact.

To gauge the effect of tailwater depth, they apparently set the weir to tailwater bed height and varied the tailwater depth for several gas transfer experiments. They concluded that there was an optimum tailwater depth at which the bubbles had plunged to their maximum depth and contact time. By increasing the tailwater depth beyond that depth there would be no additional increase in contact time while reducing the fall height. Their optimum tailwater depth, d' , then appears to be dependent on the weir and bed elevations.

The optimum tailwater depth, d' , as determined by Avery and Novak, was:

$$\frac{d'}{h} = \frac{7.5}{F_J^{0.53} h^{0.42}} \quad ; \quad (\text{h in centimeters}) \quad (\text{II-4})$$

Based on the experiments which had tailwater depths equal to or exceeding d' , they found the following equation to be a good predictor of r (at 15°C):

$$r_{15} - 1 = k_5 F_J^{1.787} R^{0.533} \quad (\text{II-5})$$

where k_5 is 0.627×10^{-4} and R , which is a Reynold's number, is equal to the jet discharge over the kinematic viscosity, or q_J/ν . The equation fit the laboratory data quite well and was shown to fit data from several prototype weirs.

In 1979, Nakasone proposed a set of four equations to predict the reaeration at weirs and free overfalls:

for $h \leq 1.2$ m and $q \leq \frac{235 \text{ m}^3}{h \cdot \text{m}}$:

$$\ln r_{20} = 0.0785 \cdot h^{1.31} q^{0.428} H^{0.310} \quad (\text{II-6a})$$

for $h > 1.2$ m and $q \leq \frac{235 \text{ m}^3}{h \cdot \text{m}}$:

$$\ln r_{20} = 0.0861 \cdot h^{0.816} q^{0.428} H^{0.310} \quad (\text{II-6b})$$

for $h \leq 1.2$ m and $q > \frac{235 \text{ m}^3}{h \cdot \text{m}}$:

$$\ln r_{20} = 5.39 \cdot h^{1.31} q^{-0.363} H^{0.310} \quad (\text{II-6c})$$

for $h > 1.2$ m and $q > \frac{235 \text{ m}^3}{h \cdot \text{m}}$:

$$\ln r_{20} = 5.92 \cdot h^{0.816} q^{-0.363} H^{0.310} \quad (\text{II-6d})$$

where r_{20} is the deficit ratio at 20°C, h is the elevation difference between headwater and tailwater (m), q is the discharge per unit length of weir (m^2/h) and H is the tailwater depth (m). The equations were the result of laboratory experiments conducted in Japan at about the same time as Avery and Novak's [1978]. The experiments were performed on a laboratory free overfall. In one set of experiments, Nakasone used a 15 cm wide overfall which fell into a 20 cm wide pool. In another set, he used a 30 cm wide overfall with a 30 cm pool. Nakasone claimed that the terms of discharge, drop height and tailwater depth were of main importance. The equations, then, were a result of a regression on those terms.

Nakasone [1987] applied his equations to a set of field data from weirs in the Netherlands. His equations performed only slightly better than the single equation given by Avery and Novak [1978] as shown in Figs. II-1a and II-1b.

The equation of Avery and Novak [1978] tended to predict higher transfers, while the errors in the Nakasone [1987] equation appear to be equally distributed between high and low. The addition of tailwater depth to the predictive equations is seen by Nakasone as an improvement.

In a discussion of Nakasone's work, Gulliver and Rindels [1987] had several objections to the form of his equations. They noted that the values of saturation concentration of oxygen used were not documented. When the

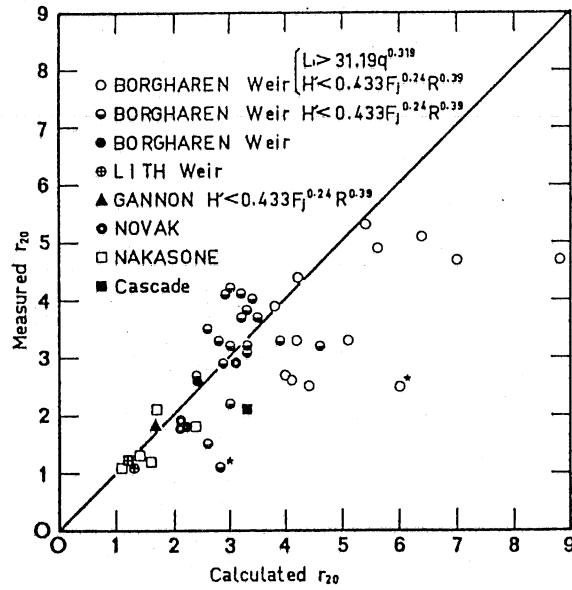
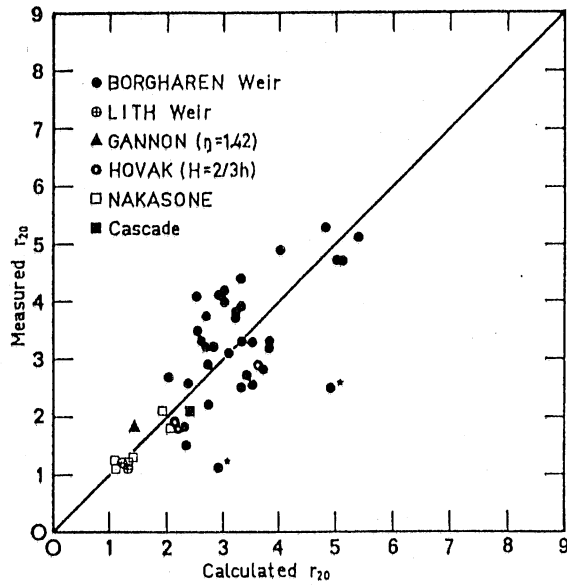


Fig. II-1a,b.

Comparison of Nakasone's [1987] and Avery and Novak [1978] equations.

initial oxygen concentration is close to saturation and therefore the deficit was small, small errors in saturation can give gross errors in the deficit ratio. They also noted the relatively complete correlation between tailwater depth and specific discharge of the field data tested shown in Fig. II-2 [Thene and Gulliver, 1988]. This could place Nakasone's equations in question if there is a similar correlation in the experimental data from which they were derived, and may make its application to prototype weirs questionable. Gulliver and Rindels concluded that the equations of Nakasone are only a slight improvement over the single equation of Avery and Novak [1978]. The marginal improvement does not justify the use of Nakasone's four equations.

The data in these studies were corrected to a single temperature for the purpose of correlation. Both studies used the temperature correction of Gameson et al. [1958] who developed an empirical equation to fit the data they measured to show the effect of temperature on oxygen transfer at small weirs:

$$\ln r_T = \ln r_{20}[1 + 0.018(T-20)] \quad (\text{II-7})$$

where r_T and r_{20} are deficit ratio at the measured temperature and 20° C, respectively, and T is the measured temperature in degrees celsius. Equation II-7 accounts for changes in $K_L a$ and molecular diffusivity due to the change in temperature. The effect of temperature on saturation concentration is removed in the definition of r (Eq. II-2).

Rindels and Gulliver [1988] developed a temperature correction with no fitted coefficients. The correction was developed from the equation of Azbel [1981] which gave an expression of the overall mass transfer coefficient, $K_L a$, for bubbly flows. Noting that $\ln r$ is proportional to $K_L a$ (Eq. II-2) and taking the ratio of $\ln r$ at one temperature to $\ln r$ at another temperature, the obtained:

$$\frac{\ln r_i}{\ln r_m} = \sqrt{\frac{D_i}{D_m}} \left[\frac{\nu_m}{\nu_i} \right]^{1/4} \quad (\text{II-8})$$

where D is the molecular diffusivity of the gas in water, ν is the kinematic viscosity of water and the subscripts i and m indicate the indexed values (oxygen at 20° C) and the value of the parameter under measured conditions, respectively. The fit of this equation and Gameson's are compared to Gameson's data in Figure II-3. The temperature correction of Rindels and Gulliver is used in this thesis.

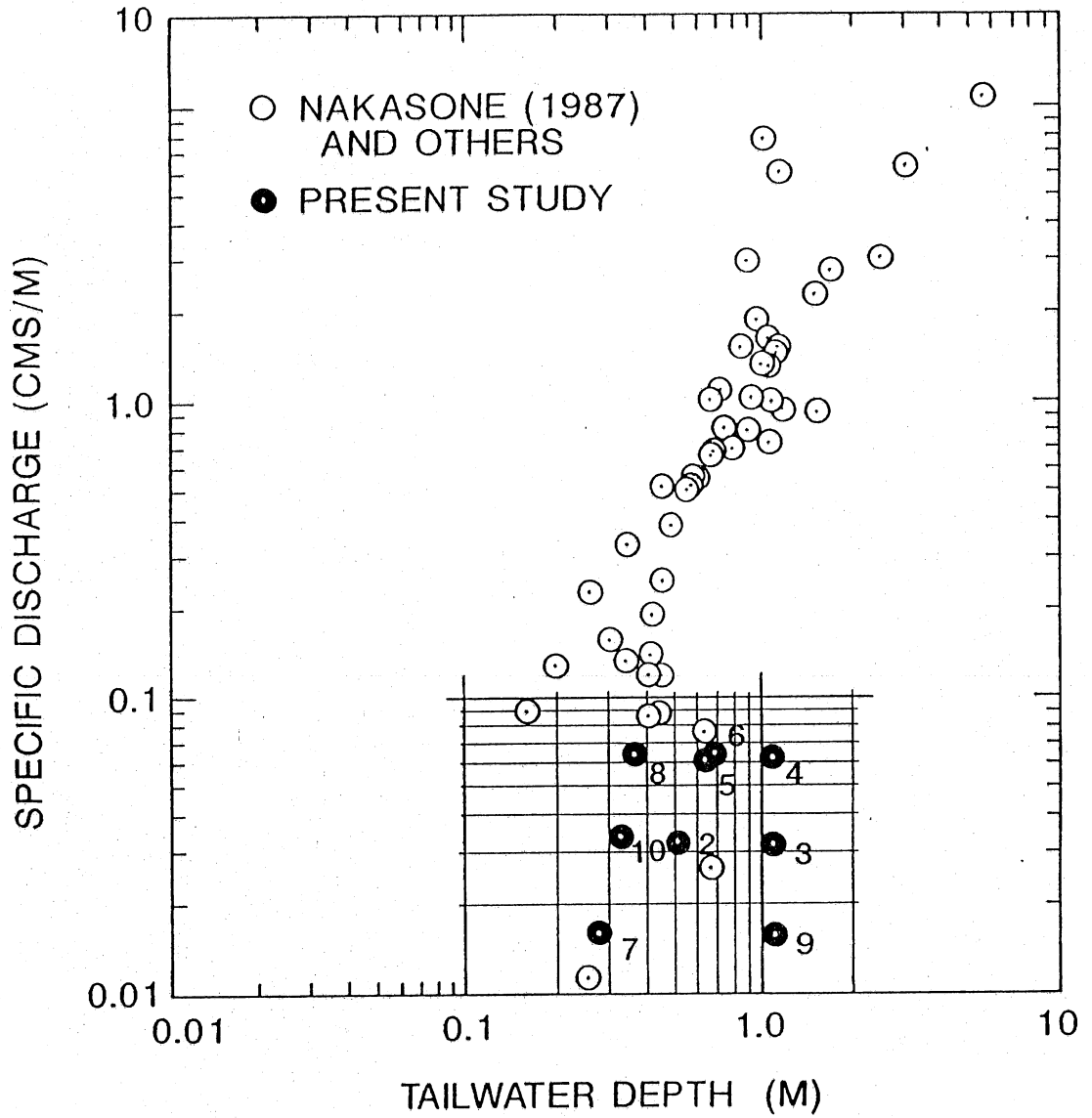


Fig. II-2 Discharge vs. tailwater depth for Nakasone [1987] and present study.

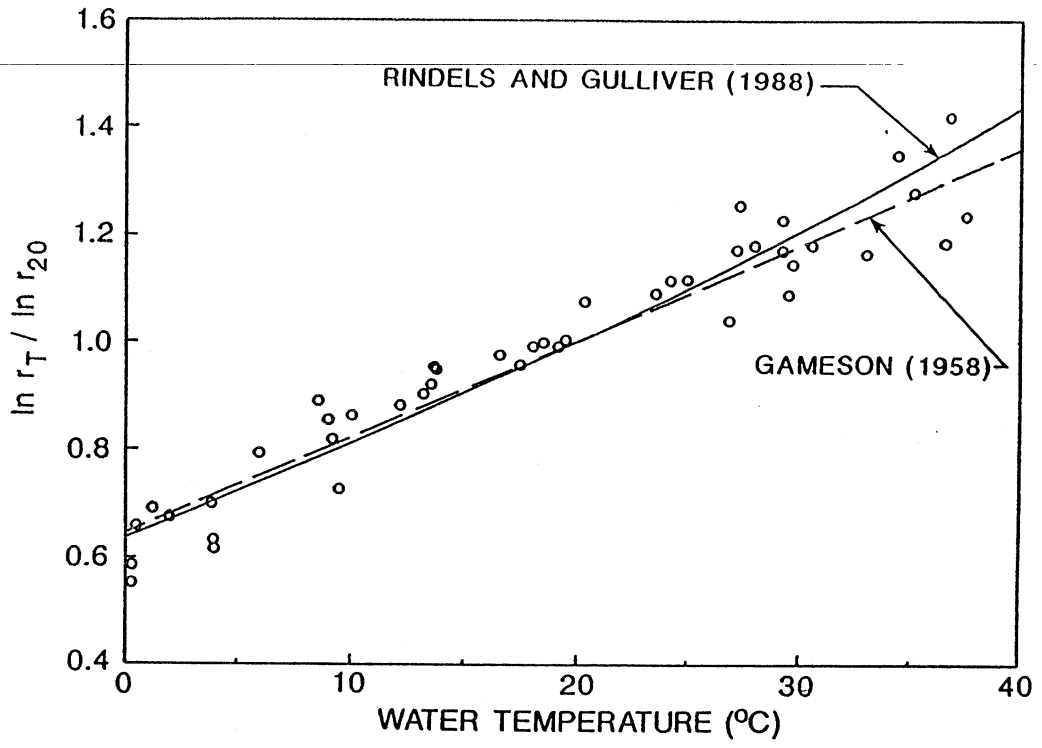


Fig. II-3 Temperature corrections compared.

Relationships for dynamic viscosity and density of water are needed for the application of this equation. The relation for viscosity of Bingham [1922] was used:

$$\mu = \{0.021482[T - 8.435 + (T^2 - 16.87T + 8149.5492)^{0.5}] - 1.20\}^{-1}$$

where μ is dynamic viscosity (cP) and T is the temperature of water (C). Gebhart and Mollendorf [1977] gave the density of water at one atmosphere:

$$\rho = 999.9726[1 - 9.297173 \times 10^{-6} |T - 277.029325|^{1.893816}]$$

where ρ is the density of water (g/L) and T is the temperature of water (K). The density given by Gebhart and Mollendorf was said to be accurate to within 0.00035 percent.

B. THEORY OF TRACER MEASUREMENT OF GAS TRANSFER

Tracer methods were originally developed because of the inadequacy of the available methods for the in situ measurement of open channel reaeration coefficients. Early methods had relied on measurement of oxygen transfer, that in turn, required the engineer to model the other in-stream processes affecting the dissolved oxygen concentration, many of which are not easily modeled. If gas transfer could be measured by means of some inert gas, then there would be no need to model the in-stream processes.

In 1965, Tsivoglou et al. proposed a gas tracer method. Their method involved the injection of radioactive krypton-85 gas as a tracer for oxygen. A conservative tracer would also be injected to measure the hydraulic and dispersive characteristics of the stream. The desorption rate for the krypton tracer would then be computed and related back to the reaeration rate for oxygen using the results of laboratory experiments which measured the simultaneous reaeration and desorption rates of oxygen and krypton, respectively.

The laboratory experiments determined the relative transfer rates for simultaneous transfer of gases in both open and closed mixing tanks. Measurements were made for krypton-85, nitrogen, oxygen, and helium. Tsivoglou determined that the ratio between gas transfer coefficients, R, was independent of mixing intensities and temperature. The krypton-85 tracer technique was subsequently field tested and proven as a valuable tool for the determination of reaeration coefficients [Tsivoglou et al., 1968]. Since that time, it has been used extensively [Tsivoglou and Neal, 1976].

Rathbun et al. [1978] proposed the use of ethene and propane as tracer gases and rhodamine WT-20% fluorescent dye as a conservative tracer. The advantages to the use of these materials were that they required little special training or licensing in their use, they were non-toxic at low levels, inexpensive and easily obtainable. Propane and ethene have molecular

diffusivities similar to that of oxygen; they are fairly soluble ($H_p = 65.9$ mg/L·atm, $H_e = 133$ mg/L·atm at 25°C, Wilhelm et al. [1977]) for ease of injection and could be measured at low concentrations [Swinnerton and Linnenbom, 1967]. Additionally, the adverse public reaction to the use of radioactive chemicals in the environment was avoided.

Rathbun et al. [1978] performed extensive laboratory experiments to determine the ratios, R_p and R_e , between the desorption rate coefficients of propane (K_p) and ethene (K_e) and the reaeration rate coefficient of oxygen (K_2). A tank was filled with distilled water which was deoxygenated either chemically with sodium sulfate and a cobalt chloride catalyst or by stripping with nitrogen bubbled through a porous tube diffuser and then spiked with concentrated ethene and propane solutions. The tank was mixed by an oscillating magnetic plate and an electric stirrer with a 2-inch blade. The oxygen concentrations were determined by Winkler titrations and the hydrocarbon concentrations by purge and trap gas chromatography [Shultz et al., 1976]. During several tests, the mixing intensity and temperature were varied. Tests were run at 20, 25, and 30°C. Rathbun et al. concluded that the ratios of gas transfer rate coefficients were independent of temperature and mixing intensity and given by:

$$R_e = \frac{K_2}{K_e} = 1.15 \quad ; \quad R_p = \frac{K_2}{K_p} = 1.39 \quad (\text{II-9})$$

The values were determined from the linear best fits to plots of K_2 vs. K_e and K_2 vs. K_p , respectively.

With a limited number of tests, they also suggested that the ratios of gas transfer coefficients were not significantly affected by the presence of phenol or detergent in the water or a surface oil film.

Rainwater and Holley [1983] performed similar tests using a stirred tank at temperatures of 4, 20 and 32°C. They were unable to confirm that the results were indeed independent of mixing intensity. They did however report values of:

$$R_e = 1.14 \quad ; \quad R_p = 1.36 \quad (\text{II-10})$$

Later Bales and Holley [1986] performed similar tests using a recirculating flume. They reported final values of:

$$R_e = 1.13 \quad ; \quad R_p = 1.36 \quad (\text{II-11})$$

Although all three studies reported similar values, the authors of the last two still expressed some reservation in the constancy of the ratios of transfer coefficients over the normal range of turbulence and temperature.

The values determined here are important in converting tracer measurement results into oxygen transfer rates. There is a variety of theoretical support for the above values. Most theories of gas transfer predict that two gases experiencing simultaneous transfer should have transfer rate coefficients related by some ratio of molecular diffusivities, namely:

$$R = \frac{K_x}{K_y} = \left[\frac{D_x}{D_y} \right]^n \quad (\text{II-12})$$

where K is the overall gas transfer coefficient, D the molecular diffusivity of the gas in water, the subscripts x and y indicate the two gases compared, and n is some constant which is said to vary from one-half to unity.

Today the most widely accepted theory of open channel gas transfer is the surface renewal theory of Danckwerts [1951]. It predicts that the transfer coefficient is proportional to $D^{1/2}$; therefore, the coefficient n should have a value of one-half. If one looks at the indexing technique of Rindels and Gulliver [1988] which was reviewed earlier (Eq. II-8), one can see that for bubbly flows such as those responsible for weir aeration, the coefficient n should also be one-half. The equation relating deficit ratios for different gases at the same temperature should be:

$$\frac{\ln r_x}{\ln r_y} = \left[\frac{D_x}{D_y} \right]^{1/2} \quad (\text{II-13})$$

Thus, values of R obtained for open channel reaeration should be applicable to bubbly flows, and therefore to hydraulic structures.

There are many theories available for the prediction of molecular diffusivities, as well as diffusivity data, which can be compared to the rate experiments reviewed above. They will be the subject of the following section.

C. USE OF DIFFUSIVITY DATA IN ESTIMATING R

Rathbun et al. [1978] compared diffusivity data available from the literature with the ratios of gas transfer coefficients, R, they had measured. They used the model of Tsivoglou et al., [1968] which predicted an exponent n in Eq. II-12 of one. The seven data points ($T = 15, 20$ and 25°C) which they found for ethene gave an average ratio of 1.29. If one uses the value of $n = 1/2$, this average becomes 1.14, which compares quite well with their experimental value of 1.15. When they performed a similar analysis of available propane data [Wise and Houghton, 1966] they obtained an average value of 1.3, whose square root of 1.1 does not compare well at all with their experimental value of 1.39. It is the author's opinion that

there are better data available than that of Wise and Houghton, as will be discussed later.

Rainwater and Holley [1984] reviewed the theoretical and experimental determinations of the ratio R and found general support for the value $n = 1/2$.

Kyosai et al. [1981] studied the simultaneous transfer of volatile substances in sewers. They developed a relationship for rate coefficient ratios by combining the work of Dobbins [1962] and Wilke and Chang [1955]. Using Eq. II-12 and the Wilke-Chang relationship for D , they arrived at:

$$\frac{K_x}{K_y} = \left[\frac{(V_c)_y}{(V_c)_x} \right]^{.629n} \quad (\text{II-14})$$

where V_c is the critical volume or the volume occupied by one mole of a substance at its critical temperature and pressure. Critical volumes of various compounds have been tabulated by Reid and Sherwood [1968]. Kyosai et al. assumed that $n = 1/2$ and found:

$$\frac{K_x}{K_y} = \left[\frac{(V_c)_y}{(V_c)_x} \right]^{.314} \quad (\text{II-15})$$

Using this equation they found good agreement with their mixing tank measurements of methylene chloride and oxygen. They measured a value of $R_{MCl} = 1.35$ while Eq. II-15, using the data in Reid and Sherwood [1968], predicted $R_{MCl} = 1.35$. Again, using the data of Reid and Sherwood [1968], Eq. II-15 predicts $R_e = 1.16$ and $R_p = 1.36$, which both agree well with the experimental results (1.15 and 1.39) discussed earlier. Equation II-15 is seen as a good predictor of the ratio between gas transfer coefficients.

Most of the work done previously in relating gas transfer ratios has relied on predictive equations for molecular diffusivities. Few results have been reported based on experimental determinations of D . Daniil [1983] reviewed the prediction, measurement techniques and available data for the molecular diffusivity of oxygen.

Daniil concluded that the best method to correlate experimental measurements of molecular diffusivity was the Einstein-Stokes equation:

$$\frac{D\mu}{T} = f \quad (\text{II-16})$$

in which μ is the dynamic viscosity of the liquid, T is the temperature of the system (K), and f is a function of the diffusing system. This can be seen as a simplification of the Wilke-Chang correlation:

$$\frac{D\mu}{T} = \frac{k(xM)^{0.5}}{V_c^{0.6}} \quad (\text{II-17})$$

where $k = 7.4 \times 10^{-8}$ is a constant, x is an association constant (2.6 for water), V_c is the critical volume [cm^3/gmol] and M is the molar mass of the diffusing gas [g/gmol]. The term on the right side of Eq. II-17 does in fact result in a constant for a given gas and liquid system. Of the data reviewed by Daniil, she concluded that the value of Goldstick and Fatt [1970] of $2.13 \times 10^{-5} \text{ cm}^2/\text{s}$ at 25°C is the best reference value to use in Eq. II-16. Using $\mu = .00894 \text{ g}/\text{cm}\cdot\text{s}$ gives $f = 6.38 \times 10^{-10} \text{ g}\cdot\text{cm}/\text{s}\cdot\text{K}$.

A similar relation was needed in the present study for the molecular diffusivity of propane. Diffusivity data were found by searching Chemical Abstracts from 1965 through 1986. Propane data were reported in the period of 1963 through 1968.

The results of several diffusivity measurements were reported by Witherspoon et al. [Saraf et al., 1963; Witherspoon and Saraf, 1965; Sahores and Witherspoon, 1966; Bonoli and Witherspoon, 1968]. Measurements were made by the capillary cell method. This method involves placing a propane solution of known concentration in a short capillary and allowing it to diffuse through one open end exposed to a large well-mixed water bath. After the diffusion period, the average concentration in the capillary was determined, and the diffusion coefficient was determined from those concentrations and the dimensions of the capillary.

Wise and Houghton [1966] measured the diffusion coefficients of propane and nine other gases at 10 to 60°C by the rate of bubble collapse technique. This technique is dependent on the saturation concentration, the rate of collapse of the bubble and a calibration coefficient of the bubble collapse cell determined from oxygen measurements. The calibration of the cell depended on values of the diffusion coefficient of oxygen measured and reported by others.

Because the method of Witherspoon et al. has no assumptions of saturation concentration or calibration coefficients, it is the method preferred by the author. Both sets of data are presented in Table II-1. The points are plotted in Fig. II-4 according to the Einstein-Stokes relation. Although it was found that each set of data fit the Einstein-Stokes relation, the Witherspoon data and that of Wise and Houghton predicted different values for f (see Fig. II-4). The data of Witherspoon et al. give $f = 3.23 \times 10^{-10} \text{ gcm}/\text{s}^2\text{K}$. The constant f was determined as the average of the f values computed for each diffusivity value of Witherspoon et al.

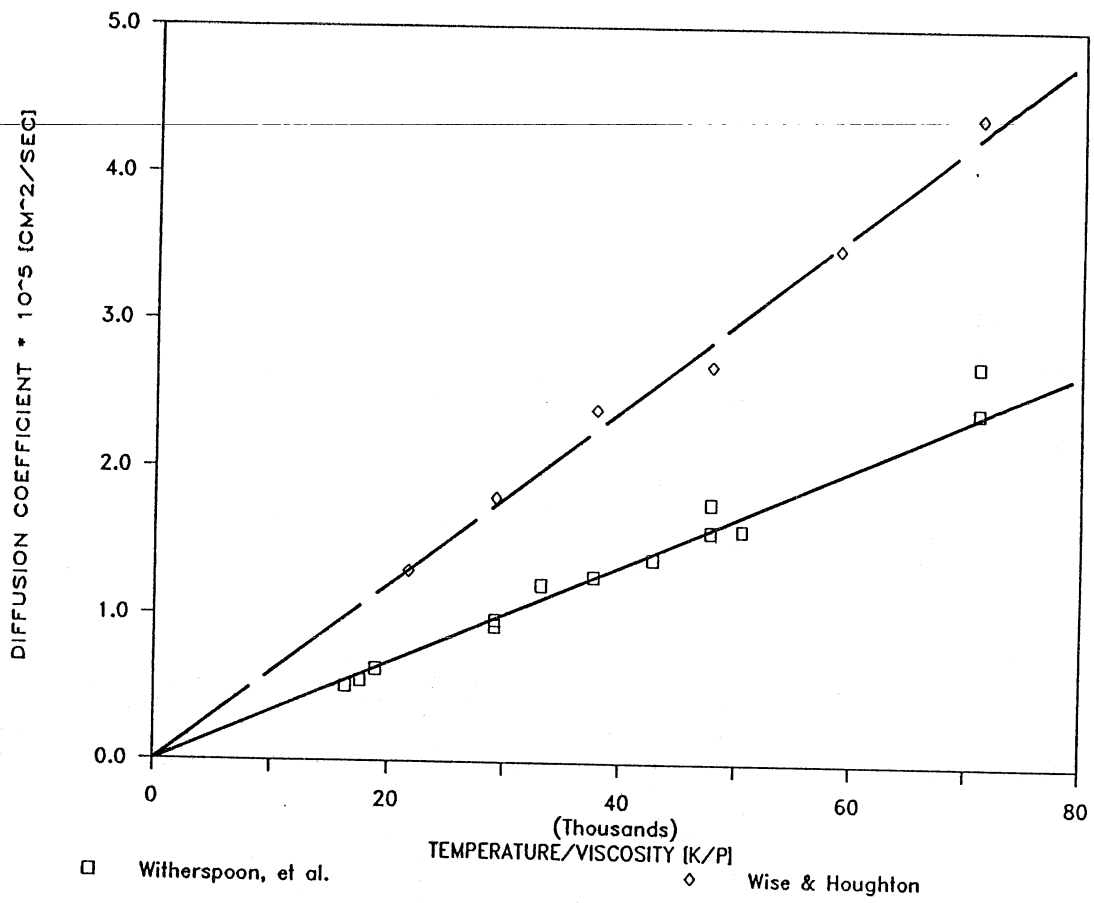


Fig. II-4 Propane diffusivity data.

Table II-1. Propane Diffusivity Data

T (° C)	Dx10 ⁵ (cm ² /s)	μ (cP)	fx10 ¹⁰ (cm ² P/sK)	T (° C)	Dx10 ⁵ (cm ² /s)	μ (cP)	fx10 ¹⁰ (cm ² P/sK)
2	0.51	1.67	3.10	10	1.3	1.31	6.00
4	0.55	1.56	3.11	20	1.8	1.01	6.17
4	0.55	1.56	3.11	30	2.4	.801	6.34
6	0.63	1.47	3.32	40	2.7	.656	5.65
20	0.93	1.01	3.18	50	3.5	.549	5.95
20	0.97	1.01	3.32	60	4.4	.469	6.19
24.8	1.21	.898	3.64				
29.9	1.27	.803	3.36				
35.1	1.39	.721	3.25				
40	1.58	.656	3.31				
40	1.77	.656	3.70				
42.6	1.59	.625	3.14				
60	2.40	.469	3.37				
60	2.71	.469	3.81				
	f, avg.:		3.34				6.05
	std. dev.:		0.23				0.24
Reference: Witherspoon et al.				Wise and Houghton [1966]			

Then, using these relations for the diffusivity of oxygen and propane, the ratio of transfer coefficients can be found to be:

$$R_p = \frac{K_2}{K_p} = \left[\frac{D_{O_2}}{D_p} \right]^{1/2} = \left[\frac{6.38}{3.34} \right]^{1/2} = 1.38 \quad (\text{II-18})$$

The above analysis is seen to give quite remarkable agreement with the data of Rathbun and Holley. Thus, Eq. II-8 with $R_p = 1.38$, will be used throughout to index the propane gas transfer measurements to oxygen transfer at 20° C

Similar results will be needed for the conversion of methane transfer measurements to propane. Analysis of 14 methane diffusivity measurements reported by Witherspoon et al. gave an average f value of 4.94×10^{-10} with a standard deviation of 27×10^{-10} g·cm/s²·K. This leads to the conversion from methane to propane given by:

$$\frac{K_p}{K_m} = \left[\frac{D_p}{D_m} \right]^{1/2} = \left[\frac{3.34}{4.94} \right]^{1/2} = 0.82 \quad (\text{II-19})$$

and, using Eq. II-16 and the oxygen diffusivity from Daniil [1983], the conversion from methane to oxygen is given as:

$$R_m = \frac{K_2}{K_m} = \left[\frac{6.38}{4.94} \right]^{1/2} = 1.08 \quad (\text{II-20})$$

The relationship of Kyosai et al. [1981] can be used to estimate K_p/K_m . Using the critical volumes $(V_c)_m = 99.5 \text{ cm}^3/\text{g}\cdot\text{mole}$ and $(V_c)_p = 200 \text{ cm}^3/\text{g}\cdot\text{mole}$ listed in Reid and Sherwood [1968], Eq. II-15 gives the following results.

$$\frac{K_p}{K_m} = \left[\frac{(V_c)_m}{(V_c)_p} \right]^{0.314} = \left[\frac{99.5}{200} \right]^{0.314} = .803$$

and, with the critical volume of oxygen from Reid and Sherwood [1968], $(V_c)_o = 74.4 \text{ cm}^3/\text{g}\cdot\text{mole}$, the conversion in Eq. II-20 is given as:

$$R_m = \left[\frac{99.5}{74.4} \right]^{0.314} = 1.10$$

The values of $K_p/K_m = 0.82$ and $R_m = 1.08$ will be used in this thesis. The author is not aware of any direct measurements of these ratios (for methane) which have been reported in the literature.

D. ANALYSIS OF DISSOLVED LIGHT HYDROCARBONS

In 1967, Swinnerton and Linnenbom reported a new method for the measurement of small amounts of light hydrocarbons (C2-C4) dissolved in sea water. The technique made use of helium gas stripping chamber where inert helium gas was bubbled through the sample in order to strip the gases from the sample. As the gases were stripped, they were condensed on -80°C cold traps. The traps were subsequently warmed and the samples were flushed into a gas chromatograph for separation. The gases were detected and quantified by a flame ionization detector.

Shultz et al. [1976] modified the technique for use with the hydrocarbon tracer technique for determination of reaeration (or gas transfer) coefficients. They trapped methane by use of a liquid nitrogen trap rather than the dry ice and acetone bath of Swinnerton and Linnenbom [1967], which did not trap methane. They tested the use of 60 mL glass bottles with ground glass stoppers and found them to be satisfactory sample

containers. More importantly they developed a technique of sample preservation. The purpose of preservation was to deter bacterial degradation of the tracer gas during storage. They studied the use of Formalin (37 percent formaldehyde, 11 percent methanol, in water) added to samples containing approximately 90 mg leaf litter each. They adopted the procedure of adding one mL of Formalin to each 60 mL sample, providing satisfactory preservation under those conditions. Typical coefficients of variation of the process, as outlined in Shultz et al. [1976], were observed to be as low as two percent.

Rathbun [1988] observed that a large volume of river water with propane dissolved in it experienced no noticeable loss of propane over a period of nine days. The water was being used for other tests at the time and was not being monitored to determine decay rates of propane. Apparently after nine days the bacteria in the river water adapted to propane and began to consume propane. Twice Rathbun attempted to repeat that phenomenon; however, propane concentrations remained steady and were not found to decay after similar periods of storage. It may therefore be assumed that microbial decay of propane during short periods of storage should be minimal.

Rainwater and Holley [1984] constructed a purge and trap apparatus similar to that described in Shultz et al. [1976] to perform analyses of the relative gas transfer rates of oxygen and the tracer gases. They tested that apparatus by analyzing several replicate samples (presumably prepared using clean water). They found a low coefficient of variation of 2.6% for ethene and 2.8% for propane based on eighteen and twenty replicate samples, respectively. Thus, as an approximation of the precision of the purge and trap analysis technique, two to three percent can be used.

Rainwater and Holley [1984] conducted further tests of the tracer technique to determine the adsorptive characteristics of five soils of varying cation exchange capacity, organic carbon content, pH, and grain size distribution. None of the tests on ethene showed any significant loss of ethene. Only one of the propane tests showed an apparent significant loss of propane, but that one result was questionable. They concluded that for the five soils tested absorptive losses were negligible.

E. HEADSPACE ANALYSIS

Headspace analysis is a gas chromatographic technique used to measure concentrations of dissolved, volatile chemicals. The technique, which was first developed as a quick method for police to determine blood alcohol concentrations, involves the sampling of a vapor phase in thermodynamic equilibrium with a liquid or solid sample. The concentration in the original sample can then be determined from the vapor phase, or 'headspace', concentration by way of a mass balance and some equilibrium partitioning coefficient such as Henry's Law constant.

Headspace analysis is particularly well-suited for sampling of gases such as methane, ethene, and propane, since the headspace concentration is generally much higher than that in the water sample. Hachenberg and

Schmidt [1977] and Ettre, Kolb, and Hurt [1983] describe the basic ideas of headspace analysis as well as more sophisticated methods to enhance results.

Bales and Holley [1984] recognized the usefulness of a headspace analysis technique for the modified tracer technique. An accurate headspace technique would eliminate the need for the complicated purge and trap apparatus of Shultz et al. [1976]. Further, it should greatly reduce the time required for analysis. Bales and Holley [1984] performed seven tests of the headspace analysis technique on several samples containing ethene and propane. The sample containers they used were 40 mL glass vials with teflon faced septa and open topped screw caps. Their first three attempts of headspace analysis failed as they searched to find a suitable method for producing equilibrium between the sample and the headspace. It was found that heating the samples at 50°C for two hours did not produce equilibrium; continuous shaking on a shaker table for two hours at 22°C did not produce equilibrium either. Finally equilibrium was produced by placing the samples on a shaker table for 24 hours at 22°C.

The samples analyzed were siphoned from the same water body and capped full without bubbles and stored approximately two weeks. Various methods for creating the headspace were tested. For two of the four remaining tests two syringe needles were inserted through the septum, one to remove water and the other to allow air to enter. The samples from the third set were uncapped, approximately 20 mL was poured off and the samples were recapped. The headspaces were created directly before the samples were placed on the shaker table for the equilibration period. The fourth set of samples was analyzed by purge and trap for comparison.

Sample vials were weighed full and empty to determine the average volume of the vials. The samples were weighed with the headspace in order to obtain the volumes of gas and water. Two-mL headspace samples were withdrawn and injected directly into the GC column and analyzed for ethene and propane. The concentrations in the original sample were computed by mass balance with Henry's Law constant. (The details are not presented here because of the similarity to those of the author, which will be presented later.)

The samples from the third set resulted in higher concentrations and lower standard deviations than those from the first two sets even though there were half as many samples. The results are summarized in Table II-2 [Bales and Holley, 1984].

As one can see, the results of the third set were more precise and appear to have lower losses, indicating that opening the samples and pouring off the liquid to create the headspace may be the preferred method. It should be noted, however, that these results may also reflect inadequacies in the equilibration technique. Although the samples analyzed in test 3 were more precise than those analyzed by purge and trap in test 4, they were not as precise as the purge and trap measurements of Bales and Holley [1984] described in Section II-D. The concentrations of test 3 were higher than those in test 4, this may indicate that headspace analysis has smaller associated losses. More importantly no comparison was made of the limit of quantitation (LOQ) for the two techniques, which is very important to the planning and success of field applications.

Table II-2. Summary of Results of Headspace Analysis of Bales and Holley [1984] (units are moles/mLx10⁹)

Test	Propane				Ethene			
	No.	Mean	Std. Dev.	Coeff. of Var.	No.	Mean	Std. Dev.	Coeff. of Var.
1	8	0.48	0.071	0.148	8	14.3	1.94	0.136
2	8	0.50	0.093	0.186	8	14.0	1.68	0.120
3	4	0.69	0.050	0.072	4	17.8	1.84	0.050
All Headspace Samples:								
	20	0.58	0.110	0.208	19	14.9	2.25	0.151
4	4	0.58	0.057	0.098	4	17.1	1.63	0.095
Note:								
Tests 1 & 2:			Headspace created using syringe withdrawal through septum.					
Test 3:			Headspace volume poured off					
Test 4:			Purge and trap (control)					

Bales and Holley [1984] concluded that headspace analysis could be made to work with the same equipment they had used. They noted that the use of new headspace autosamplers could reduce uncertainties in the method substantially.

Dietz and Singely [1979] applied headspace analysis to the measurement of chlorinated hydrocarbons in drinking water. They rigorously developed and tested the method during an 18-month period. They obtained equivalent results with the headspace and the purge and trap method. The headspace sampling resulted in much cleaner samples and reduced the possibility of column contamination. The headspace technique was shown to be two to three times faster than the purge and trap method. The headspace analysis was chosen not only as an alternative to purge and trap analysis but as the preferred method.

It is a purpose of this report to establish headspace analysis of light hydrocarbons as a viable technique for use with the modified tracer technique for the determination of reaeration coefficients. Although the analysis of light hydrocarbons (paraffins) is not as demanding as that of chlorinated hydrocarbons, the work of Dietz and Singely will be used as a model for this work.

III. DEVELOPMENT OF LABORATORY TECHNIQUE

The following section of this report will present the procedure adapted for the headspace analysis, some of the tests, problems and solutions which lead to that procedure, the data reduction and uncertainty analysis of the results, and the quality assurance/quality control documentation. The procedure is that which was finally adapted, is and recommended for future use.

A. DISSOLVED HYDROCARBON SAMPLING AND HEADSPACE ANALYSIS

All samples were taken in 40 mL borosilicate glass vials with teflon faced septa and open top screw caps. The vials used were Fisher brand "for EPA water analysis." Each vial was numbered by permanent marker for identification. It was found that each vial had a different mass and volume, therefore the volume and mass of each bottle needed to be determined and recorded because the vials also served as headspace analysis vessels. The dry mass of each vial, as well as the mass of each vial capped and full of water, were measured and recorded. With these masses and those of the septa and caps, the volumes of the vials were determined.

Because the caps and septa had varying masses also, the masses of a large sample (29, 19) of these were measured. The average masses were used in all calculations. The standard deviations were also recorded for use in a later uncertainty analysis of this procedure.

These vials are very brittle. Before sampling, the rim of each sample vial was inspected for chips; a chip in the rim can lead to bubble formation in the full vial or leaks to, or losses from, the headspace. Because the vials broke frequently, at least two samples were taken for each sampling condition. Occasionally the vials broke while the caps were being tightened.

All sampling was performed with a dissolved gas sampler designed and built similar to the standard dissolved oxygen (D.O.) sampler. The sampler (shown in Figs. III-1 and III-2) differed from the standard D.O. sampler in that it was constructed of 4-inch PVC pipe with a PVC end cap for a lid. Because of physical restraints, the sampler was larger than necessary and flushed each sample about ten times (three or more are recommended). A larger volume was necessary so that the samples could be capped under the water surface and the samples would be free of air bubbles. The flushing generally removed bubbles but at times bubbles remained. In this case, if the bubble could not be removed by rattling the vial in the sampler the sampler was emptied and the sample retaken. When a bubble-free sample was obtained, the sample was capped with a septum and cap. The cap and

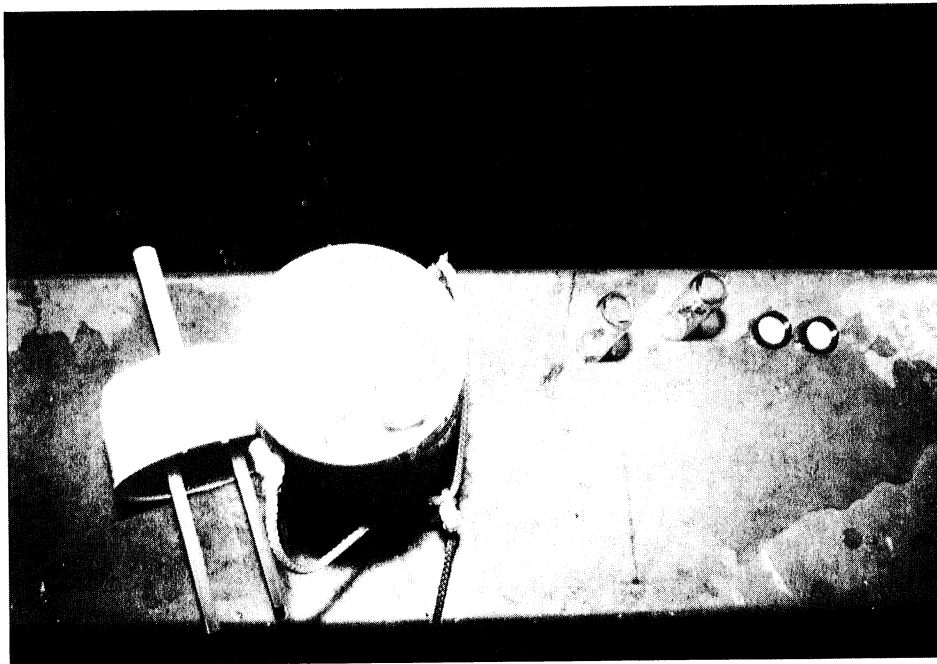


Fig. III-1 Photograph: Sampler open with vials inside.

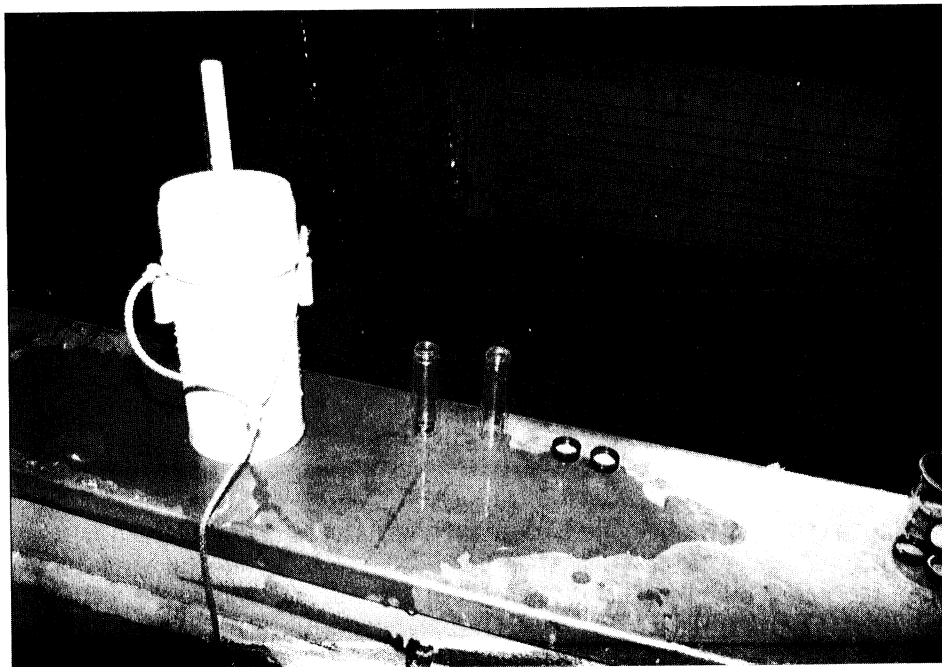


Fig III-2 Photograph: Sampler closed.

septum were tapped on the side of the sampler while submerged in order to remove air bubbles from them.

Samples were taken two at a time in the sampler. The bottle numbers were recorded at the time of sampling along with the location, time and sampling conditions. The water temperature was recorded at various times during the sampling period. After each use the vials were rinsed in hot tap water and allowed to drip dry.

Every effort was made to analyze the samples the day after they were taken. The samples were transported to the GC lab the evening before analysis. This was to ensure that the samples would reach thermal equilibrium with the surroundings and the temperature of the samples would be known. It was shown that this method was sufficient and would not cause any significant errors (see Section III-B.). Extra samples (temperature blanks) were taken for the purpose of checking the assumption of thermal equilibrium. The temperature blanks were found to be in equilibrium with the lab air during each test. Had they not been, it was planned that a temperature bath would be acquired, the samples placed in it and analyzed the following day.

The gas chromatograph (GC) used was a Hewlett-Packard model 5840A. It was equipped with a flame-ionization detector (FID), a strip chart recorder, and an electronic integrator. The injection port and the FID were both kept at 250°C. The air line to the FID was maintained at 20 PSIG and the hydrogen line at 15 PSIG. The column used was six feet by 1/8 inch stainless steel packed with Alltech brand Chemipack C18, 80/100 mesh. The oven was maintained isothermal at 90°C and the carrier gas was nitrogen at approximately 30 mL/min. The high oven temperature and high flow rate allowed for a quick analysis with a 55 second run time and a 35 second retention time for propane. Under these conditions, the column was capable of separating propane from the air injected with the headspace sample as well as the naturally occurring methane, and the ethane/ethene impurity in the injected propane gas.

The GC was calibrated using commercially prepared and certified gas standards. The standards used were 10.14 and 99.7 ppm (by volume) propane in hydrocarbon-free air and 99 ppm methane in nitrogen gas. The concentrations of these gases were certified to be within plus or minus two percent by the manufacturer, Scott Specialty Gases.

After the operating conditions for the GC were set, several volumes of the standards were injected using Hamilton 1000 series gas-tight syringes. Fixed needle syringes were used and are recommended for quantitative work such as this. The syringe sizes used for this work were 25, 100, 250, and 1000 μ L. The size actually used depended on the concentration in the samples and the response desired. Although the calibration for this test was not necessary (see Section III-C.), it was carried out for each set of samples in order to show the linearity of the GC response and indicate the quantity of gas sampled.

The 40-mL sampling vials were also used as headspace analysis vessels. The analysis proceeded as follows:

Under a ventilation hood, each sample vial was quickly opened, about half the volume of liquid was poured off, and the vial was recapped. After this, the sample was then violently shaken by hand to produce equilibrium between the dissolved gas and that in the headspace. In this step, approximately 95% of the dissolved gases originally present in the water volatilized into the headspace (based on Henry's Law constant, water temperature and mass balance, see Eq. III-5 and Section III-D).

From the headspace of the vial, a volume of 25 μL to 1 mL was removed using a gas-tight syringe through the septa cap. This volume was quickly injected into the GC column and the integrator was started simultaneously. Six samples were analyzed from each headspace. On the second and third samples of the day the volume was adjusted to one which produced a satisfactory response on the GC. The volume chosen was always that of the full capacity of the syringe used. Once this volume was determined it was used for all subsequent samples that day. This was due to concerns about the pressure in the GC column and how it might effect the volume of sample which was actually injected. By using the same volume each time, errors due to pressure should be eliminated, since only relative concentrations are required for the purposes of this study.

If, during the first six injections from the headspace of a particular sample, the analyst observed one or more samples which gave an obviously high or low response, compared to the others from that sample (see Section III.E.), the GC system would be checked for leaks and other improper operating parameters. Then another headspace sample would be analyzed from that sample so that there would be six "good" measurements made from each sample. The peak areas were recorded for later computations. The outside of the vials were then dried and the vials were weighed to the nearest .01 gram and the mass was recorded. The mass was needed for the computation of the concentration. The computations are summarized in Section III-C.

B. TESTS AND ANALYSIS OF PROCEDURE

As noted previously, a temperature bath was not needed to maintain the temperatures of the samples. Analytical and experimental support is presented here.

Only temperature is important in the conversion of the headspace concentration, C_{HS} , to the original water concentration, C . This conversion is detailed in Section III-C, with the result given by:

$$C = C_{\text{HS}} \left[\frac{R_u T}{MH} + \frac{V_{\text{HS}}}{V_{\text{W}}} \right]$$

where R_u is the universal gas constant, T is the absolute temperature of the sample, M is the molar mass of the gas, H is the Henry's law constant, and V_{HS} and V_{W} are the volume of the headspace and remaining water,

respectively. The entire bracketed expression is dimensionless because both concentrations are given as mass per volume. The portion of the total mass of propane which is in the dissolved phase is represented by R_uT/MH and the portion in the vapor phase is represented by the V_{HS}/V_W term. Using the solubility relation of Wilhelm et al. [1977], the term R_uT/MH is plotted against temperature for propane (the least volatile of the tracer gases) and methane in Fig. III-3. In a relatively wide range of room temperatures, from 15°C to 30°C (57°F to 86°F), R_uT/MH varies only from 0.05 to 0.032 for propane. With typical V_{HS}/V_W values in the range of 0.6 to 1.2, R_uT/MH is only 2.6 to 7.7 percent of the entire correction from headspace to water concentration. The result is due to the high volatility of propane, which means that the majority of the compound will be in the headspace.

Furthermore, the variation in this term is quite small for small changes in temperature. Therefore, an error in the temperature will produce only small errors in the concentration. For a range of V_{HS}/V_W from 0.6 to 1.2, the maximum error in concentration due to a one degree error in temperature (from 25°C) is 0.15% (Fig. III-4). For the most common value of V_{HS}/V_W , 0.9, the maximum error is 0.10%. Furthermore, if errors are consistently high or low, the errors will tend to cancel one another in the efficiency computation. As an example of the temperature variation which can be expected, the temperature blanks of May 30, 1987, showed very little variation:

Table III-1. Temperature of Samples without Temperature Bath

Vial No.	Time	Temp. (C)
50	10:15	25.1
43	12:27	25.0
18	13:20	25.1
52	14:35	25.1
38	14:50	25.2

The average water temperature was 25.1°C and the maximum error is 0.1°C. As will be seen later, errors in the V_{HS}/V_W term overshadow those in the R_uT/MH .

It is the author's opinion that this procedure is as good, if not better, than one using a temperature bath. Since the sample is at the air temperature, the sample temperature should not change while the headspace is created, nor while the vial is shaken or sampled. If a temperature bath were used, the temperature would most likely be different from that of the air and the sample temperature could change unpredictably during the handling and sampling. Also, the thermostat on a common water bath is often not sensitive to within 0.2°C.

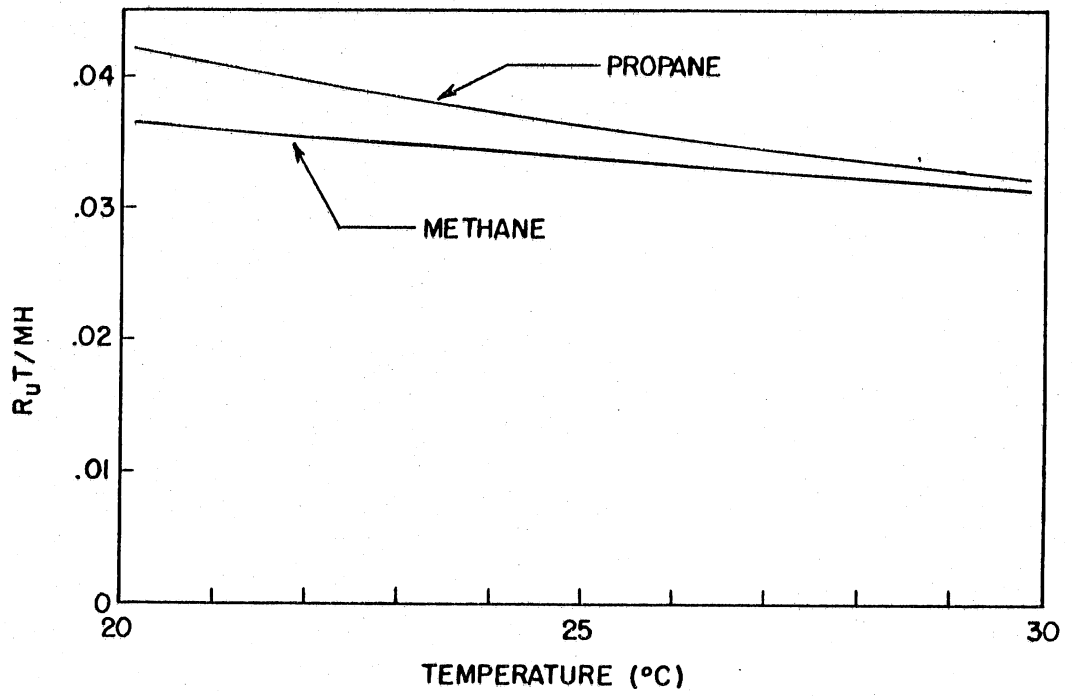


Fig. III-3 Variation of $R_u T / M_p H$ with temperature.

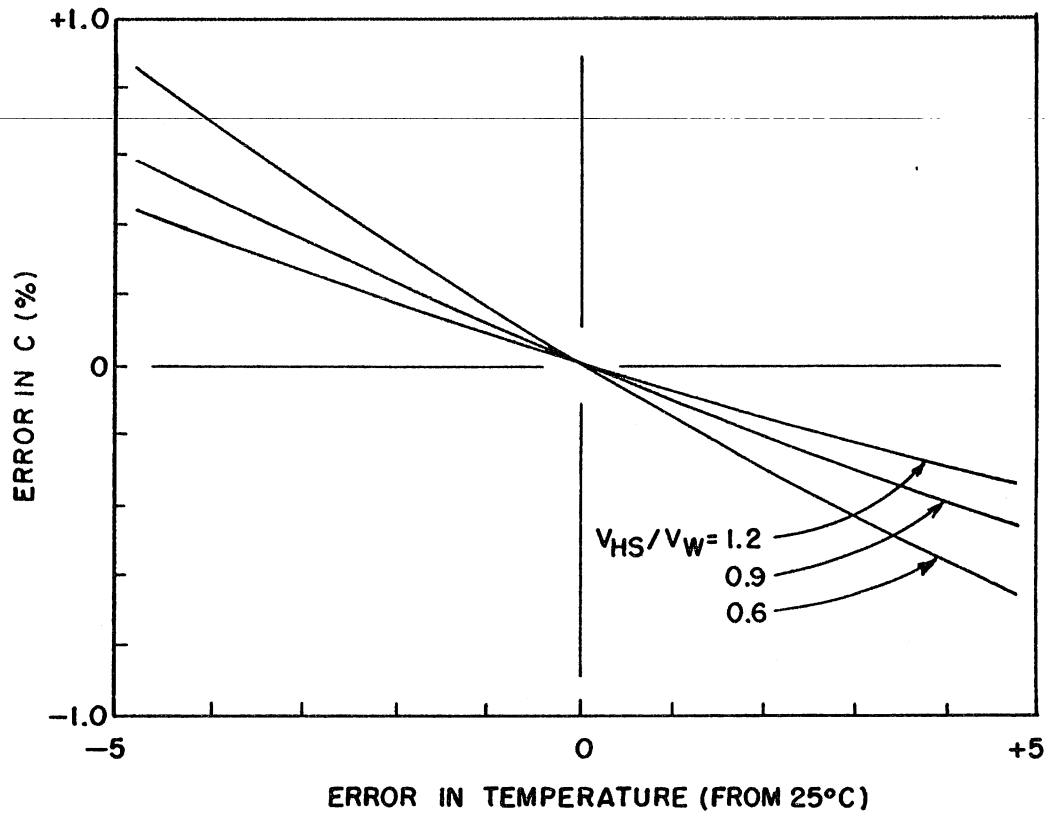


Fig. III-4 Comparison of error in concentration and error in temperature.

Because so much of the gas is in the vapor phase, it was decided that it was not important to attempt to physically verify the Henry's Law constant, H. The solubility relations of Wilhelm et al. [1977] were determined from many solubility measurements by several researchers and are believed to be reliable for this work.

Because such a small fraction of the total propane is dissolved (about 5%), it would be difficult to measure H because the 95 percent confidence level precision of the procedure is about 2 to 3 percent of the concentration. The difference between the equilibrium headspace concentration and the amount spiked would, at best, be on the order of the precision uncertainty. So, determination of H would be a futile exercise given the sampling technique described here.

Note: At the beginning of this work, when the headspace technique was being tested, there were problems with the GC column and therefore the results shown in this section are not as precise as those of the weir experiments since the column was changed before they were begun.

At the beginning of these experiments all samples were taken with the headspace poured off at the time of sampling. The reasoning behind this was that it would eliminate the need to open them later and the possible losses involved with that. It also would eliminate the worry of losses due to bubble formation in the sample vials. In an early test it was learned that samples allowed to sit 18 hours without shaking did not reach equilibrium. The vials were sampled before and after shaking one, two or three times for 15 to 20 seconds each. The shaking was done by hand; the samples were shaken violently so that bubbles would form to enhance the transfer from solution to the headspace. The results shown in Table III-2 clearly show that shaking was necessary to reach equilibrium. Subsequently all samples were shaken for one to two minutes after they were taken. This is in contrast to the 24 hours required by a shaker table (Bales and Holley, 1984) which was probably not violent enough to mix turbulently or to entrain bubbles.

Table III-2. Concentrations Showing Need for Shaking

Vial No.	15	9	36	64
	Concentration ($\mu\text{g}/\text{L}$)			
Unshaken	2150	2075	4230	4130
Shaken 1x	2550	2550	4810	5400
Shaken 2x		2450	5070	5550
Shaken 3x			5060	5590

In the third trial of this technique, samples were taken and equilibrated with vials half full, or "with headspace". The rms error for six samples was approximately 5%. However, later it was decided that

full-bottle sampling should be tested and compared to with-headspace sampling.

In the fifth test, it was determined that the losses occurring while creating the headspace in full samples should be small. It took less than five seconds to open the vial, pour off the headspace, and recap the vial. The headspace of two vials were sampled one minute after the headspace was created but before they were shaken. The headspace concentrations were 5.3 and 14 percent of the concentrations after shaking. Since these concentrations were measured one minute after the headspace was created, and that step took only five seconds, it was concluded that losses in that step were small and negligible for future tests.

Also in that test, it was found that samples could be brought into equilibrium in as little as 15 seconds of shaking. A few samples were not in equilibrium after 15 seconds but all were after 30 seconds of shaking. It was decided that subsequent samples would be shaken for one minute.

In a comparison of full-vial sampling and with-headspace sampling, it was shown that samples taken with the headspace gave consistently lower concentrations in four pairs of samples (Table III-3).

Table III-3. Full Sampling Compared with Headspace Sampling

	Concentration ($\mu\text{g/L}$)			
	Samples taken full:	44.5	41.8	47.5
Samples taken with Headspace:	37.7	41.1	18.1	31.6

Each pair of samples in Table III-3 was taken in the same sampler at the same time. These results were used to specify that all future samples would be taken full and the headspace created in the GC laboratory.

Considering the number of samples required for gas transfer measurement, a significant cost advantage could be realized by the re-use of the teflon faced septa. Therefore, the re-use of septa was tested. Four pairs of samples were taken, one sample was capped with a new septum and one with a used septum. The used septa had been punctured by needles 14 to 18 times each. The samples were stored approximately 72 hours before analysis.

As can be seen in Table III-4, all the samples with holes had slightly lower concentrations. But compared to the random scatter of the measurements, this difference is insignificant in three of the four cases. As a result of this test, it was concluded that the septa could be re-used.

As the extreme case, the teflon was removed from the septa so that the silicone rubber rather than the teflon faced the sample. The resulting measured concentrations were approximately one third as high as those with the teflon facing the sample. Therefore, it appears that there is a limit to the number of holes which can be allowed in the septa. It was not

Table III-4. New Septum Compared to Used Septum

Pair:	1	2	3	4
No Holes				
Conc. ($\mu\text{g/l}$)	369.7	363.4	348.0	345.6
Std. dev.	7.9	13.6	7.0	7.7
n	5	4	4	4
14 to 18 Holes				
Conc. ($\mu\text{g/l}$)	347.4	361.3	347.3	341.2
Std. dev.	13.3	17.3	7.9	4.7
n	4	4	4	4

n: number of samples from each headspace

attempted to find that limit in this work, but the limit set was 18 holes. Few samples, if any, were taken with 18 holes, most were taken with septa with 12 or fewer holes.

During the weir experiments, septa with and without holes were used quite interchangeably with no noticeable consequences. It is noted that at the time of the test described, the GC was not performing as well as it did with the new column.

C. DATA REDUCTION

The data reduction and error analysis for this experiment was performed by a FORTRAN computer program. The measured data used includes ambient temperature, pressure, calibration data, sample masses, volumes injected on the GC column and the GC area responses.

First, the calibration data were converted from a volume and concentration of standard injected to a mass of propane in (μg):

$$M_{\text{INJ}} = \frac{V_{\text{INJ}} M_p P C_i}{R_u T} \quad (\text{III-1})$$

where V_{INJ} is the volume of standard injected (μL), M_p is the molar mass of propane (g), P is the pressure (atm), C_i is the concentration of the standard expressed in volume propane at standard temperature and pressure per volume of standard, R_u is the universal gas constant (.082057 ℓ atm/K), and T is the ambient temperature ($^{\circ}\text{K}$).

These masses, M_{INJ} , were then plotted against the GC area responses. An approximate line is drawn through the points, and outlying points were eliminated visually. This is justified by the experience that the GC at times will give erratic responses. The remaining points are used to find a least-squares calibration line. The line is forced through the origin and the slope is calculated as

$$s = \frac{\sum M_{INJ}A}{\sum A^2}$$

where A is the GC area response. This line has a y -intercept equal to zero, and a slope, s , in μg propane per area count.

The calibration is used only to verify that the calibration response is linear over the range of measured responses, and that it goes through the origin. Since only relative concentrations are required in this work, the requirements stated are the only ones required for calibration. The calibrations were used to show the propane concentrations that were measured.

As noted earlier, when the samples are analyzed, the vials are half-filled with water. For each sample, then, the volumes of the headspace V_{HS} and water remaining in the vial, V_W , were determined using the mass of the sample, mass of the vial, and the density of water.

Several samples are taken, by syringe, from the headspace of each vial. The first step is to calculate the concentration of propane in air in the syringe. That concentration is given by:

$$C_{SYR,i,j} = \frac{A_{i,j} \cdot s}{V_{SYR,i,j} \cdot 10^6 \text{ L}/\mu\text{L}} \quad (\mu\text{g/L}) \quad (\text{III-2})$$

where i is the sample number, j is the injection number, $V_{SYR,i,j}$ is the for the j th injection from bottle i .

To correct the concentrations for the dilution caused by sampling, $C_{i,j}$ was multiplied by the following factor, F_D :

$$F_D = \prod_{k=1}^j \left[1 + \frac{V_{INJ,i,k}}{V_{HS,i}} \right] \quad (\text{III-3})$$

The adjusted concentration is equal to the propane concentration C_{HS} ($\mu\text{g/L}$) in the headspace before sampling began, so $C_{HS,i} = C_{i,j} \cdot F_D$. Note that it has been assumed that no additional propane volatilizes between samplings. This assumption is justified because propane volatilization is relatively slow without shaking when compared to the short time between samples (see Section III-B); additionally, the equilibrium is not upset very far, and there is little dissolved propane available to volatilize (3-6%).

Next, these headspace concentrations were adjusted to the concentrations before the headspace was created. The mass of propane in the headspace is given by:

$$M_{HS} = C_{HS} V_{HS}$$

Henry's law is given as:

$$P_{HS} = C_W H$$

where P_{HS} is the partial pressure of propane in the headspace (atm), C_W is the equilibrium concentration of propane dissolved in the water ($\mu\text{g/L}$), and H is Henry's Law constant ($\text{atm} \cdot \text{L}/\mu\text{g}$). The headspace concentration must be converted to a headspace partial pressure by the ideal gas law:

$$P_{HS} V_{HS} = n R_u T$$

where n is the amount of gas in moles, and

$$P_{HS} = C_{HS} \frac{R_u T}{M_p}$$

Then, the concentration in the water is:

$$C_W = \frac{P_{HS}}{H} = C_{HS} \frac{R_u T}{M_p H}$$

Then, the mass in the dissolved phase is

$$M_W = C_{HS} \frac{R_u T}{M_{pH}} V_W$$

Adding the two masses and dividing by the volume of water, we get the concentration:

$$C_W = C_{HS} \left[\frac{R_u T}{M_{pH}} + \frac{V_{HS}}{V_W} \right] = C_{HS} F_W \quad (\text{III-4})$$

This equation defines F_W , the correction factor converting a gas phase concentration to the original dissolved concentration. Note that both quantities in the brackets are dimensionless.

With all the concentrations converted to concentrations in the water, the concentrations from each vial were averaged. Next, all of the upstream samples and all of the downstream samples from one experiment were averaged together to give C_u and C_d , respectively. Then the transfer efficiency E is calculated by Eq. I-4:

$$E = 1 - \frac{C_d}{C_u} \quad (\text{I-4})$$

D. UNCERTAINTY ANALYSIS

The calibration for this experiment served two purposes. One purpose was to show the linearity of the GC response. The second was to assign concentration units to the individual concentration measurements made. The calibration was not necessary for reporting the final gas transfer efficiencies. Because the efficiency, E , is computed from a ratio of concentrations, the concentrations could have been (and effectively are) reported as GC area counts per liter instead of micrograms per liter.

Because the calibration data play no role in determining the transfer efficiency, the uncertainty in E , due to the calibration, need not be considered.

1. Syringe Volume Bias

The syringes used to withdraw samples from the headspaces each have an associated bias. That bias can cause errors or uncertainties if the syringes are not used in a systematic way. In this experiment, only one syringe was used to withdraw samples from all the headspaces in a given test.

The concentration in the syringe is determined by:

$$C_{\text{SYR}} = \frac{A \cdot s}{V_{\text{SYR}}} \quad (\text{III-5})$$

The final result of the data reduction are the upstream and downstream concentrations, which can be characterized as

$$C_u = \sqrt{\frac{\lambda_u}{V_{\text{SYR}}}} \quad , \quad C_d = \sqrt{\frac{\lambda_d}{V_{\text{SYR}}}} \quad (\text{III-6})$$

where λ represents the results of the remaining data reduction. When the efficiency is calculated, the V_{SYR} terms drop from the expression:

$$E = 1 - \frac{C_d}{C_u} = 1 - \frac{\lambda_d}{\lambda_u} \cdot \frac{V_{\text{SYR}}}{V_{\text{SYR}}} \quad (\text{III-7})$$

Because V_{SYR} drops from the result, there is no need to consider its bias in this uncertainty analysis.

In some cases, different syringes may be used in one experiment. Because of this, a detailed treatment of the biases in syringe volumes is included in following paragraphs. The use of a single syringe is recommended for best results.

Hamilton Syringe Company claims their syringes have a bias of plus or minus one percent. This bias must be propagated in the calibration curve and in the sampling from the vials. The precision of the syringes will be addressed subsequently.

Hamilton was not specific with what this $\pm 1\%$ represents. It is logical that a bias would represent some percentage of the total volume of the syringe. The syringes were not used with less than 40-60% of their total volumes, and most often near their full volumes, except during calibration. Consequently, one percent of the volume used, not the volume of the syringe, will be used as the bias.

If one syringe and one volume were used for the entire experiment, the bias here would cancel, as will the bias due to the standard gas. When several syringes with several biases are used, the biases must be treated in detail. Since the signs of the biases are unknown, the biases here will be added as squares.

The concentration in the syringe is given as

$$C_{\text{SYR}} = \frac{A \cdot s}{V_{\text{SYR}}}$$

We can find the bias in C_{SYR} now due to bias in V_{SYR} :

$$\begin{aligned} B_{C_{\text{SYR}}}^2 &= \left[\frac{\partial C}{\partial V} B_V \right]^2 \\ &= \left[\frac{AS}{V^2} \cdot .01V \right]^2 = (.01)^2 C^2 \end{aligned}$$

$$B_{C_{\text{SYR}}} = .01 C \quad (\text{III-8})$$

Then, the concentration in the syringe is multiplied by the dilution factor:

$$F_D = \prod_{k=1}^j \left[1 + \frac{V_{\text{INJ},i,k}}{V_{\text{HS},i}} \right]$$

With V_{HS} approximately equal to 20 mL and V_{INJ} most often (much) less than 1000 μ L, this term (for $j = 1$) is rarely as great as 1.05.

The bias in this term can be estimated using the 1.0 percent bias in V_{SYR} and .083 mL in V_{HS} , which is equivalent to .005 V_{HS} :

$$B_{F_D}^2 = \left[\frac{\partial F_D}{\partial V_{\text{SYR}}} B_{V_{\text{SYR}}} \right]^2 + \left[\frac{\partial F_D}{\partial V_{\text{HS}}} B_{V_{\text{HS}}} \right]^2 \quad (\text{III-9})$$

and for $j = 1$

$$\begin{aligned}
 &= \left[\frac{1}{V_{HS}} \cdot .01 V_{SYR} \right]^2 + \left[\frac{V_{SYR}}{V_{HS}^2} \cdot .005 V_{HS} \right]^2 \\
 &= (.01^2 + .005^2) \left[\frac{V_{SYR}}{V_{HS}} \right]^2 = (.011)^2 \left[\frac{V_{SYR}}{V_{HS}} \right]^2
 \end{aligned}$$

for the maximum $V_{SYR}/V_{HS} = .05$, $B_{F_D} = .0006$ or 0.06%. When j is greater than one, F_D is given approximately by:

$$F_D = \left[1 + j \frac{V_{INJ}}{V_{HS}} \right] \quad (III-10)$$

This will give a bias of $j(0.0006)$, and with j less than or equal to 6, the maximum bias in F_D will be .0036 or .36%. Since this error is small and is for the worst possible case, it is neglected.

Returning to the bias in E due to bias in syringe volume, B_{ES} , it is found to be:

$$B_{ES}^2 = \left[\frac{\partial E}{\partial C_u} B_{C_u} \right]^2 + \left[\frac{\partial E}{\partial C_d} + B_{C_d} \right]^2 \quad (III-11)$$

Since the bias in C_{SYR} is a proportion of C_{SYR} , the bias in C_u and C_d will be that same proportion:

$$B_{C_u} = .01 C_u \quad , \quad B_{C_d} = .01 C_d$$

So then,

$$B_{ES} = .014 \frac{C_d}{C_u} \quad (III-12)$$

2. Precision Uncertainty in Samples

As noted before, six headspace samples were analyzed from each vial and for each, an average concentration was calculated. (The errors in concentration calculation will be addressed later.) If some concentrations were obviously in error, or there was suspicious GC output, the concentrations were not included in the average.

The standard error was calculated for the concentration of each vial:

$$s_i^2 = \frac{1}{n_i-1} \sum_{j=1}^{n_i} C_{i,j} - \bar{C}_i \quad (\text{III-13})$$

That standard error was then adjusted to a 95% confidence interval using the students' t score:

$$W_{\bar{C}_i} = t(n_i-1)s_i \quad (\text{III-14})$$

Next, the average concentrations are averaged to give the average upstream and downstream concentrations:

$$C_u = \frac{1}{n_u} \sum_{i=1}^{n_u} \bar{C}_i \quad (\text{III-15})$$

Propagating the errors, we get

$$\frac{\partial C_u}{\partial C_i} = \frac{1}{n_u}$$

so that

$$W_{C_u}^2 = \sum_{i=1}^{n_u} \left[\frac{\partial C_u}{\partial C_i} \right]^2 W_{C_i}^2$$
$$W_{C_u}^2 = \sum_{i=1}^{n_u} \frac{1}{n_u^2} W_{C_i}^2 = \frac{1}{n_u^2} \sum_{i=1}^{n_u} W_{C_i}^2 \quad (\text{III-16})$$

Finally, with W_{C_d} defined in the same manner, the precision uncertainty in E is given as:

$$W_{EP}^2 = \left[\frac{C_d}{C_u} W_{C_u} \right]^2 + \left[-\frac{1}{C_u} W_{C_d} \right]^2 \quad (\text{III-17})$$

3. Standard Gas Bias

The concentration of the propane gas standard is certified to be within plus or minus two percent of the quoted value, the actual error is a bias and unknown. For this analysis, the slope and y-intercept can be given by

$$s = C_{STD} K_1 \quad \text{and} \quad y_0 = C_{STD} K_2 \quad (\text{III-18})$$

where K_1 and K_2 are constants.

The concentration can then be characterized by:

$$C_i = A_i C_{STD} K_1 + C_{STD} K_2 = C_{STD} K_i$$

so

$$C_u = C_{STD} K_u \quad ; \quad C_d = C_{STD} K_d \quad (\text{III-19})$$

Then the bias in concentration due to the standard are:

$$B_{C_u} = K_u (.02 C_{STD}) \quad , \quad B_{C_d} = K_d (.02 C_{STD})$$

The biases in C_u and C_d can be added algebraically to give the bias in E because there is a single definite bias for C_{STD} . The bias is unknown, but always acts with the same sign, thus, the bias in E is:

$$B_E = \left[\frac{\partial E}{\partial C_u} B_{C_u} + \frac{\partial E}{\partial C_d} B_{C_d} \right] \quad (\text{III-20})$$

giving

$$B_E = \left[-\frac{C_d(K_u)(.02 C_{STD})}{C_u^2} + \frac{(K_d)(.02 C_{STD})}{C_u} \right] = .02 \left[-\frac{C_d C_u}{C_u^2} + \frac{C_d}{C_u} \right]$$

$$B_E = 0 \quad (III-21)$$

Thus, as could be expected, the transfer efficiency is independent of the standard concentration, C_{STD} . Furthermore, since pressure is also a multiplier in the slope and intercept calculations, a bias of αP , where αP is a small portion of P , will result in no bias in E . Temperature is also a factor in slope, but it is an inverse factor. The same analysis as above can be performed to show that a bias of βT , where βT is a small portion of T , will result in no change in E .

Bias in these quantities will, however, result in biases in the concentrations; these bias were not calculated or reported here.

4. Bias in Headspace Correction Factor, F_W

The headspace concentration, C_{HS} , was corrected to the water concentration before the headspace was created, C , by the headspace correction factor, $F_W = (R_u T / M_p H + V_{HS} / V_W)$. The uncertainty due to that term is addressed here.

First, we will address the V_{HS} / V_W term and call it R_V . The first step was to find the volume of each vial. The vials were labelled and weighed full of water (with the temperature and density known) with caps and septa in place, then they were weighed a second time, dry and without caps. Several septa and caps were weighed. The average weight of the septa and caps were found along with their standard deviations. Then the volume of each vial could be determined by:

$$V_V = \frac{M_{FULL} - M_{EMPTY} - M_{CAP} - M_{SEPTUM}}{\rho} \quad (III-22)$$

The value of density, ρ , was given by Gebhart and Mollendorf [1977] in a representation accurate to $3.5 \times 10^{-4}\%$:

$$\rho = 999.9726 [1 - 9.297173 \times 10^{-6} |T - 277.02935|^{1.894816}] \quad (III-23)$$

The error introduced by this equation was negligible.

The bias uncertainty in V due to the uncertainty of the mass was given as:

$$B_V^2 = \rho^{-2} [W_{M_{FULL}}^2 + W_{M_{EMPTY}}^2 + W_{M_{CAP}}^2 + W_{M_{SEPTA}}^2] \quad (III-24)$$

$W_{M_{FULL}}$ and $W_{M_{EMPTY}}$ are assumed to be two times the smallest division on the balance, or 0.02 grams. $W_{M_{CAP}}$ and $W_{M_{SEPTA}}$ are taken as their standard deviations multiplied by their t scores or 0.0213 g and 0.0751 g, respectively.

Using these values, the uncertainty in V is:

$$B_V = .083 \text{ mL} \quad (III-25)$$

Similar analysis for the volume of water with headspace present gives the same uncertainty, $B_{V_W} = 0.083 \text{ mL}$.

R_V is reduced to terms of V_V and V_W :

$$R_V = \frac{V_{HS}}{V_W} = \frac{V_V - V_W}{V_W} = \frac{V_V}{V_W} - 1 \quad (III-26)$$

The bias in the individual bottles is:

$$B_{R_V}^2 = \left[\frac{\partial R_V}{\partial V_V} B_{V_V} \right]^2 + \left[\frac{\partial R_V}{\partial V_W} B_{V_W} \right]^2 \quad (III-27)$$

then,

$$B_{R_V}^2 = \left[\frac{1}{V_W} 0.083 \right]^2 + \left[-\frac{V_V}{V_W^2} 0.083 \right]^2 \quad (\text{III-28})$$

For a typical range of R_V from 0.6 to 1.2, B_{R_V} ranges from .0068 to .0117. As a percentage, the range is from 0.98% to 1.1% of R_V . As an approximation for B_{R_V} , $0.01 R_V$ will be used.

In terms of a single sample vial, the uncertainty in R_V is a bias. When several vials are averaged together, the uncertainty in R_V can be treated as a precision uncertainty, W_{R_V} .

The other term in the correction factor is $R_u T / M_p H$. The only variable in this equation is T , additionally Henry's Law constant is a function of temperature.

Wilhelm [1978] fitted a semi-empirical equation to several researchers' data giving saturation concentration, C_s , of propane in water under one atmosphere propane (in units of mole fraction):

$$C_s = \exp \left[\frac{A+B/T+C \ln(T)}{R_u} \right] \quad (\text{III-29})$$

where $A = 628.866$ cal/K·mol, $B = 31638.4$ cal/mol, and $C = 88.0808$ cal/K·mol are the fitted constants and $R_u = 1.9872$ cal/K·mol is the universal gas constant. To find Henry's Law constant in units of L·atm/g, we convert C_s by:

$$H = \frac{P}{C_s} = \frac{M_w P}{C_s M_p \rho} \quad (\text{III-30})$$

where P is pressure (1 atm), M_w and M_p are the molar masses of water and propane, respectively, and ρ is the density of water.

In order to find the uncertainty in H due to errors in T , a 2°K temperature uncertainty was assumed. This is an over-estimation since it was estimated to be on the order of 0.2 to 0.3°K in the methods development section (III-A). For this change of 2°K, the error in H due to ρ is negligible. So the uncertainty in $R_u T / M_p H$ is given as:

$$W_{R_u T / M_p H} = \frac{\partial \frac{R_u T}{M_p H}}{\partial T} W_T = - \frac{R_u T}{M_p H} \left[\frac{T}{H} \frac{\partial H}{\partial T} + 1 \right] W_T \quad (\text{III-31})$$

With an uncertainty of 2°K at a temperature of 298°K, $W_{R_u T / M_p H} = 0.003$. When this uncertainty is combined with the uncertainty in V_{HS}/V_W (.01), it is found to be negligible:

$$W_{F_W}^2 = W_{R_u T / M_p H}^2 + W_{R_V}^2$$

$$W_{F_W} = [.003^2 + .01^2]^{1/2} = 0.0104 \quad (\text{III-32})$$

So, the total uncertainty due to the correction term F_W will be estimated to be 1% of F_W .

This one percent in F_W will give a one percent uncertainty in C_u and C_d . Then, the uncertainty in E , due to the uncertainty in F_W will be:

$$W_{EF} = \left[- \frac{C_d}{C_u} 0.01 C_u \right]^2 + \left[\frac{1}{C_u} 0.01 C_d \right]^2 = 0.014 \frac{C_d}{C_u} \quad (\text{III-33})$$

5. Henry's Law Bias

Wilhelm et al. [1977] gave a standard error in C_s equal to 4.6% for 15 points. The 95% confidence interval then will be $4.6 t(15) = 9.8\%$. An error in C_s , and hence H , will cause a bias in E due to H . H is given as

$$H = \frac{M_w P}{C_s M_p \rho} = \frac{k}{C_s} \quad (\text{III-34})$$

and the bias in H should be given by

$$\begin{aligned}
B_H &= \left[\left(\frac{\partial H}{\partial C_s} \right)^2 B_{C_s}^2 \right]^{1/2} \\
&= \frac{k}{C_s^2} C_s (.098) = \frac{k}{C_s} (.098) = H (.098)
\end{aligned} \tag{III-35}$$

Then, propagating this error into an error in C:

$$\begin{aligned}
C &= C_{HS} \left[\frac{R_u T}{M_p} \frac{1}{H} + \frac{V_{HS}}{V_W} \right] \\
\frac{\partial C}{\partial H} &= - C_{HS} \frac{R_u T}{M_p} \frac{1}{H^2}
\end{aligned} \tag{III-36}$$

Then the bias in C, due to H, is:

$$\begin{aligned}
B_{CH} &= \left[\left[- C_{HS} \frac{R_u T}{M_p} \frac{1}{H^2} 0.098 H \right]^2 \right]^{1/2} \\
B_{CH} &= C_{HS} \frac{R_u T}{M_p H} 0.098
\end{aligned} \tag{III-37}$$

This bias is of unknown sign, but it is of the same sign for both upstream and downstream concentrations, thus the biases can then be added algebraically. Noting that H is only assumed to hold before the sampling starts, we use the \bar{C} from each vial and back-calculate C_{HS} for each sample,

then the bias in \bar{C} due to H is calculated for each sample. The biases in the upstream and downstream average concentrations can be shown to be the average of the individual biases.

Then these biases will be combined in a bias for E as follows:

$$B_{EH} = \left[\frac{\partial E}{\partial C_u} B_{C_u} + \frac{\partial E}{\partial C_d} B_{C_d} \right] \tag{III-38}$$

$$= \left[\frac{C_d}{C_u^2} B_{C_u} - \frac{1}{C_u} B_{C_d} \right] \tag{III-39}$$

In this case, $B_{C_u} \neq B_{C_d}$, so they will not cancel, but one will reduce the other. A typical bias in C is small, approximately .004C. With this small bias in C, it can be seen from Eq. III-39 that B_d approaches zero for all values of C_d/C_u .

6. Total Uncertainty in E:

First, to summarize, we present a list of the uncertainties in E calculated thus far:

- B_{ES} - due to a bias uncertainty (BU) in concentration due to a BU in syringe volume, equal to zero if only one syringe is used.
- W_{EP} - due to a precision uncertainty (PU) concentration - accounts for PU in syringe volume and GC response.
- W_{EF} - due to PU in C introduced as a result of F_W , which converts the concentration in the headspace to that in the water.
- B_{EH} - due to a BU in Henry's Law constant, H.

Thus, the total uncertainty in E, U_E , is:

$$U_E^2 = W_{EP}^2 + W_{EF}^2 + B_{ES}^2 + B_{EH}^2 \quad (\text{III-40})$$

E. QUALITY ASSURANCE/QUALITY CONTROL

Quality assurance (QA) is defined as the setting of allowable limits on data quality. Quality control (QC) is a set of steps taken if the QA limits are not met. The QA/QC for the measurement of gas transfer at weirs (and other hydraulic structures) by the propane tracer method will be detailed in the following pages.

For these experiments, several QA/QC measures were undertaken including the following:

1. Analytical blanks

The first analytical blank was an air blank. Laboratory air in a syringe was injected on the QC column. It was necessary to test the lab air for propane content because it was the air used to create the headspace. This blank should give no propane response. Experience shows there will

not be a propane response, but it was tested once each day. In each test, no propane response was detected.

If propane were found in the air blanks, it would first be determined if that response was significant compared to responses expected from the headspace samples to be analyzed. If the responses were insignificant ($\leq 1\%$), the analysis would proceed as usual. If the response to air blanks was significant, the headspace should either be created at another location without propane in the air, or by another method. One such method could involve removing the water through one needle through the septum while injecting pure nitrogen under pressure through another needle. With this technique, one should be careful not to create bubbles or do it so violently as to increase mixing and gas transfer during that step.

The second analytical blank was a distilled water headspace blank. A vial was filled with distilled water at the time of field sampling. In the GC laboratory, half the sample was poured off and the vial was shaken to produce equilibrium between the headspace and water. Then the headspace was sampled and analyzed to assure that water itself gave no "propane" response. A distilled water headspace blank was only analyzed once in Test 3. Earlier tests had shown no propane response to air, distilled, tap, or river water. With no propane response or interference in those samples, there is no reason to suspect it in a distilled water sample. (This procedure should be capable of detecting a carry-over in the sampling containers.)

2. Field blanks

Field blanks were taken above the weir before the propane injection had begun. These blanks were analyzed as usual. It is inconsequential whether propane was found in these samples or not; propane was added to the flow in an unknown quantity, therefore additional propane should not matter. It is important if another gas with a retention time similar to that of propane is present. Such a gas could interfere with the propane peak integration and alter the results. The GC output was checked for such results. Field blanks were analyzed in Tests W1 and W3. No response was detected around the retention time of propane in the eight headspace samples analyzed.

If a gas (other than propane) were found that would interfere with the propane peak, it would first be quantified. When the propane response in the downstream samples was determined, it should be at least 100 times the response to the field blank. In that case, the interfering gas would then be ignored. If the response in the field blank was greater than 1% of the downstream concentration, the response should be subtracted from the propane response in the data reduction. Results of tests which had propane interference should be noted wherever reported.

3. Calibration

The calibration should be inspected at the time of analysis. The calibration should be linear and go nearly through the origin. Only a visual inspection and a line drawn by hand is required. If it is not, the GC should be checked for operational problems. Additionally, the sampling port on the standard gas bottle should be flushed several times to ensure that

the propane had not adsorbed into the septum. Then the calibration should be retried. If the calibration is still not linear, or does not go through the origin, a curve shall be fitted to the calibration data and used in the data reduction.

4. Limit of detection and limit of quantitation

The limit of detection, LOD, is defined as the lowest concentration that is statistically different than the blank. The limit of quantitation, LOQ, is the concentration level above which quantitative results can be obtained with confidence. In most cases the detection limit is defined as three times the standard deviation of the response to blank runs [American Chemical Society, 1983]. Experience has shown that there is no "propane" response to blank runs. Consequently, a different procedure was required.

Since there was no propane response, a small amount of propane was spiked to a distilled water sample, such that the resulting concentration should be as low as detectable. From experience with GC response to propane, the minimum mass of propane which gives a significant response was estimated. A syringe volume was chosen as large as possible. The volume was not chosen to be so great as to disturb the normal chromatogram. With these two quantities, the syringe (or headspace) concentration was estimated. From that, the sample concentration was computed.

A vial half-filled with distilled water was spiked with a volume of propane gas which would yield the concentration computed above. The vial was then shaken to produce equilibrium. From that bottle, seven samples were run on the GC. The mean water concentration, \bar{C} , and the standard deviation, σ , were calculated. The limit of detection is then be defined as:

$$\text{LOD} = \bar{C} + 3\sigma \quad (\text{III-41})$$

When the operator felt the spike was too large and a lower LOD could be measured, the test was retried with a smaller spike.

As with the LOD, the limit of quantitation (LOQ) is generally defined as ten times the standard deviations of blank runs [American Chemical Society, 1983], therefore:

$$\text{LOQ} = \bar{C} + 10\sigma \quad (\text{III-42})$$

All reported concentrations should be greater than the LOQ. The LOD and LOQ will be reported in Section IV-E this thesis.

When one or more samples from a tracer gas transfer test result in concentrations less than the LOQ, the results of that test should be set off from others with a note wherever reported. If possible, that test should be

repeated with a larger propane injection rate. If a sample(s) results in concentrations less than the LOD, the results should be reported as not detectable (ND) or below LOD.

5. Field samples

All field samples were taken in duplicate (i.e. two at a time in the same sampler). Six pairs of samples were first taken upstream of the weir with their locations distributed across the weir. The first upstream samples were taken at $t = 0$, and then at four subsequent intervals equal to the hydraulic retention time of the tailwater pool, t_r , and the sixth at some time in between. This will give an impression of the steadiness of the upstream concentration and an average value of what has passed into the tailwater pool. Five pairs of samples were then taken in rapid succession at the downstream end of the tailwater. The downstream sampling was done at a time at least four times the hydraulic retention time ($4t_r$) of the tailwater pool after the propane injection had begun. Assuming a well-mixed pool, the concentration should reach at least 98% of the equilibrium concentration. After the downstream samples were taken, one pair of samples was taken upstream of the weir to check that the concentration was maintained throughout the test.

The maximum number of holes in a re-used septum was, and for future use, shall be 18. Samples capped with re-used septa were tested and no significant difference with new septa was detected (see Section III-B).

One sample from each of the pairs was analyzed as described earlier. Additionally, one of the duplicates to those six was analyzed in order to show that pairs are duplicable. If that duplicate did not prove to be duplicable, the remaining duplicates for that experiment were to be analyzed. Because many samples were already analyzed and the results were good, analyzing the further samples was not necessary. The extra samples allowed the analyst to choose only bubble free samples for analysis.

6. Instrument performance

Instrument performance was monitored directly in tests W5, W8, and W10. The calibration standard was analyzed at the beginning of the GC analysis and 2, 6, and 4 standard samples, respectively, were analyzed at the end of the analysis. In those tests, the GC response at the end of analysis (approximately 4 hours later) was about 92-96% of that at the beginning of the analysis. During the tenth test, after samples from the standard were found to give 85% response, the sampling port on the standard gas bottle was flushed. Two more samples were then analyzed and they were found to give a response equal to 99.7% of the initial response. It is believed that, while the sampling port sits during the analysis of samples, propane gas was selectively absorbed into the septum of the sampling port. This could be responsible for the low (92-96%) responses in tests W5, W8, and W10 when the sampling port was not flushed. The results from W10 demonstrate that the GC performance is quite good.

Although the above procedure should be the preferred one, another method of verifying GC performance is available. At the beginning of each GC analysis day, the upstream samples were analyzed. The last sample

analyzed each day was the sample taken upstream after the downstream samples were taken. If this sample gives the same concentration as those of the other upstream samples, it should be concluded that the GC performance is good. Of the eight tests in which these samples were analyzed, only tests W5 and W7 gave significant deviations (Table III-5). The sample from test W7 had a large bubble in it which may account for the large deviation. It should be noted that a low final sample concentration may indicate a drop in propane injection rate during the weir test itself, and therefore may not imply a change in instrument performance. For each test, as in test W5, the upstream and downstream samples can be seen to have no trends (Appendix A). During test W7, however, a negative trend was apparent in the upstream samples, but no trend was noticeable in the downstream samples. This indicates a change in propane injection rate, rather than a change in instrument performance. For these reasons, GC performance was determined to be adequate.

Table III-5. Use of Final Samples to Evaluate GC Performance

Test	$C_u(\mu\text{g/L})$	C_u , end	Notes:
W1	47.4	46.7	Center samples, tests failed due to inadequate mixing.
W2	180	—	Problem with GC did not allow analysis of final sample.
W3	72.0	71.5	
W4	32.1	31.2	
W5	97.6	92.1	
W6	53.2	52.0	
W7	273	236	Large bubble in sample before analysis.
W8	84.0	82.1	
W9	81.8	80.3	
W10	129	130	

7. Identification

All sample containers have a number permanently enscribed. At the time of sampling, all samples were recorded with the bottle number, the bottle number of its mate, the time and location of the sample, along with depth and other sampling conditions when appropriate.

The data taken in the GC laboratory was recorded on the original data sheets. For each headspace sample (injection) the following data was recorded: injection number, the volume injected, the GC run number, the GC area counts and any notes on GC performance. The mass of each sample was recorded to the nearest 0.01 g.

The data on the data sheets was transferred to a computer file for analysis. The data was checked thoroughly at least once before the computer analysis was executed.

8. Data quality - concentrations

Six headspace samples were analyzed from each vial. From time to time, the GC will give an erratic response with no apparent cause. If a concentration obtained in that way did not fall within the 95% confidence limits described by the others, it was dropped from the analysis. It should appear in the tabulation of results with an explanation of why it was dropped. When the operator noticed a possible outlier such as this, or some strange output from the GC, an additional headspace sample was analyzed.

With the dropping of outliers described above, it may appear that all samples would have a low precision uncertainty. This, however, may not always be the case because the variation in headspace samples is used to determine which measurements are outliers. A set of headspace samples with a high precision uncertainty logically has less of a tendency to have outliers.

The sample in the group of upstream or downstream samples may have an extraordinarily large precision uncertainty (based on replicate injections from the same headspace). If its error band is greater than two times the next highest band in that group, it was dropped from the analysis. Typically, the operator will notice a highly imprecise sample. The operator should then check the sample for apparent problems such as leaks. Additionally, he should check that all GC operating parameters are set correctly, and check the column and septum, etc., for leaks. Then the operator should analyze the mate of the defunct sample. No samples were eliminated for this reason, but the procedure is included for future use.

Additionally, if the concentration of a single upstream or downstream sample lies outside the 95% confidence interval of the total upstream (or downstream) concentration, it may be dropped from the analysis. Again, if the operator notices this, he should analyze the mate of any sample which could possibly be dropped later.

One remaining quality control step is to increase the number of samples analyzed; either the number of headspace samples, the number of samples or both can be increased. Increasing the number of headspace samples is promising, because it reduces the t -score applied and the coefficient $n^{-1/2}$. The number six was chosen as a number where both the t -score and $n^{-1/2}$ curves begin to level off with increasing n (Fig. III-5). Because the slopes of both these curves decrease with increasing n , little is to be gained by increasing the number of samples analyzed.

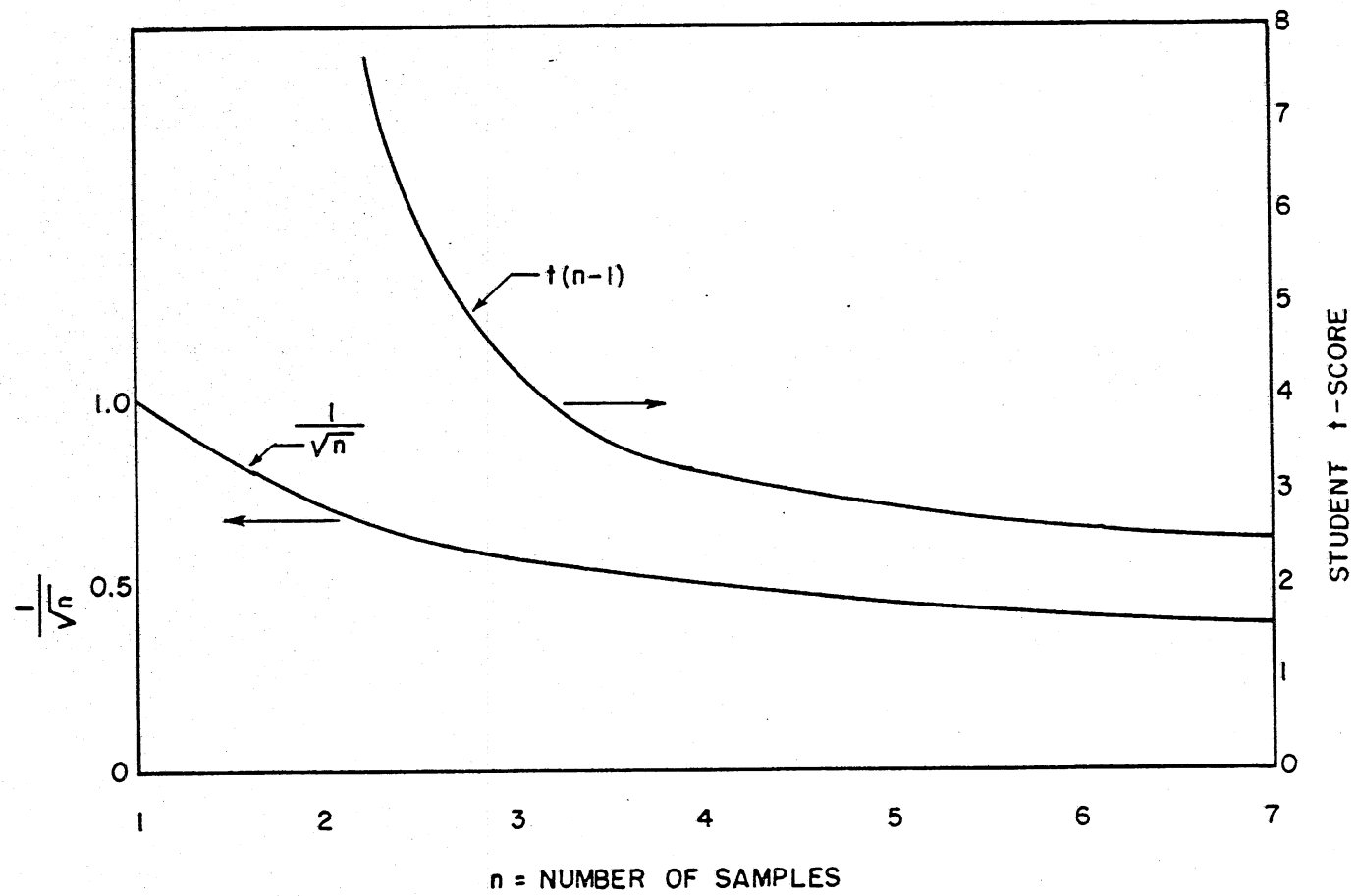


Fig. III-5 Student t-score vs. number of samples.

The alternative of analyzing more samples reduces the uncertainty in C by way of the $n^{-1/2}$ factor. After initial experiments, the number of samples analyzed might have been increased. All unanalyzed samples were retained until the results were computed and the quality was assessed. Those samples would then have been analyzed, had it appeared beneficial to do so.

9. Comparison with another laboratory/technique

It should be desirable to show that this technique gives the same results as others. For the purpose of this work, the desired results were not the actual values of the concentrations but the relative concentrations. Therefore, for this work, it is not necessary to check the concentrations against another laboratory.

10. Limitations of data

There is little one can say in advance about what quality of data is needed or what uncertainty is acceptable. The quality is largely determined by the technique, as it has been described up to this point. It will be up to subsequent researchers to decide if the technique and data produced here is of high enough quality for their modeling purposes. The results obtained by the author are seen to be of very high quality. The quality is seen as especially good in light of the difficulties associated with measurements of oxygen transfer.

IV. WEIR EXPERIMENTS

In order to test the procedure outlined in Section III, a field scale laboratory weir was constructed. In this section the construction, the tracer gas transfer tests, and their results will be discussed.

A. WEIR CONSTRUCTION

The weir used for this work was constructed in the main test channel of the St. Anthony Falls Hydraulic Laboratory. That channel is nine feet wide and six feet deep, it is fed by water from the Mississippi River and has a capacity of 300 cubic feet per second. Because the channel had other users, a full width weir could not be constructed. Also, the fall height or the tailwater depth of a weir constructed across the channel would be very limited. Furthermore, the side walls of the channel are permanent and a full width weir could not be ventilated properly. An alternative weir was designed such that other users of the channel could continue their work unimpaired by the presence of the weir (Fig. IV-1).

The weir was constructed 0.908 m wide and 0.52 m high across the end of a 3.05 m long by 0.908 m wide by 0.71 m high tank. The tank was placed at the center of the channel on steel bridges which were laid across the top of the channel walls (Figs. IV-1, IV-2 and IV-3). The weir was constructed of 3/4 inch plywood with an approximately 3 mm thick sharp-edged aluminum crest bolted to the upstream face of the plywood. In order to avoid the bursting of the nappe at the ends, it was necessary to extend 10 cm "fins" downstream from the crest (see Fig. IV-4).

Water was supplied to the weir from the main supply channel of the laboratory through a 15-cm I.D. PVC pipe. The flow in the pipe was controlled by a gate valve 11 m upstream. The pipe fed the weir tank about 30 cm from the upstream end of the tank (Fig. IV-1). The pipe was capable of supplying flows of up to 0.058 m³/s. Two bundles of chicken wire mesh, each 30 cm thick, were placed across the section of the tank to control waves and reduce turbulence.

Discharge was determined using a point gauge to determine the head on the weir and the weir equation [Henderson, 1966] was used to determine the specific discharge:

$$q = \frac{2}{3} C_d \sqrt{2g} H_w^{3/2} \quad (\text{IV-1})$$

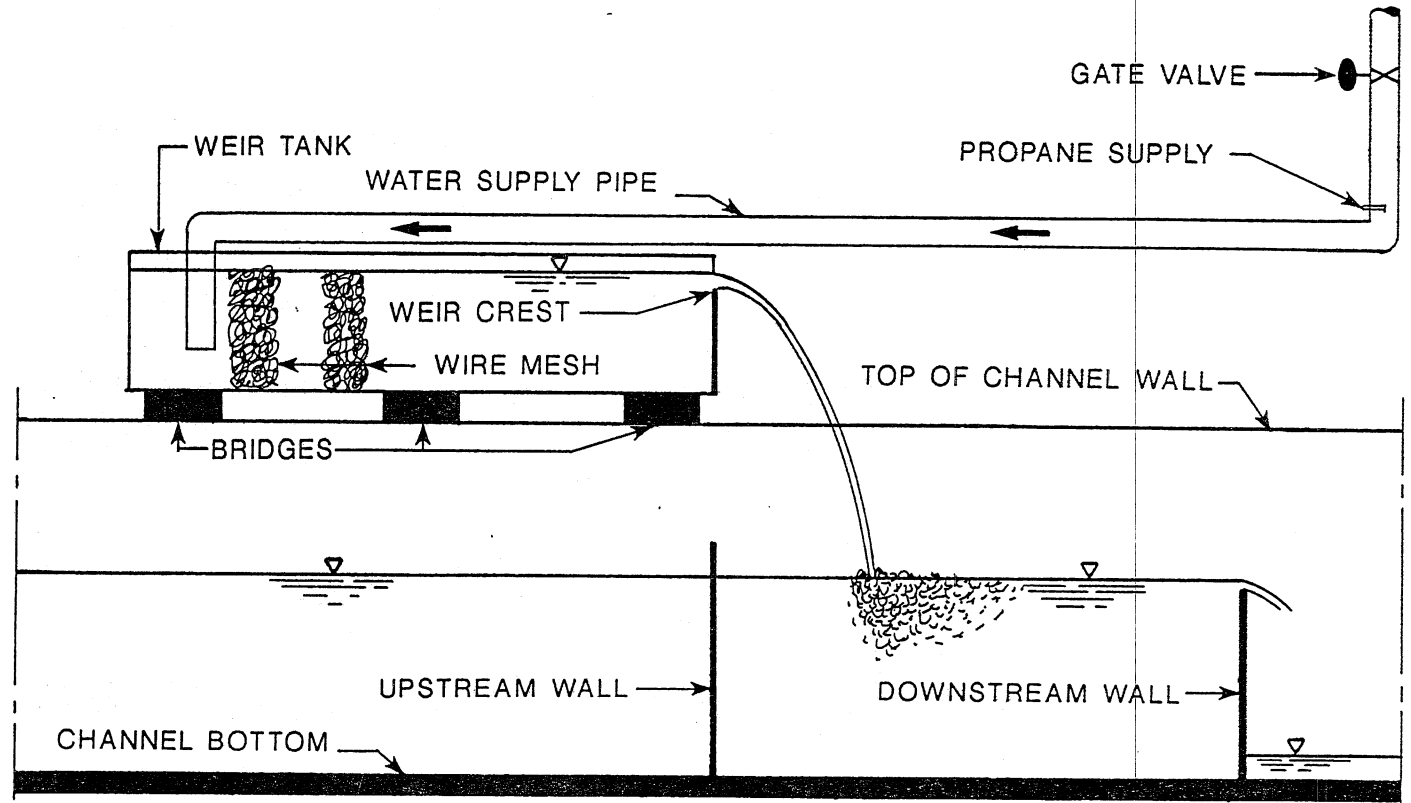


Fig. IV-1 Elevation of weir tank and channel.

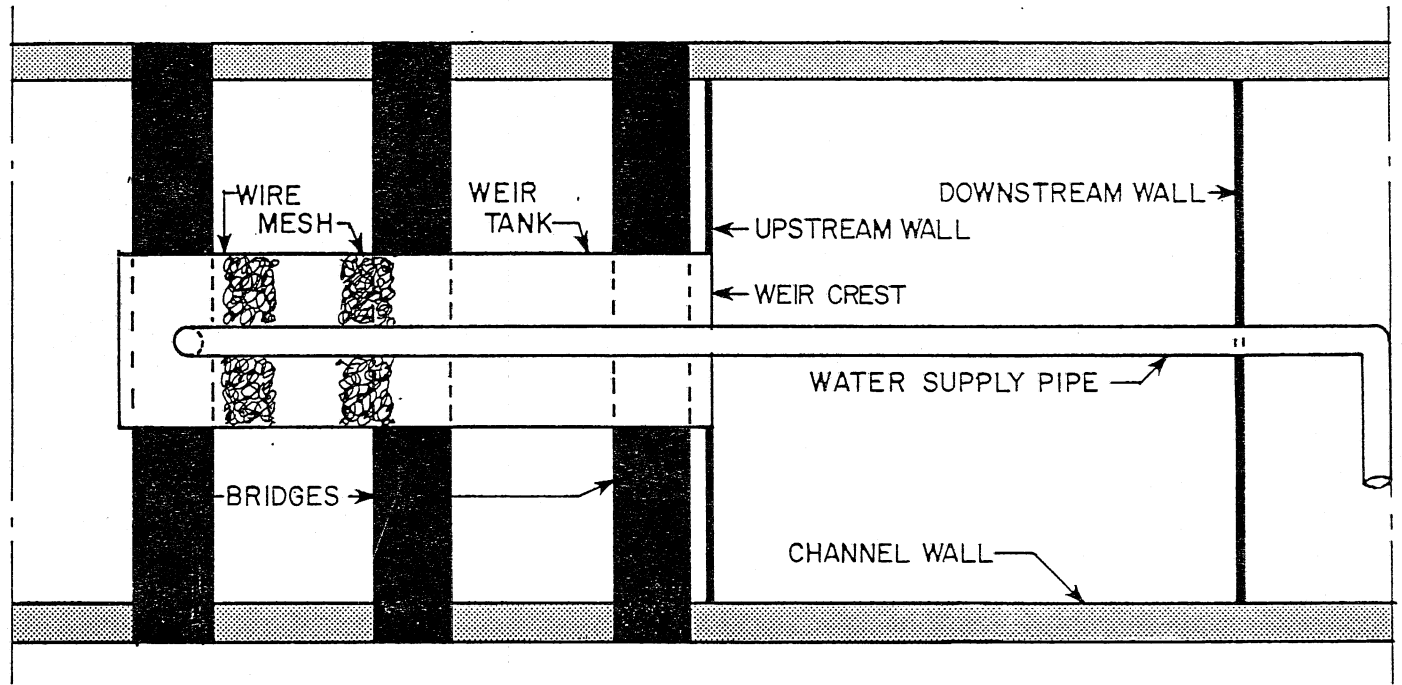


Fig. IV-2 Plan view of weir tank and channel.

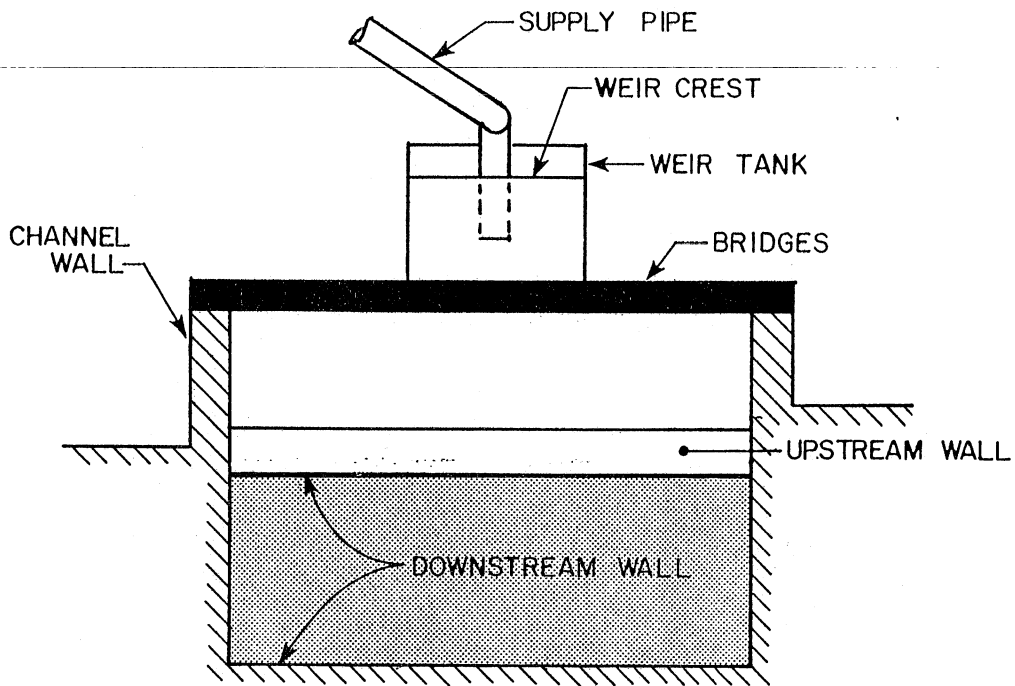


Fig. IV-3 Front view of weir tank and channel.

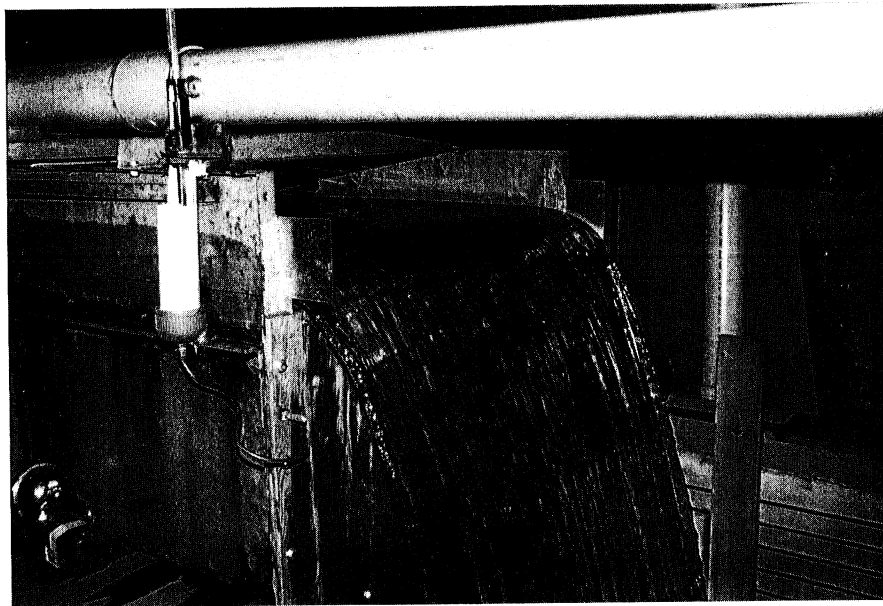


Fig. IV-4 Photograph of weir showing fins, point gage and well.

where q is the specific discharge (m^2/s), H_w is the head on the weir (m), and C_d is the contraction coefficient given by Henderson [1966]:

$$C_d = 0.64 + 0.08 \frac{H_w}{a} \quad (\text{IV-2})$$

where a is the height of the weir above the bed of the approach channel (m). To measure the head on the weir, a point gage was placed in a 5 cm diameter well on the side of the weir tank (Fig. IV-4). The pressure tap was located at four times the maximum head on the weir [Ackers et al., 1978], or 40 cm upstream of the weir face. The pressure tap was a 1/4-inch copper tube through the side of the tank. It extended 5 cm perpendicular to the side wall of the tank; the other end was connected to the well.

The zero reading on the point gage was determined by filling the tank to the level of the weir crest and measuring the water surface in the well by the usual method; the point gage was lowered until the first disturbance in the water surface was observed. The point gage was equipped with a vernier scale capable of measurements to 0.001 feet (0.3 mm). The precision of the point gage is estimated to be less than .002 ft.

The nappe from the weir fell into a pool in the main channel. The dimensions of the tailwater pool and the volume available for mixing were controlled by placing two temporary walls across the channel. At the upstream end of the pool (under the crest of the weir) a nine foot by four foot piece of 3/4-inch plywood was placed across the channel. This wall was not water-tight and only served to restrict mixing to the area downstream of the weir. The wall was placed in the channel when the tailwater had reached the desired level for the test.

To control the tailwater elevation and determine the tailwater control volume, a second wall of 1.5-inch by 5.5-inch boards was constructed across the channel. A heavy plastic sheet was placed over the upstream face to control leaking. The wall was 4.5 m downstream of the weir crest. The water was allowed to flow over the top of the wall and down the channel to the outfall. The depth of the tailwater was determined simply by lowering a tape measure to the bed and reading it at the water surface.

A concentrated propane solution was injected into the supply pipe approximately nine meters upstream of the weir tank. The solution was injected into the center of the pipe with a 10-mm tap through the side of the pipe. The first experiment failed due to inadequate mixing when the propane was injected at the downstream end of the supply pipe. The propane solution was injected far upstream to supply the necessary mixing.

The propane solution was prepared outdoors, one and a half floors above the weir in a 400-L steel tank. The solution was siphoned down to the weir in a 1/2-inch hose and the discharge was controlled by a valve on the hose. Because these tests were performed in the winter, the portion of the hose which was outdoors was insulated to prevent freezing which could cause the discharge to vary. Although the head in the propane tank may

have varied by up to 30 cm during a test, the change in the discharge was found to be small. Discharge through a closed conduit, such as the hose used here, varies with the pressure head to the $1/2$ power. Because the head was large (5.7 m) a variation of 0.3 m would not cause a large change in discharge. For the worst case, with the initial head of 5.7 m and a final head of 5.4 m, the ratio of the initial discharge to the final should be $(5.7/5.4)^{1/2} = 1.03$, thus the greatest variation in flow to be expected would be three percent. In each of the experimental runs the variation of the initial six upstream samples was less than three percent over the time in which they were taken. In all tests except W7 there was no noticeable trend in propane concentration. In test W7 (the test with the longest retention time, and therefore the longest test) a small trend was noticed; the last upstream sample was approximately three percent lower than the first.

B. PROCEDURE FOR PROPANE GAS TRANSFER MEASUREMENTS

Several measurements of propane gas transfer were made using the experimental set-up described above. The procedure used for those measurements is outlined in this section.

On each day that a measurement was made, the intake gate to the main channel was checked for leaks and resealed if necessary. The water for the test came from a different source, so it was important that there were no other sources of water to the system.

The next step was to install the downstream wall and hang the plastic sheet over the upstream face. The boards of the wall were installed up to the desired tailwater level. The gate valve was then opened and the flow was set. After the flow was set, the point gage was checked to determine if the weir was operating at the desired discharge. The channel was allowed to fill to the top of the downstream wall while the propane solution was prepared. Two field blank samples were taken from the weir tank and their numbers were recorded.

The propane solution was prepared in the 400-L tank. First the tank was filled with tap water, then a Sanitare brand fine bubble porous stone diffuser was placed on the bottom of the tank. Commercial heating grade propane gas was obtained from a local supplier in a 20-lb tank equipped with a variable-flow regulator. Half-inch tygon tubing fed the propane gas through a rotameter-type flow meter and to the diffuser. The gas was bubbled at approximately 5 L/s for 20 to 30 minutes. This injection was probably excessive, but it was done to ensure high concentrations of propane. To alleviate concerns that the excess gas would concentrate somewhere and pose an explosive hazard, the gas was burned as it escaped the water surface. The gas was simply lit with a welding torch lighter and the flame maintained itself as long as the wind was not too strong or the propane flow rate too small.

After the propane solution was prepared, a 1/2-inch hose was run from the tank through a window and down to the level of the weir. A siphon was started and the flow was controlled by a valve at the end of the hose, the discharge from the hose was checked by measuring the time to fill a

one-liter bottle. The exact discharge was not required, it was only necessary that enough solution was used to get a high enough concentration and that so much was not used that the solution would expire before the test was completed. After the flow was set, the hose was connected to the tap in the pipe. At that time, a stopwatch was started to monitor the progress of the test.

When the tailwater pool had been filled and was overtopping the downstream wall, the upstream wall was lowered into position. This wall only separated the tailwater control volume and the water on the upstream side of the wall so they would not mix. The head on the weir was checked once more before sampling began.

The sampling started when the time on the stopwatch was at least two times the hydraulic retention time of the weir tank. The times at which the six upstream samples were taken are as described in Section III-E., Field Samples. The six samples were taken 60 cm upstream of the weir crest and at locations 15, 45 and 75 cm across the tank and 25 cm above the bottom and 10 cm below the water surface. For each sample, the sample vial number, the time of sampling, the location, and its partner were all recorded. Then the downstream samples were taken as quickly as possible. The samples were taken 30 cm upstream of the downstream wall and at locations of 30, 80, 135, 190 and 240 cm across the tailwater pool and 10 cm below the water surface. The final sample was taken 60 cm upstream of the weir in the center of the channel and 10 cm below the water surface. It was important to take these samples as quickly as possible so that the propane discharge into the weir tank would not change or expire.

After all the samples had been taken, the water temperature was measured above and below the weir, the tailwater depth was measured and the head on the weir was checked once more.

Later, on the evening of the test, the samples were transported to the GC laboratory where they would be analyzed the next day. The next day the samples were analyzed, as described in Section III-A. Subsequently the data were reduced as in Sections III-C., III-D., and III-E. using a FORTRAN computer program written for that purpose. The conditions under which the measurements were made and the results of that analysis will be the subject of the next section.

C. RESULTS OF PROPANE GAS TRANSFER MEASUREMENTS

Measurement of gas transfer at weirs is relatively precise and simple, providing an excellent stage for testing the measurement techniques developed herein. In addition, the equations available in the literature perform reasonably well with the data to which they have been applied, and it was believed that the results of this test could be used to test and verify the application of the equations. The equations were not seen as a way to test the applicability of tracers because they were not sufficiently precise. Furthermore, the data sets used to develop the equations are not sufficiently comprehensive. In fact, the prototype data used by Nakasone [1987] to verify his predictive equations, which incorporated tailwater depth (and were

based on the results of laboratory experiments), has shown a relatively complete correlation between discharge and tailwater depth [Gulliver and Rindels, 1987]. It was therefore decided to choose a set of tailwater depth and discharge combinations which did not agree with that correlation. In Fig. II-2 [Thene and Gulliver, 1988] the discharge and tailwater depths of Nakasone [1987] and the author are compared. It was felt that the discharge and tailwater depths chosen should test the limits of the equations of Nakasone, and the results could be used to give greater insight into the effects of tailwater depth on reaeration at weirs.

Ten tests of the hydrocarbon gas tracer technique for weirs were made at St. Anthony Falls Hydraulic Laboratory during the period of February 10 to March 25, 1988. The first test failed due to incomplete mixing upstream of the weir. The test was repeated (Test W2) when the propane solution was injected into the water supply pipe upstream of the weir as shown in Fig. IV-1. No significant difference in concentration was found across the weir for the later tests, indicating that mixing was adequate. The last nine tests gave very good results. The uncertainties, to the 95% confidence interval, were computed for the transfer efficiencies and were found to be very low, ranging from 0.009 to 0.014. These values range from 1.7 to 5.4 percent of the transfer efficiency. The results, at the temperature measured, are reported in Table IV-1, and in Appendix A.

TABLE IV-1. Propane Gas Transfer Measurement Results

Exp. Run	q (m ³ /m/s)	Fall Height (m)	Tailwater Depth (m)	Temp (°C)	Efficiencies at Field T		
					Propane E (-)	Unc. (-)	Methane E* (-)
W2	0.0325	2.09	0.50	2.8	0.506	0.012	0.307
W3	0.0321	1.52	1.08	2.6	0.313	0.013	0.284
W4	0.0629	1.56	1.08	2.5	0.414	0.014	0.189
W5	0.0626	1.99	0.65	3.5	0.491	0.009	0.339
W6	0.0637	1.98	0.65	5.8	0.499	0.010	0.372
W7	0.0147	2.29	0.28	3.2	0.530	0.009	(neg)
W8	0.0643	2.28	0.35	4.0	0.439	0.011	0.501
W9	0.0145	1.50	1.07	3.4	0.259	0.014	0.173
W10	0.0341	2.28	0.31	5.3	0.453	0.012	

*Methane efficiency corrected to propane by Eq. IV-3
(see Section IV-D.)

Two tests, W5 and W6, were performed at the same discharge, fall height, and tailwater depth. The purpose of this was to show that the technique was repeatable; the results in Table IV-1 confirm that it is. The two tests show just a 0.008 difference between the two efficiencies.

At the time of weir test W10, the dissolved oxygen was measured by Winkler titration above and below the weir. The water at that time was lightly supersaturated as the upstream values were higher than those downstream. The difference in concentrations was only approximately 0.5 mg/L. These measurements confirm the usefulness of a tracer technique. If these measurements had been made with oxygen, the results would be subject to large errors due to the small surplus of oxygen.

The results from Table IV-1 were converted to transfer efficiencies of oxygen at 20°C by the indexing method of Rindels and Gulliver [1988] given by Eq. II-8. The results of the propane weir tests, converted to 20°C and oxygen are presented along with the values predicted from Eq. II-5 [Avery and Novak, 1978, converted from 15°C to 20°C by Eq. II-8] and from Eq. II-6 [Nakasone, 1987] in Table IV-2. The discharge used in Eq. II-5 is the discharge per unit width of the nappe at impact. The width of the nappe was measured for each test and the discharge used for Eq. II-5 is given as q_i in Table IV-2.

TABLE IV-2. Propane Gas Transfer Measurement Results and Values Predicted from Avery and Novak [1978] and Nakasone [1987].

Exp. Run	q (m ³ /m/s)	q_i (m ³ /m/s)	Fall Height (m)	Tailwater Depth (m)	Efficiencies (oxygen at 20°C)			
					Meas. (-)	Unc. (-)	Avery [1978] (-)	Nakasone [1987] (-)
W2	0.0325	0.0347	2.09	0.50	0.764	0.012	0.726	0.623
W3	0.0321	0.0329	1.52	1.08	0.537	0.018	0.632	0.612
W4	0.0629	0.0608	1.56	1.08	0.645	0.017	0.528	0.724
W5	0.0626	0.0611	1.99	0.65	0.742	0.009	0.665	0.738
W6	0.0637	0.0622	1.98	0.65	0.731	0.011	0.663	0.741
W7	0.0147	0.0178	2.29	0.28	0.783	0.009	0.795	0.463
W8	0.0643	0.0635	2.28	0.35	0.682	0.012	0.704	0.715
W9	0.0145	0.0163	1.50	1.07	0.454	0.021	0.687	0.486
W10	0.0341	0.0364	2.28	0.31	0.687	0.013	0.746	0.603

The results of the tracer tests are compared with the computed values in Figs. IV-5 and IV-6. The propane gas transfer measurements give reasonable agreement with the predictive theories for oxygen transfer. A standard error (based on the measured minus the predicted efficiency) of 0.1 is found for Avery and Novak's equation and one of 0.13 is found for the Nakasone equation. Thus there was a 2/3 chance that predictions of transfer efficiency from Avery and Novak's equation would be within 0.1. It appears, however that there may be some room for improvements in the theories, especially if one considers run numbers W7 and W9, where the prediction of gas transfer was off considerably.

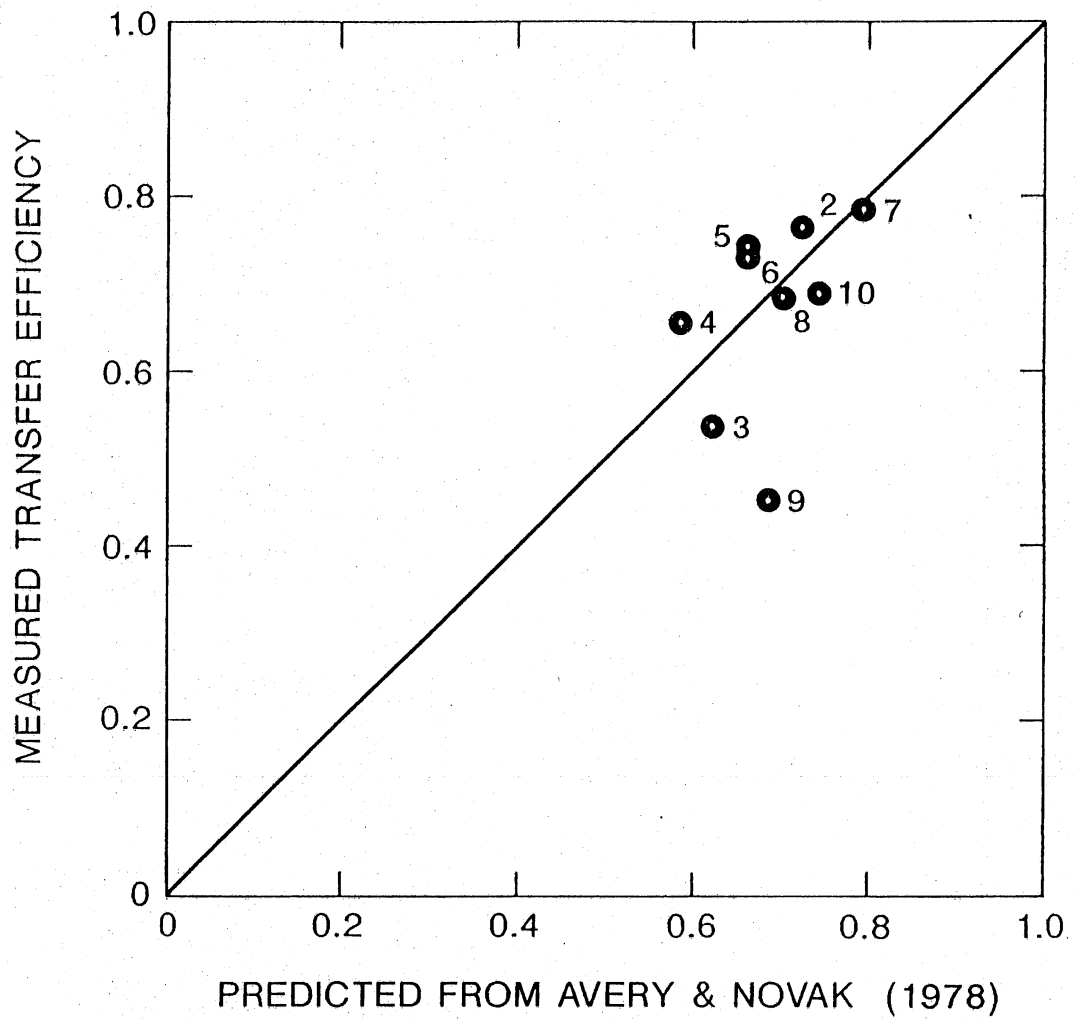


Fig. IV-5 Comparison of results of tracer tests and predictions from Avery and Novak [1978].

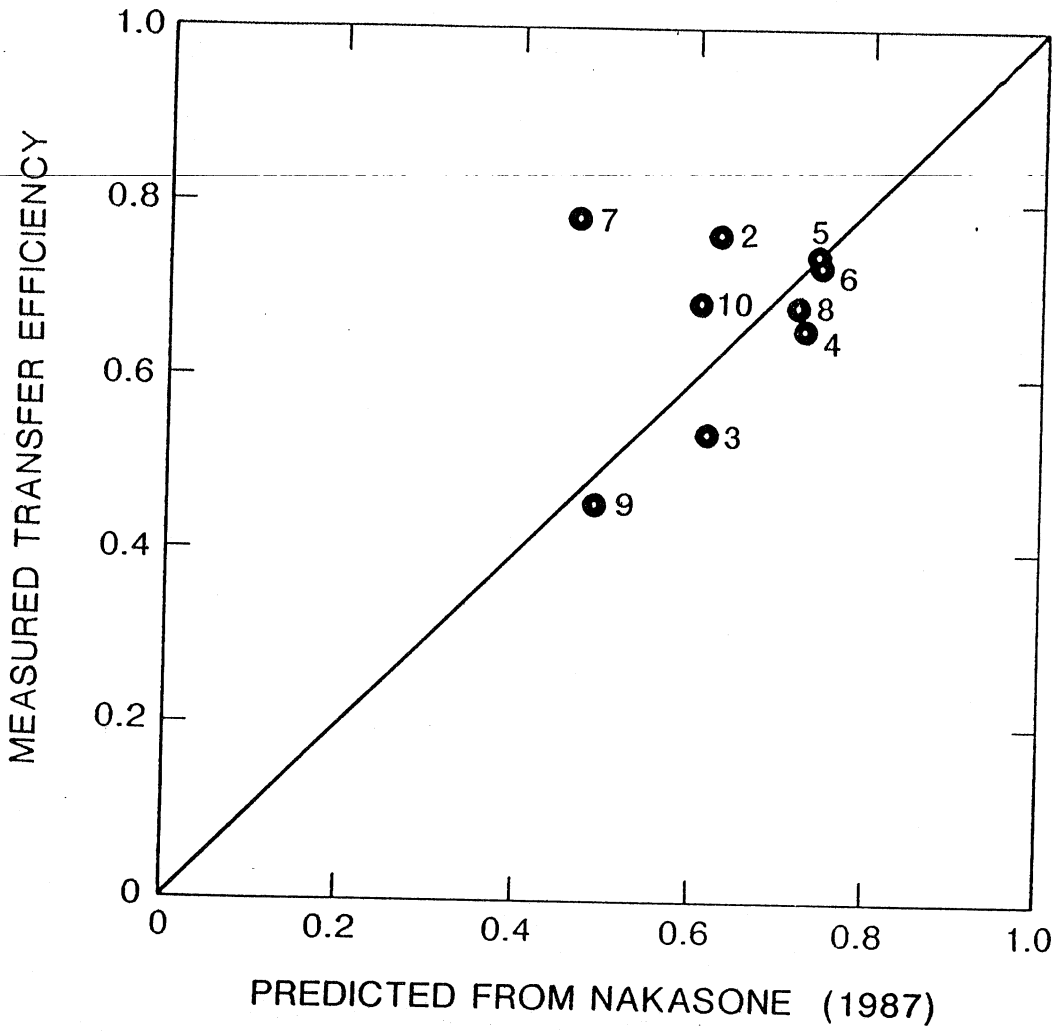


Fig. IV-6 Comparison of results of tracer tests and predictions from Nakasone [1987].

D. RESULTS OF METHANE GAS TRANSFER MEASUREMENTS

Methane gas was present in the river water samples taken for the weir experiments described above. When the samples were analyzed for propane, the gas chromatograms showed methane responses as well. It was thought that additional gas transfer data could be acquired if the methane responses of the samples were analyzed as the propane responses were and the methane gas tracer technique could be tested, however the methane responses were not as good as the propane responses. A typical chromatogram (Fig. IV-7) shows that there was a dip in the baseline of the chromatogram that lead into the rising leg of the methane peak. This dip caused significant errors in the integration of the methane response.

The dip was likely caused by a pressure wave resulting from the large volume of air injected with the sample or by the air itself which should elute before the methane. The gas chromatographic column used for this test was not capable of separating this dip from the methane peak. A different column may be capable of separating the methane from the pressure wave.

The solubility of methane used was that reported by Wilhelm et al. [1977]. There was one difference in the computational analysis of methane, and that was that there is an atmospheric component of methane. The approximate concentration is given in the *CRC Handbook of Chemistry and Physics* [Weast, 1980] as 2 ppm by volume, or 1.3 $\mu\text{g/L}$. That concentration was subtracted from the headspace concentration before it was inserted into Eq. III-5 to compute the water concentration. It was not attempted to find a more exact concentration of atmospheric methane because the results of the methane analysis were so imprecise anyway. In future tests, it is recommended that the headspace be created using some pure hydrocarbon-free gas such as nitrogen. In this way there should be no concern about the atmospheric component of methane.

The problems mentioned above resulted in intolerable uncertainties in the methane transfer efficiencies. The precision uncertainties were so large that the assumptions of the uncertainty analysis were no longer applicable; however, the uncertainties computed ranged from 0.16 to 0.8 with an average of 0.34 for the nine tests (W1-W9) analyzed. The dip most likely introduces a bias in the integration of the methane peak, thus even if a low precision uncertainty was realized, a large unknown bias would probably exist. The methane efficiencies were converted to propane efficiencies for comparison. The results of the literature review of in Section II-C., which related the overall gas transfer coefficients of methane and propane, were used to make the conversion from methane to propane. The conversion is given by:

$$\frac{\ln r_p}{\ln r_m} = 0.82 \quad (\text{IV-3})$$

where the subscripts m and p denote methane and propane respectively. The methane results are given in Table IV-1 with the original propane data, and the methane results (converted to propane efficiencies) are compared to

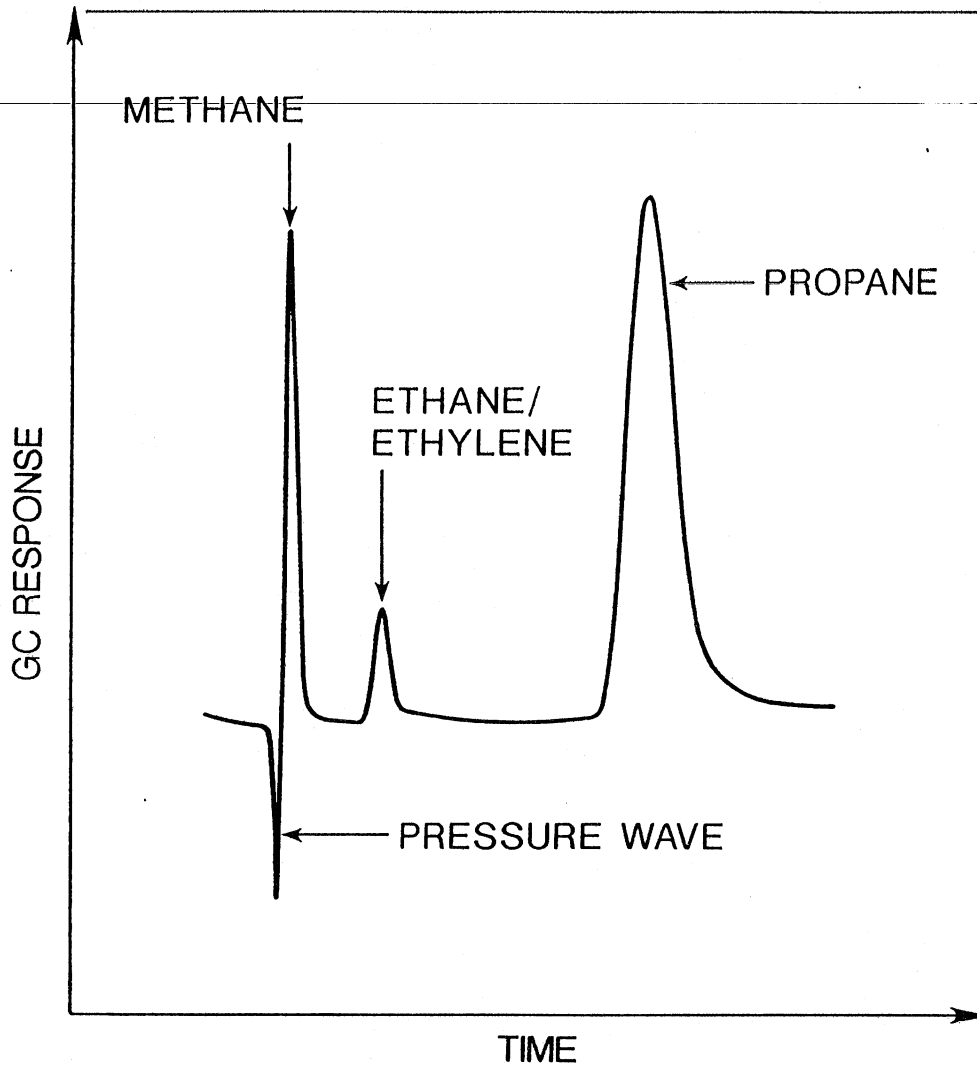


Fig. IV-7 Typical chromatogram.

propane results in Fig. IV-8. The bias in the integration plus the uncertainty in the atmospheric component of methane probably lead to the low transfer measurement (relative to propane).

Although the application of the methane tracer technique appears to have failed in this trial, it does show some promise. In seven of the eight tests analyzed, there was a transfer detected, i.e., the downstream concentration was lower than the upstream value. A longer column or one designed to analyze methane may be capable of measuring methane by the headspace technique. A capillary column may be able to pass this pressure wave (if indeed it is one) before the methane elutes from the column.

If it is found that methane cannot be analyzed by the headspace technique, the methane gas tracer method should be successful if the purge and trap technique of Shultz et al. [1976] is used.

The needs for further research and testing of the methane gas tracer method will be discussed in Section VII.

E. LIMITS OF DETECTION AND QUANTITATION

The limits of detection (LOD) and quantification (LOQ) were determined as outlined in Section III-E. at the same time that the samples from weir tests W7 and W10 were analyzed. The results of those tests are given in Table IV-3.

Table IV-3 Limit of Detection and Quantitation Samples

Weir test/Sample No.:	W7/52	W7/37	W10/11	W10/5
Conc. ($\mu\text{g/L}$):	1.90	0.69	0.35	0.33
	1.89	0.71	0.39	0.34
	1.90	0.77	0.31	0.38
	1.90	0.69	0.45	0.45
	1.92	0.65	0.40	0.46
	1.86	0.69	0.45	0.43
	1.85	0.66	0.43	0.51
Average	1.89	0.69	0.42	0.41
Std. Dev.	0.025	0.039	0.055	0.067
LOD	1.96	0.81	0.59	0.61
LOQ	2.14	1.08	0.97	1.08

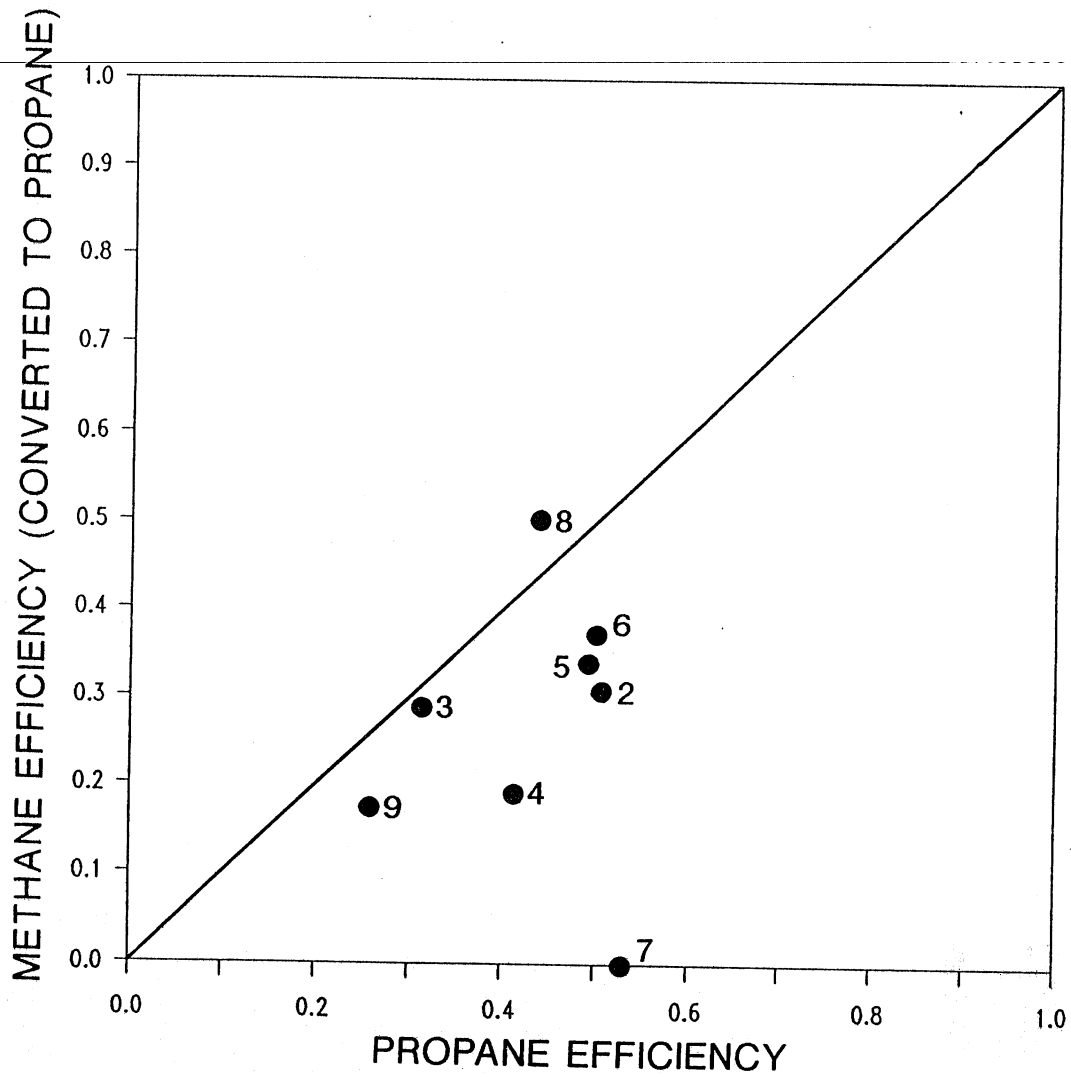


Fig. IV-8 Comparison of methane and propane results.

The samples were analyzed using 0.25 mL headspace samples. From the attempts made here to find these limits, they are determined to be:

$$\text{LOD} = 0.6 \quad , \quad \text{LOQ} = 1.0 \quad (\text{IV-4})$$

These results are good and compare well with the results of Rathbun [1986]. He claimed his purge and trap apparatus was capable of analyzing samples down to $0.1 \mu\text{g/L}$. The LOD and LOQ might be reduced by analyzing 1.0 mL headspace samples.

V. ANALYSIS OF WEIR EXPERIMENTS

In this section the results reported in the preceding sections, along with the data compiled by Nakasone [1987], will be compared to the predictive equation of Avery and Novak [1978]. Avery and Novak's equation will be altered by adding a term to account for the effects of tailwater. Another equation will be developed by the author which utilizes the results of Ervine and Elsayy [1975] and Elsayy and McKeogh [1977].

The analysis in this section will use the deficit ratio, r , as the variable which is predicted from hydraulic parameters. It is chosen because it is the variable used in the literature and because it is the solution (Eq. II-2) to Eq. II-1.

The performance of the predictive equations will be evaluated based on the errors in predicted transfer efficiency, $E = 1 - 1/r$. Transfer efficiency is chosen because its value is proportional to the amount of gas exchanged; therefore, errors in E will reflect the errors in downstream gas concentration predicted by the equations. Errors in the deficit ratio lead to prediction error in the downstream concentration which depends on r , as well as the error in r . As an example, an error of 0.2 in r can give widely varying errors in concentration depending on the value of r itself. If the true r value is 1.5 and 1.7 is predicted, the gas transfer predicted will be high by 19 percent of the upstream gas concentration (or deficit in the case of atmospheric gases). If r is 3.0 and is predicted to be 3.2, the gas transfer predicted will be high by only three percent of the upstream concentration. Thus, absolute errors in r are not indicative of the errors in predicted gas transfer.

If an erroneous value of E is predicted, the error in the amount of gas transferred remains the same regardless of the value of E . If the true value of E is equal to 0.5 and an erroneous value of 0.55 is predicted, the error in the gas transfer is equal to five percent of the upstream concentration. If E is equal to 0.7 and 0.75 is predicted, the error in gas transfer predicted will still be five percent of the upstream concentration. Thus, efficiency is a better indicator of the predictive capabilities of predictive equations of gas transfer at hydraulic structures.

A. ANALYSIS OF EQUATION OF AVERY AND NOVAK [1978]

In this section the data compiled by Nakasone [1987] along with those of the author are used in testing several equations. The data from Nakasone which were used are included in Appendix B. Some points were not used because they did not fit the constraints of the equations or because Nakasone himself had criticized them. Thirty-eight measurements from Nakasone [1987] were used. Nakasone lists only the physical characteristics

of the weir, the discharge, water temperature, and upstream and downstream oxygen concentrations. The saturation values used by Nakasone were not documented, nor were the computed deficit ratios, so saturation values from *Standard Methods* [American Public Health Association et al., 1980] were used to calculate the deficit ratios for this work.

The equation of Avery and Novak [1978] gives the deficit ratio at 15°C in terms of a Froude number and Reynolds number of the jet at the point of impact:

$$r_{15} - 1 = 0.64 \times 10^{-4} F_j^{1.787} R^{0.533} \quad (\text{II-5})$$

The standard error, s , of the efficiency to be used in this analysis is defined by:

$$s^2 = \frac{1}{n-1} \sum_{i=1}^n (E_m - E_c)^2 \quad (\text{V-1})$$

where E_m is the measured efficiency, E_c is the computed efficiency, and n is the number of observations ($n = 47$). The standard error computed for the data using Eq. II-5 is 0.120. The computed efficiencies from Avery and Novak are compared to the measured efficiencies in Fig. V-1. The error found by using the equation of Nakasone is 0.112. The efficiencies predicted from Eq. II-6 [Nakasone, 1987] are compared with measurements in Fig. V-2. The error calculated using the Nakasone equation is considered high since it had a tailwater depth term in it and there were four equations instead of one.

It was thought that a significant improvement could be made in the equation of Avery and Novak by adding a term to account for the effects of tailwater. A hypothesis was made that gas transfer should increase and then level off with increasing tailwater depth. The explanation is that, as tailwater depth increases, bubbles are entrained to greater depths and therefore the contact time and gas transfer are increased. This should hold as long as the bubbles are propelled to the bottom of the tailwater pool. As tailwater depth increases further, the bubbles will still be entrained only to the maximum depth possible (as determined by the discharge and impact velocity) and no increase in contact time or further transfer will be realized. A function which decreases r for low tailwater depth, H , but has decreasing effect for increasing H may improve the prediction. Therefore the form of the function was chosen as:

$$1 - \beta_3 \exp\left[-\beta_4 \frac{H}{h}\right] \quad (\text{V-2})$$

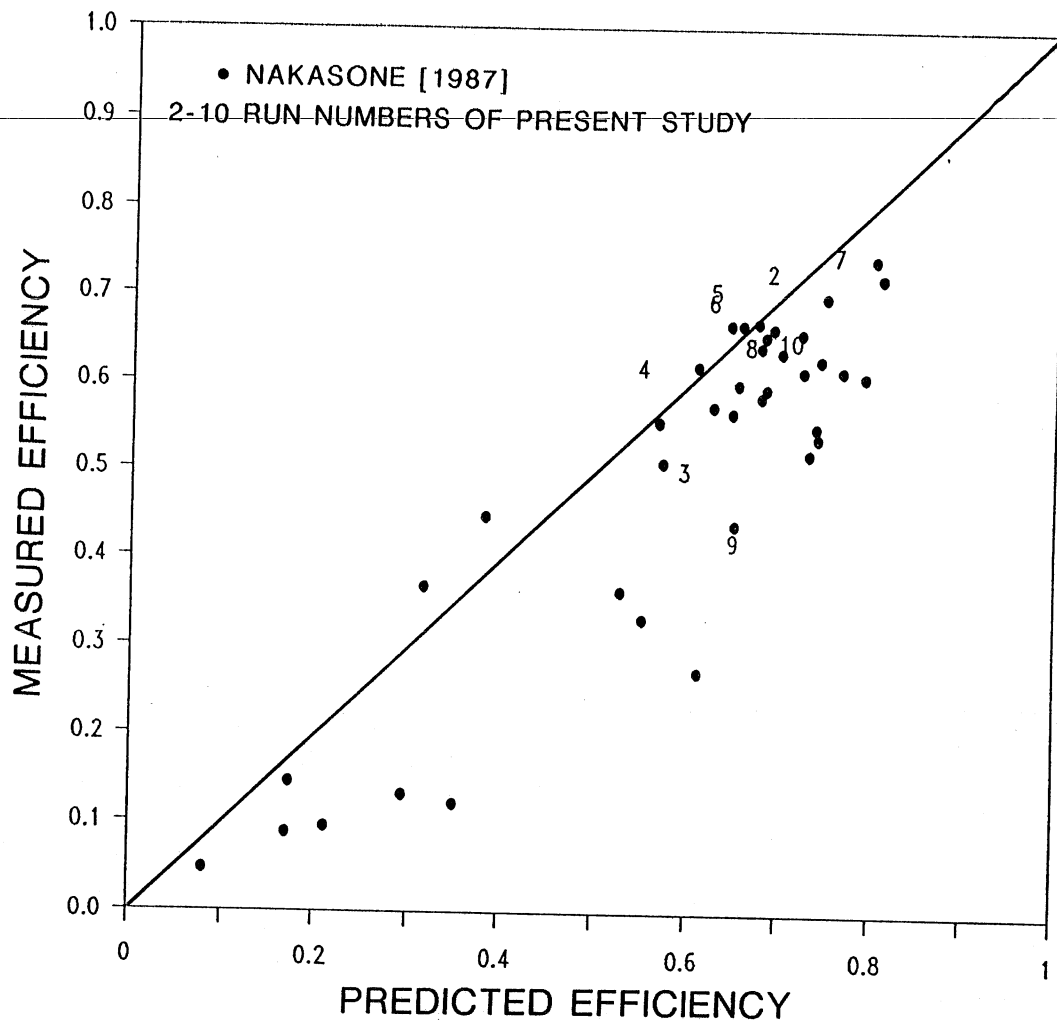


Fig. V-1 Comparison of measured transfer efficiencies with prediction of Avery and Novak [1978].

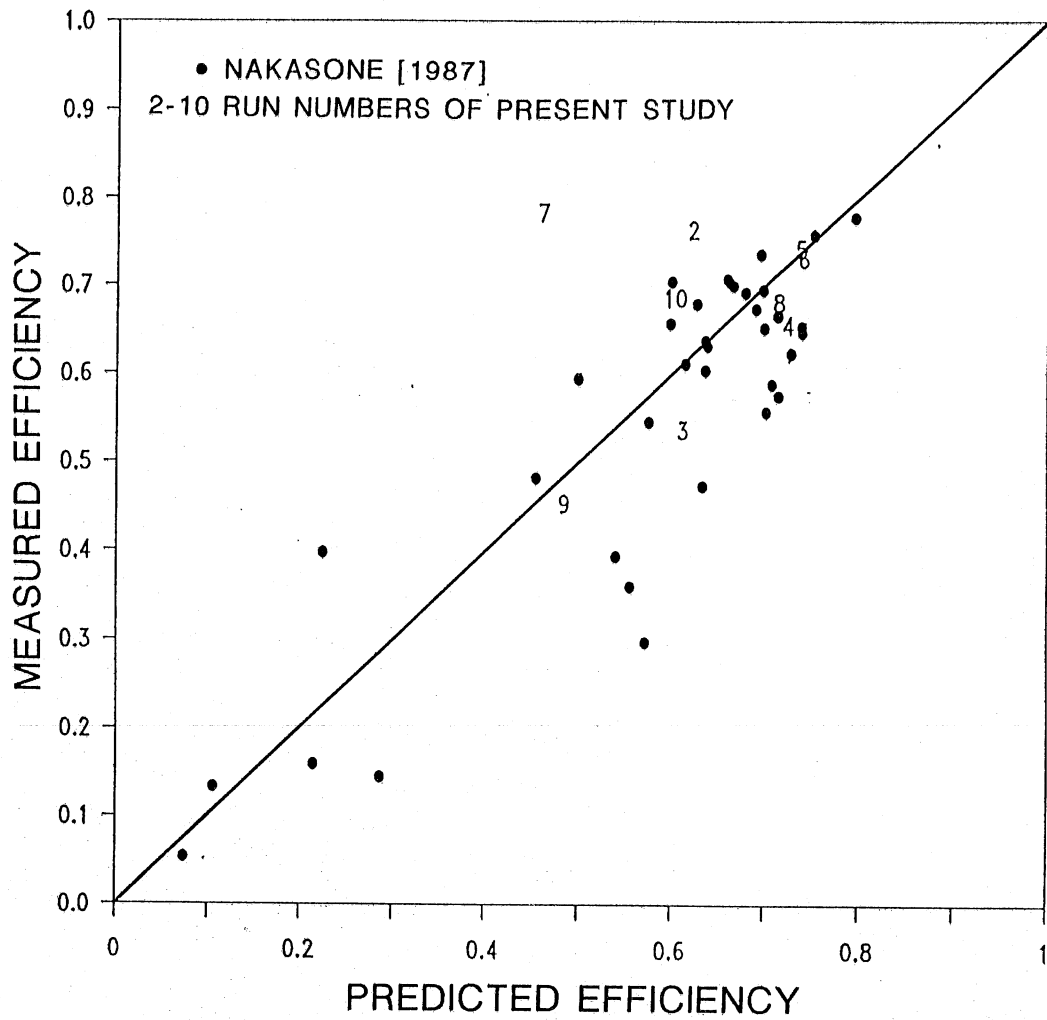


Fig. V-2 Comparison of measured transfer efficiencies with prediction of Nakasone [1987].

Where β_3 and β_4 are fitted constants, H is tailwater depth, and h is the fall height. In order to achieve geometric similitude, the tailwater depth term is non-dimensionalized by dividing by the fall height: H/h . Fall height, h , is the appropriate parameter to non-dimensionalize tailwater depth because it determines the impact velocity of the jet and therefore influences the depth to which bubbles may be propelled. In order to choose the terms β_3 and β_4 , the measured $(r_{15}-1)$ divided by the predicted $(r_{15}-1)$ was plotted versus H/h in Fig. V-3. A curve was chosen by hand which would have the form of Eq. V-2 and fit the data as well as possible. That curve is shown in Fig. V-3. The coefficients in Eq. V-2 were determined by choosing two points on that curve and computing them from Eq. V-2. The coefficients were $\beta_3 = 0.6$ and $\beta_4 = 3.7$. These coefficients gave the next result in this analysis:

$$r_{15} - 1 = (0.64 \times 10^{-4}) F_J^{1.787} R^{0.533} \left[1 - 0.6 \exp \left[-3.7 \frac{H}{h} \right] \right] \quad (V-3)$$

which is the Avery and Novak equation (Eq. II-5) multiplied by the function in Eq. V-2.

A log-linear regression was performed on an equation of the form given below:

$$r_{15} - 1 = \beta_0 F_J^{\beta_1} R^{\beta_2} \left[1 - 0.6 \exp \left[-3.7 \frac{H}{h} \right] \right] \quad (V-4)$$

where the coefficients β_0 , β_1 , and β_2 replace the coefficients in the original equation. In that regression β_0 , β_1 , and β_2 were allowed to vary. The final form of that equation was:

$$r_{15} - 1 = (1.005 \times 10^{-5}) F_J^{2.08} R^{0.63} \left[1 - 0.6 \exp \left[-3.7 \frac{H}{h} \right] \right] \quad (V-5)$$

The standard error in the efficiencies computed from Eq. V-5 was determined to be 0.095. This is an improvement of 0.025 in the Avery and Novak equation and 0.010 over the Nakasone equations. The predictions of Eq. V-5 are presented in Fig. V-4.

The improvement realized above is not significant enough to determine whether this equation describes the phenomenon better or merely fits the data better. The reason for that uncertainty can be seen in Fig. V-2. In that figure, it is seen that the data seem to cluster around the function of Eq. V-2; however, there does not seem to be enough data to confirm this form of the equation. It may be, for example, that the scatter in the region from $H/h = 0$ to $H/h = 0.5$ would continue to higher values of H/h if additional data were taken. In that case, merely changing the lead coefficient in Eq. II-5 may result in a similar improvement. Even with the

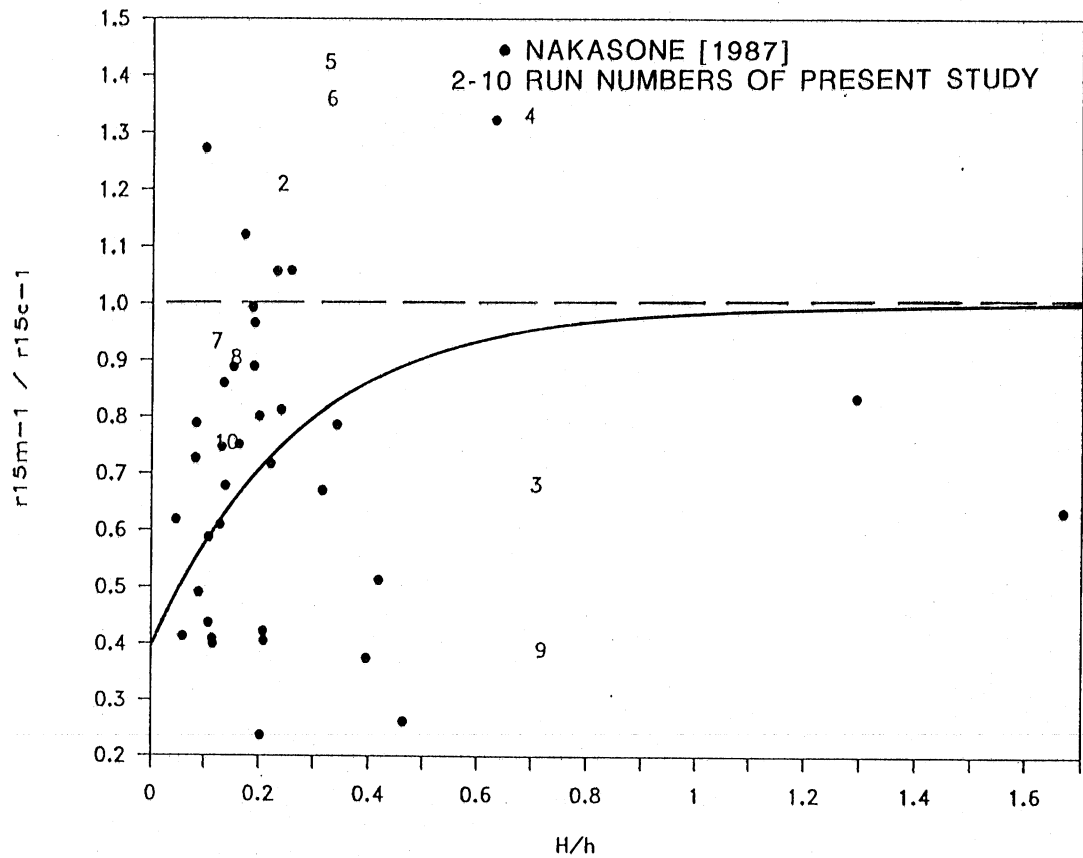


Fig. V-3 Errors in Eq. II-5 vs. H/h.

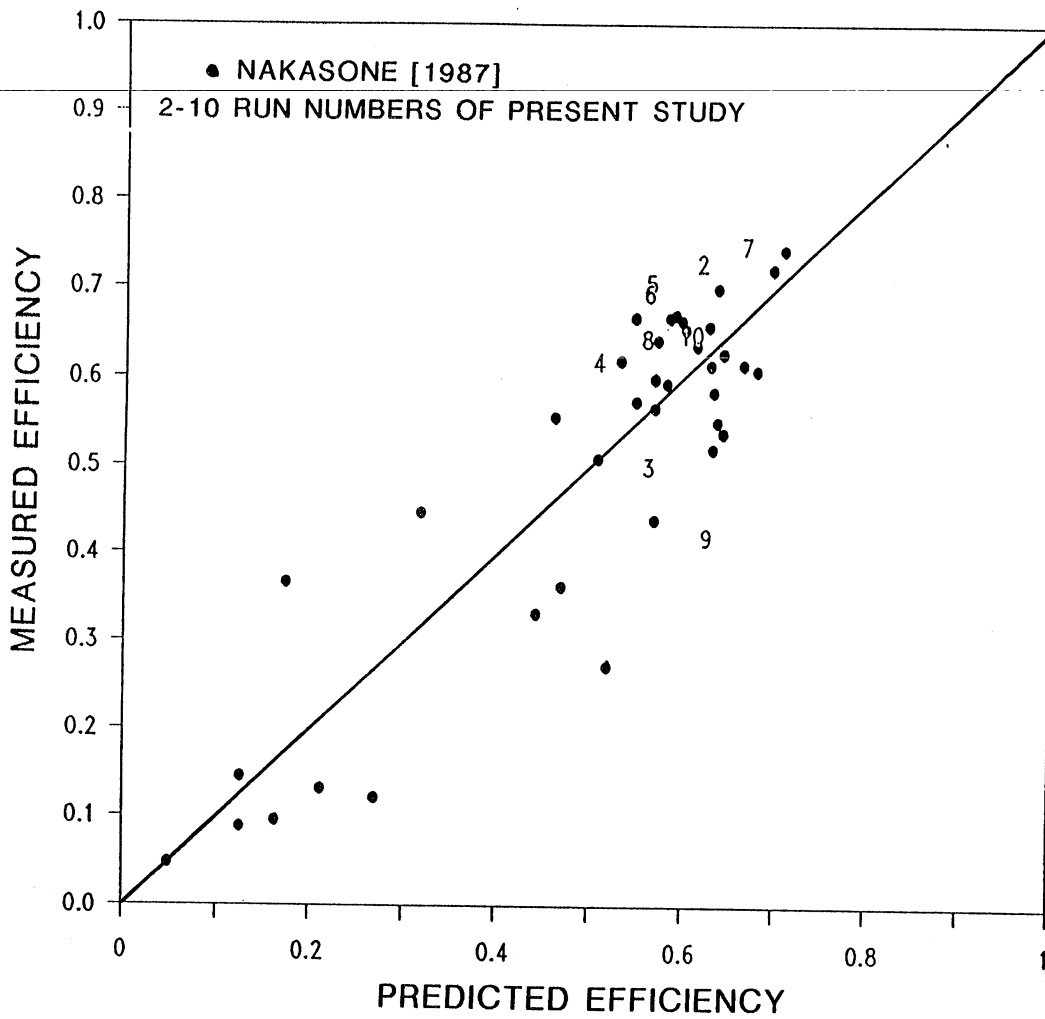


Fig. V-4 Predictions from Eq. V-5.

question raised above, the tailwater function computed here is seen to be at least as valid as that of Nakasone. With one equation, Eq. V-5 performs better than the four of Nakasone.

B. ANALYSIS OF WORK OF ELSAWY ET AL.

In the mid-1970's Elsayy et al. [Ervin and Elsayy, 1975; Elsayy and McKeogh, 1977] studied the air entrainment of water jets impinging on a free water surface. Ervin and Elsayy [1975] studied the rate of air entrainment caused by a rectangular jet impinging on a free water surface. Elsayy and McKeogh [1977] studied the volume of air entrained by a circular jet impinging on a free water surface. The equations resulting from those studies will be used here to find a relation to predict the gas transfer at weirs.

Ervin and Elsayy [1975] found the following relation predicted the rate of air entrainment for a rectangular jet:

$$\frac{Q_a}{Q_w} = 0.26 \left[\frac{b}{p} \right] \left[\frac{h}{t} \right]^{.446} \left[1 - \frac{v_0}{v} \right] \quad (V-6)$$

where Q_a is the discharge of entrained air, Q_w is the water discharge of the jet, b is the width of the jet, p is the perimeter of the jet, h is the height of fall, t is the thickness of the jet, v is the velocity of the jet at impact, and v_0 is the minimum velocity required to entrain air. The minimum velocity needed to entrain air, v_0 , was found to be 1.1 m/s.

Elsawy and McKeogh [1977] found the volume of air entrained by a circular jet to be:

$$V_a = 1.2 \left[\frac{Fr_i}{0.5 Fr_1 + 5.2} \right]^{3.7} d^3 Fr_1^{1.66} \quad (V-7)$$

where Fr_i is the Froude number of the jet at impact, Fr_1 is the Froude number of the jet as it exits the nozzle, and d is the diameter of the jet.

The two results above can be used to give a sort of average contact time, $t_c = V_a/Q_a$, of the bubbles entrained. The average contact time could be used to calculate the deficit ratio if the liquid film coefficient for the bubbles entrained, $K_L a$, was known. The contact time is related to the deficit ratio by Eq. II-2:

$$r = \exp(K_L a \cdot t_c) \quad (II-2)$$

Equations V-6 and V-7 could not be applied to wide weirs in the forms they are given in. Several modifications and assumptions were required to obtain a gas transfer equation for weirs, as outlined below.

The equation of Ervine and Elsayy only needed slight modifications to be applied to weirs. The perimeter, p , is given as $p = 2b + 2t$. For a long weir, the ratio t/b goes to zero and p becomes $p = 2b$. In that case, the b/p term in Eq. V-6 becomes $1/2$. In the case of a long weir Q_a/Q_w can be expressed as q_a/q_w where q is the discharge per unit width of weir. With these modifications, Eq. V-6 becomes:

$$\frac{q_a}{q_w} = 0.13 \left[\frac{h}{t} \right]^{.446} \left[1 - \frac{v_0}{v} \right] \quad (V-8)$$

The equation of Elsayy and McKeogh [1977] presented greater problems. In their equation, Froude number was defined as:

$$Fr = \frac{v}{\sqrt{gd}} \quad (V-9)$$

where v is the velocity of the jet, g is the acceleration due to gravity, and d is the diameter of the jet at the point where the Froude number is defined. The first approximation was to replace the diameter in the Froude number with the thickness of the rectangular nappe. This is accomplished by noting that diameter can be approximated as $4R_h$, where R_h is the hydraulic radius (which is the area of the jet divided by the perimeter). For a wide rectangular jet, R_h is equivalent to $t/2$. With that result the Froude number is defined as:

$$Fr = \frac{v}{\sqrt{gt}} \quad (V-10)$$

The constant $\sqrt{2}$ is removed from the Froude number and will be incorporated into the constant.

The next problem to be considered was the use of this Fr_1 in Eq. V-8. In the experiments which lead to that relation, a jet was issued from a nozzle at various values of Fr_1 and allowed to fall various heights before impinging on the water surface at Fr_1 . This exit Froude number apparently characterizes the flow conditions at the nozzle which are not simply related to the velocity at the point it is measured. Since the conditions near the crest of a weir vary widely, it was desirable to remove Fr_1 from the equation entirely. The method chosen to do that was to note that at every weir the flow goes through critical depth somewhere near the crest, thus, Fr_1 was defined as equal to unity, but the location where Fr_1 is taken is not

specified. The Froude number at impact is easily determined from energy conservation and continuity.

The only remaining problem then is the use of diameter in Eq. V-8. In order to find the volume of air entrained per unit width of weir, the volume equation is divided by the perimeter of the jet on each side. The left side is divided by the perimeter of a long rectangular jet, $2b$, divided by 2, or b . The right side of the equation is divided by the perimeter of a circular jet, πd , divided by 2, or $\pi d/2$. Finally, the remaining d^2 term on the right side is changed to $(2t)^2$ through the assumption of equivalent hydraulic radii. This analysis gives the result:

$$\frac{V_a}{b} = \frac{Fr_i^{3.7} t^2}{1193} \quad (V-11)$$

Now with the equations for discharge and volume in compatible forms, we divide volume by discharge to give the average contact time:

$$t_c = \frac{V_a}{b q_a} = \frac{Fr_i^{3.7} t^2}{1193} \frac{1}{0.13 q_w} \left[\frac{t}{h} \right]^{.446} \left[1 - \frac{v_0}{v} \right]^{-1} \quad (V-12)$$

In addition, $t/h = 2/Fr_i^2$. Then the relation for t_c , with the substitution for t/h is plugged into Eq. II-2 to give:

$$\ln r = \frac{K_L a}{114} \frac{Fr_i^{2.81} t^2}{q_w} \left[1 - \frac{v_0}{v} \right]^{-1} \quad (V-13)$$

It is necessary to define the manner in which the terms of Eq. V-13 were determined. The velocity at impact, v , was computed from the fall height and kinematics: $v = (2gh)^{1/2}$. The nappe thickness was determined by continuity: $t = q_w/v$. The Froude number was then computed from v and t as in Eq. V-9.

As a way to test this equation, the transfer coefficient, $K_L a$, was crudely assumed to be a constant. Equation V-12 was then fitted to the data of Nakasone and that of the present study by modifying just the lead coefficient, $K_L a/114$. (The discharge per width of nappe at impact, q_i in Table IV-2, was used for the testing of Eqs. V-13 through V-15. The discharges of Nakasone [1987] were used as they are tabulated in Appendix A.) A linear regression gave the following result:

$$\ln r = 0.0836 \frac{Fr_i^{2.8} t^2}{q_w} \left[1 - \frac{v_0}{v} \right]^{-1} \quad (V-14)$$

The error associated with the efficiencies calculated by Eq. V-14 is equal to 0.122.

Equations V-14 and V-13 indicate that $K_L a = 9.5 \text{ s}^{-1}$, assuming that the conversion from a circular jet to two dimensional jet through equivalent hydraulic radii is proper. For comparison, in an aeration column only 5 cm in diameter, Barnhart [1969] varied bubble diameter and found a maximum $K_L a$ of 6.5 s^{-1} at a bubble diameter of 2 mm. Bewtra et al. [1970] measured $K_L a$ values at 20°C of approximately 7.4 s^{-1} for saran tube diffusers. The above predictive equation, therefore, implicitly uses a value of $K_L a$ that is of the same order as those found through laboratory experimentation.

A further log-linear regression on Froude number gave:

$$\ln r = 0.156 Fr_i^{2.69} \frac{t^2}{q_w} \left[1 - \frac{v_0}{v} \right]^{-1} \quad (V-15)$$

The error associated with this equation was 0.113 which compares very well with Eqs. II-5, II-6 and V-5, which had errors of 0.120, 0.112 and 0.095, respectively. The efficiencies predicted from the preceding result are shown in Fig. V-5. The agreement between Eq. V-15 and the data is quite remarkable considering the assumptions needed to arrive at it and that only two coefficients were fitted. One of those coefficients, the exponent on Froude number, was only changed from 2.8 to 2.69. The other was needed to account for the liquid film coefficient and any other deficiencies. This equation should be tested against another set of data before being accepted and used for further work. Even this single equation, with no tailwater depth term at all, performs as well as the equations of Nakasone. For this reason, and those stated previously, the Nakasone equation should not be perpetuated.

Equation V-15 was tested to see if some relation between the errors in it could be related to tailwater depth. The errors were plotted against the tailwater depth over fall height term, H/h , in Fig. V-6. Apparently no simple function of H/h is capable of accounting for those errors; therefore, Eq. V-15 is the final form that will be reported here. Equation V-15 may be preferred to others because it has been derived from two equations which describe the physical process of air entrainment.

In their study of the volume of air entrained by a solid circular jet of water, Elsayy and McKeogh [1977] noted that, based on their early tests, two distinct types of air entrainment may occur, laminar and turbulent. For a given discharge and fall height, either mechanism could occur,

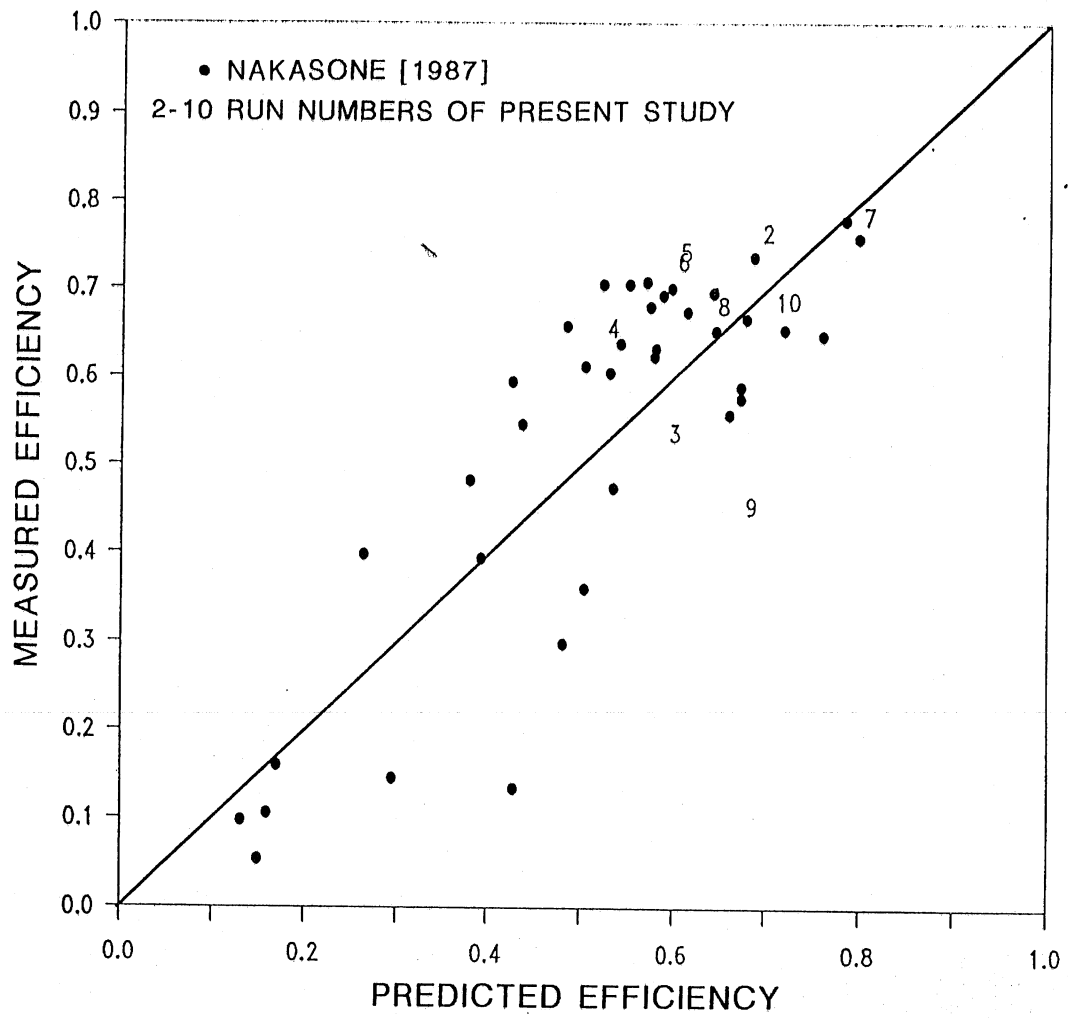


Fig. V-5 Predictions from Eq. V-15.

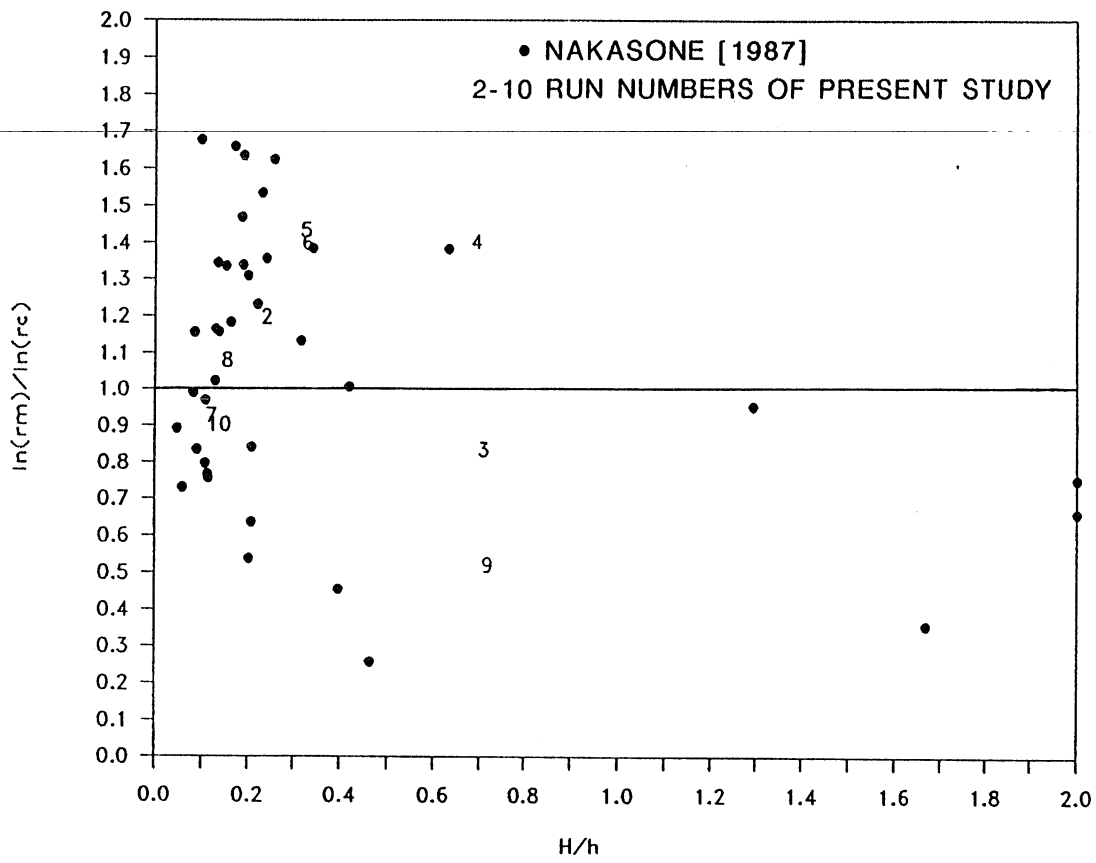


Fig. V-6 Errors in Eq. V-15 vs. H/h .

depending on the turbulence level in the jet as it issued from the nozzle. They noted the depth to which the jet would penetrate was also dependent on turbulence intensity. To test this idea, they varied the turbulence level in the supply tank and measured the volume entrained at different turbulence levels. They measured the velocity of the jet at the point of impact using a laser doppler anemometer. They then computed the percentage turbulence level by:

$$\epsilon = \frac{(\overline{u'^2})^{1/2}}{\bar{u}} \cdot 100\% \quad (\text{V-16})$$

where \bar{u} is the mean velocity and u' is the instantaneous deviation from the mean. Their results, shown in Fig. V-7 [Elsawy and McKeogh, 1977], display the pronounced dependence of the volume entrained on the turbulence as defined in Eq. V-16. They realized a seven-fold increase in the volume entrained when the turbulence was increased from one to three percent. The results confirmed qualitatively that the turbulence level was very important in their characterization of the air entrainment and therefore can be a significant factor in gas transfer at weirs. Thus, while the impact Froude number in Eq. V-15 represents the velocity of the impacting jet, the Fr_1 in Eq. V-7 represented the velocity and apparently, the initial turbulence level of the jet as it issued from the tank.

Some insight into the question of turbulence may be gained by investigating the data of the present study. The tests W9, W3 and W4 were performed using essentially the same tailwater depth, 1.08 m, and varying discharges of 15, 32, and 63 L/m/s, respectively. Because of the feeding system for the weir tank, some flows were quite turbulent. As discharge increased, the turbulence in the nappe also increased. Although the turbulence was not measured, a qualitative measure of the turbulence can be made visually in Figs. V-8a,b,c. These photographs show the front of the nappe for the various experiments. As the discharge (and turbulence) increases from the minimum value in test W9 to the maximum in W4, the ratio of measured efficiency to that predicted can be seen to increase in Figs. V-4, V-5 and V-6.

The effect of turbulence has either been ignored or not considered to be important by modelers before this time. There is still quite a bit of scatter in all of the predictions reviewed thus far and it is the author's opinion that this turbulence effect may be the primary reason for the errors in the prediction of gas transfer. Turbulence is a parameter that would be very difficult to monitor or predict in field weirs. It is therefore concluded that, although slight improvements in the predictive equations may be made in the future, the predictive power of equations for gas transfer at weirs may be nearly exhausted. Put another way, the errors associated with predictive equations will not be reduced much further without studying the effects of turbulence on air entrainment.

Although tailwater depth is seen to be an important parameter in the characteristics of weir aeration, it has not been entirely effective in the

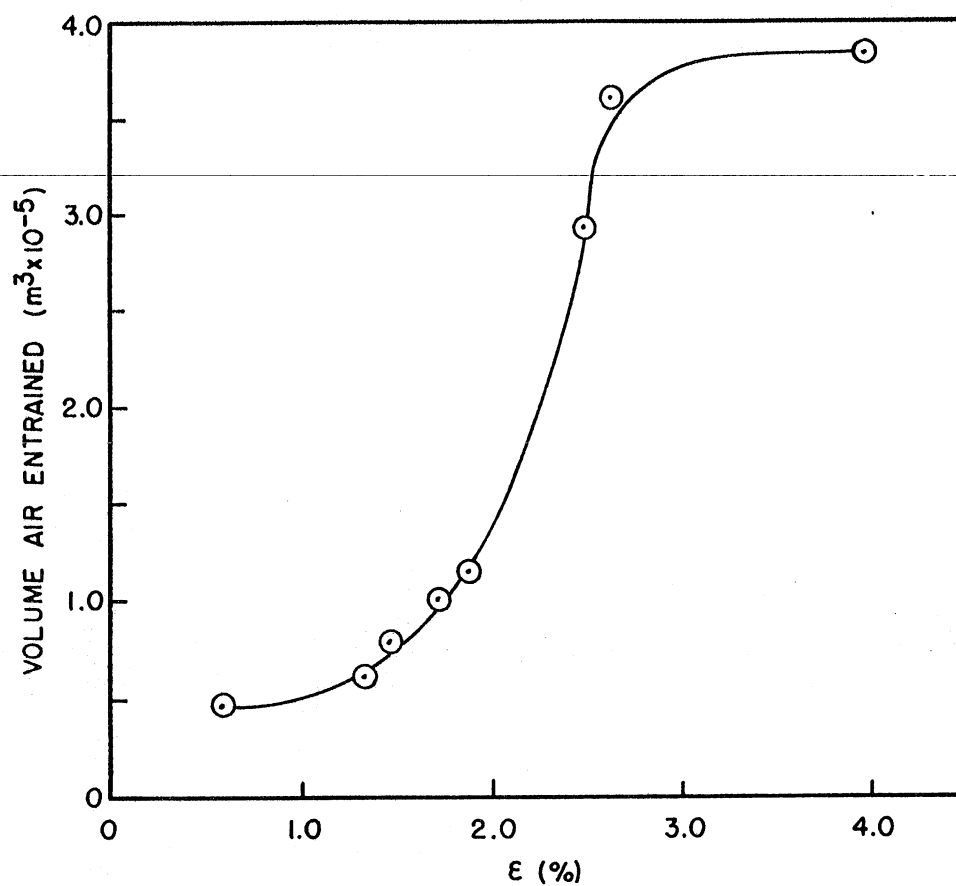


Fig. V-7

Volume of air entrained vs. turbulent intensity [Elsawy and McKeogh, 1977].

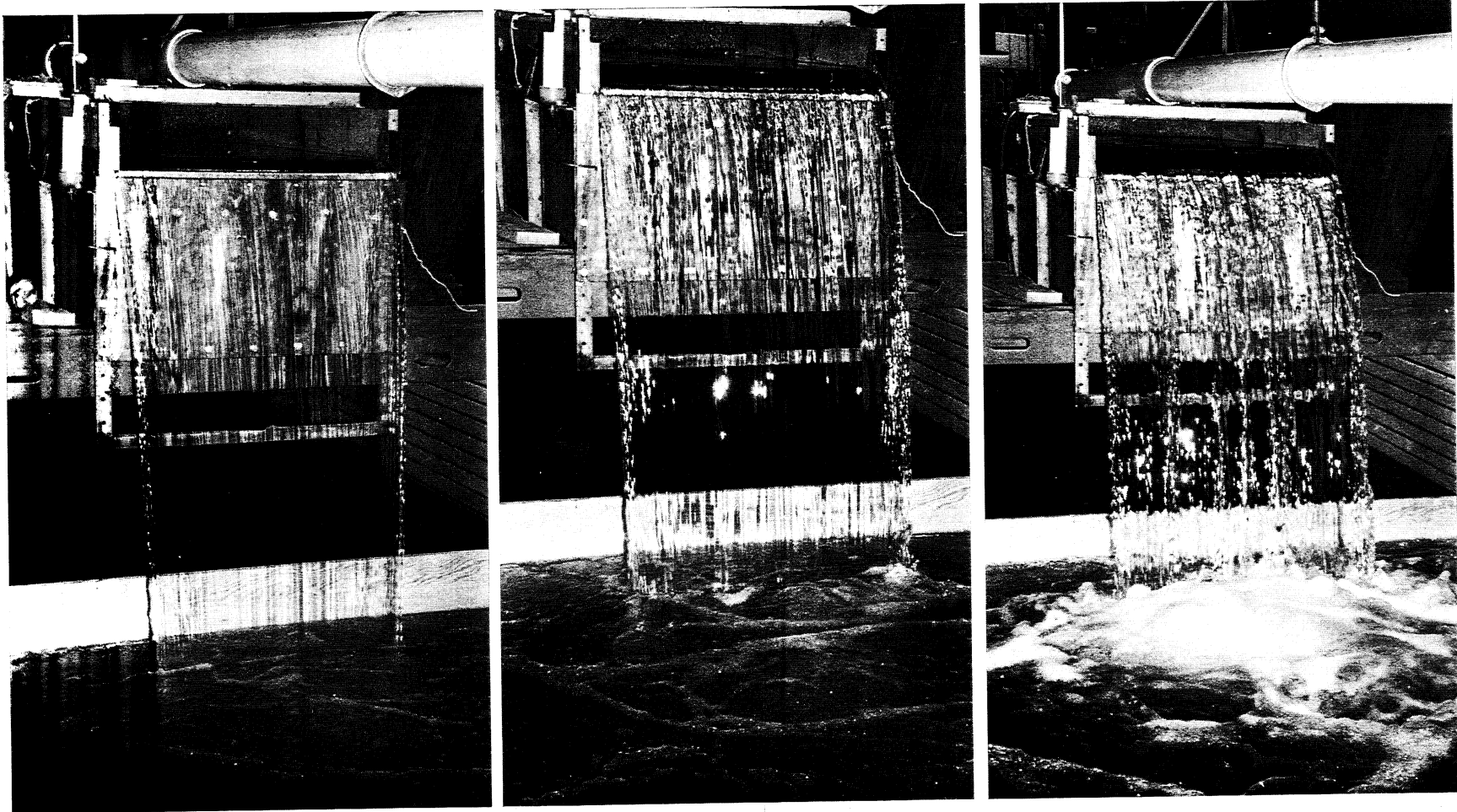


Fig. V-8a,b,c Photographs of nappe: Weir tests W9, W3, and W4, respectively.

predictive equations. Even though the four Nakasone equations have tailwater depth in them, it does not fit the data significantly better than Eq. V-14 or the equation of Avery and Novak, or significantly worse than Eq. V-5 or Eq. V-15. The Avery and Novak equation, when fitted with a tailwater function, fit the data somewhat better than any other presented. The tailwater function which was used did not account for the errors convincingly enough to prove that it truly represented effects of tailwater depth. In fact, the function chosen to adjust for tailwater depth fit the data only marginally. The equation developed here (Eq. V-15) did not show any systematic error with tailwater depth. As a result of these observations it may be concluded that although tailwater depth does influence gas transfer at weirs, is not an effective parameter in predicting gas transfer at weirs.

One reason for the ineffectiveness of tailwater may be that its effect is small and, when compared to the scatter due to turbulence, it is simply over-shadowed. Another possible explanation may lie in the assumption that, as tailwater decreases, the contact time of bubbles decreases. This increase is generally believed to be caused by the greater depth and the longer time it takes for the bubble to rise to the surface. It can be observed that, as the tailwater depth decreases and as the jet impinges on the pool, a greater level of turbulence is realized in the pool itself. This increased turbulence in the tailwater pool may, in fact, increase the contact time by keeping the bubbles in suspension longer, thus countering the obvious effect of tailwater depth.

As an example of this, weir tests W7 and W9, which had approximately laminar jets, may be compared. In test W9 the tailwater was high and quite still and the bubbles which were entrained travelled downward with the jet and then rose to the surface relatively unimpeded. Test W7 had the same discharge as W9 but had a small tailwater depth. In that test the tailwater was seen to be quite a bit more turbulent near the jet and much more air was kept in suspension. The two tailwater pools are compared in Figs. V-9a,b. Because the fall heights were different (2.29 m for W7 vs. 1.50 m for W9), the transfer efficiencies cannot be compared directly. However, they may be compared to the predicted efficiencies in Fig. V-2. Test W9, which was run at a high tailwater depth was predicted well by the Nakasone equation, however test W7 with its low tailwater depth was significantly underpredicted. This may substantiate the above hypothesis, that the increased turbulence, with decreased tailwater depth compensates for the supposed decrease in residence time associated with a shallow tailwater.

From the analysis of this section it may be concluded that tailwater depth is not an effective factor in the prediction of gas transfer. The four equations of Nakasone [1987] which included tailwater depth were not a significant improvement over the one of Avery and Novak [1978]. Efforts to add a tailwater term to the equation of Avery and Novak (and the alteration of the coefficients in the original equation) showed only a small improvement which was not significant enough to justify its use. Equation V-15, which was developed here, showed no systematic errors with tailwater depth. Tailwater depth is still believed to influence gas transfer at weirs, although its effect on the turbulence in the pool may partially reduce the

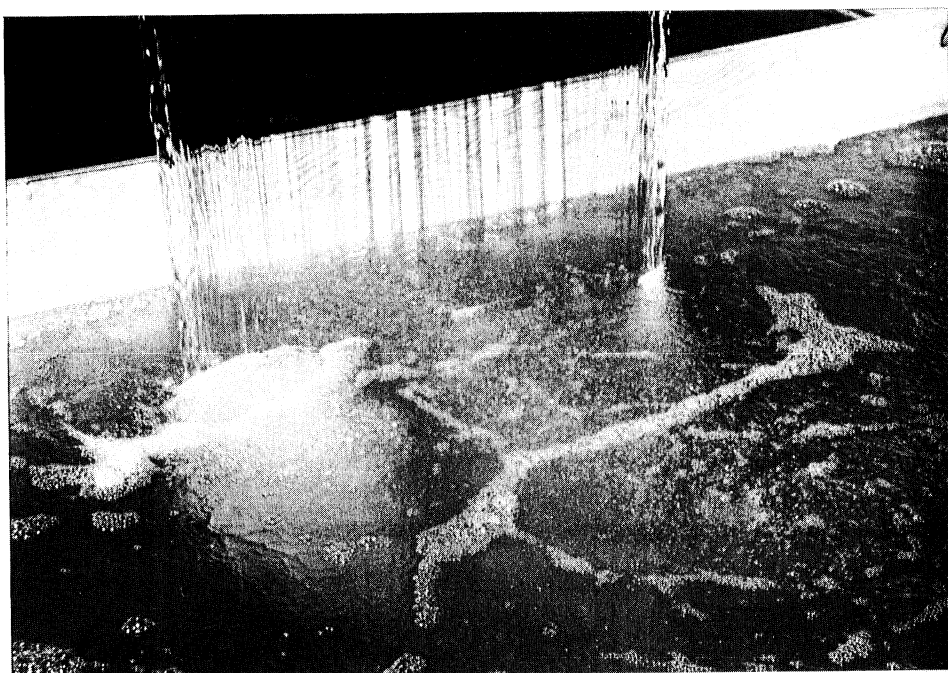


Fig. V-9a,b Photograph of tailwater: Weir tests W7 and W9.

decrease in residence time of bubbles associated with a smaller tailwater depth.

Finally, the turbulence intensity level in the nappe is believed to be a more important factor. Because of its pronounced effect on the volume of air entrained (Fig. V-7) it should influence the gas transfer at weirs significantly. The scatter in the data caused by varying turbulence may, in fact, mask the effect of tailwater depth, making it even more difficult to detect.

VI. CONCLUSIONS

Tracer methods are useful for the measurement of gas transfer at hydraulic structures as well as across the surface of open channels. Because tracer methods are not practical for wide structures, the use of naturally occurring methane should be studied for use as the preferred tracer used at hydraulic structures. Recommendations for that study are presented in Section VII.

The review of Section II has shown that, for the conversion of propane deficit ratios to oxygen deficit ratios, the value $R_p = 1.38$ should be used. For the methane conversion the value of $R_m = 1.08$ should be used, as it is predicted by two different theories. Equation II-8 is seen to be a good correction for both temperature and diffusivity with no fitted coefficients.

Headspace analysis of propane samples for use with the hydrocarbon gas tracer technique has been shown to be a viable, simple, and quite practical alternative to purge and trap analysis. The technique requires only equipment found in most GC laboratories and can be performed successfully with minimal preparation. The technique has a typical precision uncertainty of 1 to 3 percent of the concentration and has a limit of quantitation of 1.0 $\mu\text{g/L}$.

The data reduction and uncertainty analysis included in this thesis have been executed to show that the technique is very precise and produces results accurate enough for most applications. Further it was shown that the introduction of additional errors is unlikely.

Quality Assurance/Quality Control documentation was included to ensure that the results of the gas transfer measurements performed here would prove to be satisfactory. Modifications to that documentation will be necessary for other applications such as field use or the methane gas tracer method.

Gas transfer measurements utilizing the propane gas tracer technique were performed on a field-scale weir constructed at the St. Anthony Falls Hydraulic Laboratory. In those tests, river water from the Mississippi River at Minneapolis was used. The results of the gas transfer measurements were compared with two predictive equations from the literature. Headspace analysis of the methane in the river water was not successful, however there is some promise that the technique can be adapted to work for methane.

The predictive equations of Nakasone [1987] and of Avery and Novak [1978] were evaluated based on transfer efficiency. The effect of tailwater depth on gas transfer at weirs was investigated. Although the effect has been hypothesized to be important [Nakasone, 1987], tailwater depth was found to be an ineffective parameter in the prediction of gas transfer at

weirs. The equation of Avery and Novak is preferred because it is only one equation (as apposed to Nakasone's set of four) and does not include tailwater depth. It is also more versatile because it can account for changing nappe shape.

An alternative equation was developed from the work of Elsayy et al.. The performance of this equation was approximately equal to the others evaluated. It may be preferred because it was derived from two equations describing the physical process of air entrainment, that is the volume of air entrained and the rate of air entrainment.

VII. RECOMMENDATIONS FOR FURTHER STUDY

This study has established a good starting ground for the use of tracers at hydraulic structures. There is, however, work that still needs to be done to back up this work and move the method forward for future use. Most of the further developments concentrate on the methane gas tracer method.

- 1) The first requirement in the improvement of the headspace analysis of methane is the pressure wave. A longer column should be tested to see if it can separate the two responses. If that is not successful, a capillary column may be able to pass the pressure wave before the methane elutes from the column. As a third alternative one might insert a small chamber in the carrier gas line. A four-way valve should be connected so that the carrier gas can either bypass the chamber or flush it into the GC. An injection port with a septum should be located on the side of the chamber. With the valve in the bypass position, the headspace sample will be injected into the chamber. Then the valve will be rotated to the flush position and the sample will be carried into the GC. This method of introducing the sample should cause smaller pressure fluctuations than the quick syringe injection directly onto the column. To facilitate a rapid analysis, two chambers might be used so that while one is flushing the next sample can be introduced into the chamber.

In order to create a headspace without atmospheric methane the headspace should be made either in an environment made up of the carrier gas or by another technique utilizing two syringe needles. One needle should be connected to a hose from a bottle of carrier gas. The other needle should allow water to escape to form the headspace. Both methods should be tested using propane against the method outlined in Section III-A. This will determine whether the methods result in losses. Then distilled water samples should be tested to show that there is no methane response.

- 2) Once a repeatable methane response has been obtained, river water samples should be taken to determine whether the methane in samples decays or accrues during the storage of samples. If the sample concentrations are not stable for overnight storage, a sample preservation technique should be explored. The formalin technique of Shultz et al. [1976] may be effective. Whatever preservation technique is adopted, its effects on the GC response and Henry's Law equilibrium should be studied. It should be

desirable to add propane to the samples to test its decay simultaneously.

- 3) Having a methane analysis technique available, a survey of reservoirs should be made to determine how many reservoirs can be expected to have levels of methane sufficiently above the limit of quantification so that the tracer method can be successful at prototype hydraulic structures. The vertical and horizontal profile of dissolved methane should also be measured to determine whether it is uniform.
- 4) Thus far the tracer measurements of gas transfer have been converted to oxygen values using the results of theories coupled with diffusivity data or the results of mixing tank tests for free surface reaeration. Tests should be made to measure the R_m and R_p values for reaeration at weirs and other bubbly flows. These tests can be made in several ways. The limiting resource for these tests is deoxygenated water. Because deoxygenated water is consumed at such a rapid rate in these tests, one is forced to work on a small scale. There are probably no problems with this, as the scale should not change the characteristics of gas transfer from bubbles.

Each of the tests involves de-oxygenating a small batch of water and then dissolving (bubbling) small amounts of methane and propane. The volume of water might be on the order of one cubic meter. The tank should be well mixed and then sampled for both oxygen and hydrocarbons. A siphon from that tank should be connected to a constant flow pump. The jet from the end of the hose should impinge on the surface of a small tank, perhaps of 50 liters. The jet shall be run for a sufficient time such that equilibrium conditions will prevail in the small tank. The overflow will then be sampled for both oxygen and the hydrocarbons. The oxygen samples will then be titrated by the Winkler method and the hydrocarbon samples will be analyzed for methane and propane by the headspace technique developed herein. The jet should be run at various discharges, velocities, turbulence levels and thicknesses. These concentrations can then be used to compute new R_m and R_p values which should be used in future tests uses of the tracer method at hydraulic structures.

In order to test the general applicability of the R values to hydraulic structures, the same test might be conducted on a small aerated spillway face or at a hydraulic jump.

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APPENDICES

APPENDIX A. CONCENTRATION DATA

The results from the ten measurements of propane gas transfer are reported in this appendix. Three pages, each numbered W1, for example give the results from each measurement. In the first lines some notes about the test are given. Then the physical characteristics from the test are given. Following that are the average upstream and downstream concentrations, the measured transfer efficiency and the uncertainty computed for that value, and a list of some individual uncertainties. The transfer efficiencies are also given as oxygen at 20°C.

Following that is a list of the results from each individual sample analyzed in that test. The sample number, description, average of the (six) concentrations, the 95% precision confidence interval or uncertainty, $W_{\bar{C}_i}$, and the concentrations from the individual headspace samples and the GC run number. The following notation was used in the description of the sampling conditions:

HW	Indicates that sample was taken upstream of the weir (headwater)
TW	Indicates that sample was taken in tailwater
RT	Sample was taken in right 1/3 of weir tank or at right end of downstream wall
LT	Sample was taken in left 1/3 of weir tank or at left end of downstream wall
CTR	Sample was taken at center of weir tank or tailwater pool
FR	Indicates distance sample was taken from given wall
US	Indicates distance sample was taken upstream of weir or downstream wall
AB	Indicates distance sample was taken above bottom of weir tank or floor tailwater pool
BS	Indicates distance the sample was taken below the water surface
PAIR	Indicates the sample number which was taken along with that sample
6:00	The time of sampling given in minutes and seconds from the time that the propane injection began

- CH K Indicates last sample taken upstream after downstream samples, used to check if the concentration remained constant
- CH P Indicates sample analyzed to check against pair, duplicate sample
- ESI Early stop integration, GC stopped run before integration of peak was finished
- DROP Indicates headspace sample dropped because it was an outlier or for other reasons listed

The FORTRAN computer program, HSC2, which was used to analyze the raw data, is included at the end of the concentration data.

W1

PROPANE-WEIR TEST ONE
LEAK IN GATE APPROX 10 L/MIN
TEST FAILED DUE TO INCOMPLETE UPSTREAM MIXING

HEAD [M] .0677
SPECQ [M³/S/M] .0323
TOTALQ [M³/S] .0293
NOVAK SPECQ [M³/S/M] .0345
TAILWATER DEPTH [M] .492
FALL HEIGHT 2.104
WATER TEMPERATURE [°C] 2.1

UPS CONC [UG/L] 42.65
DNS CONC [UG/L] 23.54
TRANSFER EFF, E [-] .448
TOTAL UNC IN E [-] .011
PERCENT UNC [-] 2.451
PREC UNC IN E .00775
WE DUE TO CALIB 0
WE DUE TO FW .00778
BE DUE TO SYR VOL 0
BE DUE TO H -.00021

TRANSFER EFF., DEF RATIOS:, OXYGEN AT 20°C

MEASURED E .711 R: 3.46
TOTAL UNC IN E .012 R: .14
AVERY & NOVAK E .727 R: 3.67
NAKASONE E .621 R: 2.64

SAMPLE NO 11

DESCRIPTION:

HW,RT,60 CM US,25 CM AB,PAIR:56, 6:00

AVG CONC [UG/L] 34.83

UNCERTAINTY 1.37

PERCENT UNC 3.93

INDIVIDUAL G.C. RUNS:

34.25 GC RUN# 297,GC IS FINE
34.77 298
35.09 299
34.19 300, DROP
33.16 301, DROP
35.21 302

SAMPLE NO 56

DESCRIPTION:

HW,RT,60 CM US,25 CM AB,PAIR:11, 6:00

AVG CONC [UG/L] 35.32

UNCERTAINTY .94

PERCENT UNC 2.65

INDIVIDUAL G.C. RUNS:

35.01 303
35.40 304
35.81 305
35.49 306
34.79 307
35.42 308

SAMPLE NO 2

DESCRIPTION:

HW,CTR,60 CM US,25 CM AB,PAIR:59, 10:30

AVG CONC [UG/L] 46.93

UNCERTAINTY .57

PERCENT UNC 1.22

INDIVIDUAL G.C. RUNS:

45.92 309, DROP
46.64 310
47.08 311
47.15 312
46.83 313
46.97 314

SAMPLE NO 59

DESCRIPTION:

HW,CTR,60 CM US,25 CM AB,PAIR:2, 10:30

AVG CONC [UG/L] 47.80

UNCERTAINTY 1.17

PERCENT UNC 2.44

INDIVIDUAL G.C. RUNS:

48.11 334, 1 4-5MM BUBBLE
48.03 335
47.55 336
48.10 337
46.98 338, EARLY STOP INT.,DROP
48.01 339

W1

SAMPLE NO 12
DESCRIPTION:
HW,LT,60 CM US,25 CM AB, PAIR:63, 15:20
AVG CONC [UG/L] 50.32
UNCERTAINTY .39
PERCENT UNC .78
INDIVIDUAL G.C. RUNS:
49.32 315, DROP
50.40 316
50.48 317
50.21 318
50.39 319
50.14 320

SAMPLE NO 45
DESCRIPTION:
HW,CTR,60 CM US, 10 CM BS, PAIR:54, 19:30
AVG CONC [UG/L] 46.88
UNCERTAINTY 1.04
PERCENT UNC 2.22
INDIVIDUAL G.C. RUNS:
45.76 321, DROP
46.86 322
46.29 323
47.55 324
46.86 325
46.77 326
46.94 327

SAMPLE NO 27
DESCRIPTION:
HW,RT,60 CM US,10 CM BS, PAIR:32. 24:00
AVG CONC [UG/L] 31.99
UNCERTAINTY .62
PERCENT UNC 1.92
INDIVIDUAL G.C. RUNS:
32.11 328
31.96 329
32.26 330
31.74 331
31.67 332
32.18 333

SAMPLE NO 48
DESCRIPTION:
HW,CTR,60 CM US,25 CM AB, PAIR:47, 38:54
AVG CONC [UG/L] 47.16
UNCERTAINTY .88
PERCENT UNC 1.87
INDIVIDUAL G.C. RUNS:
46.90 377
46.77 378
47.45 379
47.63 380
46.94 381
47.25 382

SAMPLE NO 40
DESCRIPTION:
TW,RT,30 CM US, 25 CM BS,PAIR:67, 27:20
AVG CONC [UG/L] 23.61
UNCERTAINTY .71
PERCENT UNC 3.01
INDIVIDUAL G.C. RUNS:
23.47 346
24.11 347
23.64 348
23.53 349
23.65 350
23.28 351

SAMPLE NO 67
DESCRIPTION:
TW,RT,30 CM US, 25 CM BS,PAIR:40, 27:20
AVG CONC [UG/L] 23.06
UNCERTAINTY .91
PERCENT UNC 3.97
INDIVIDUAL G.C. RUNS:
22.63 340,D.S. DUPLICATE
23.33 341
23.43 342
23.32 343
23.01 344
22.65 345

W1

SAMPLE NO 1
DESCRIPTION:
TW,CTR,30 CM US,25 CM BS, PAIR:60, 29:30
AVG CONC [UG/L] 23.67
UNCERTAINTY .83
PERCENT UNC 3.51
INDIVIDUAL G.C. RUNS:
23.72 352
23.79 353
23.33 354
23.78 355
15.77 356, DROP
24.13 357
23.26 358

SAMPLE NO 16
DESCRIPTION:
TW,.8M FR LT,30 CM US,25 CM BS,PAIR 30,36:05
AVG CONC [UG/L] 23.51
UNCERTAINTY .37
PERCENT UNC 1.55
INDIVIDUAL G.C. RUNS:
23.34 371
23.62 372
23.47 373
23.65 374
23.36 375
23.62 376

SAMPLE NO 9
DESCRIPTION:
TW,LT,30 CM US,25 CM BS, PAIR:42, 31:22
AVG CONC [UG/L] 23.20
UNCERTAINTY .60
PERCENT UNC 2.58
INDIVIDUAL G.C. RUNS:
23.09 359, ~4MM BUBBLE
23.41 360
23.54 361
23.13 362
23.08 363
22.92 364

SAMPLE NO 30
DESCRIPTION:
TW,.8M FR LT,30 CM US,25 CM BS,PAIR 16,36:05
AVG CONC [UG/L] 24.21
UNCERTAINTY .49
PERCENT UNC 2.01
INDIVIDUAL G.C. RUNS:
24.19 365
24.04 366
24.43 367
24.28 368
24.36 369
23.94 370

W2

PROPANE WEIR TEST TWO - 2/17/88
NOTE HIGH US CONC, GC PROBLEMS FORCED EARLY STOP
LEAK IN GATE LESS THAN 10 L/MIN

HEAD [M] .0680
SPECQ [M³/S/M] .0325
TOTALQ [M³/S] .0295
NOVAK SPECQ [M³/S/M] .0347
TAILWATER DEPTH [M] .502
FALL HEIGHT 2.094
WATER TEMPERATURE [°C] 2.8

UPS CONC [UG/L] 179.84
DNS CONC [UG/L] 88.81
TRANSFER EFF, E [-] .506
TOTAL UNC IN E [-] .012
PERCENT UNC [-] 2.373
PREC UNC IN E .00978
WE DUE TO CALIB 0
WE DUE TO FW .00696
BE DUE TO SYR VOL 0
BE DUE TO H .00009

TRANSFER EFF., DEF RATIOS:, OXYGEN AT 20°C

MEASURED E .764 R: 4.24
TOTAL UNC IN E .012 R: .21
AVERY & NOVAK E .726 R: 3.65
NAKASONE E .623 R: 2.65

SAMPLE NO 50

DESCRIPTION:

HW, 60 CM US, RT, BOT, PAIR:59,10:00

AVG CONC [UG/L] 184.34

UNCERTAINTY 3.84

PERCENT UNC 2.08

INDIVIDUAL G.C. RUNS:

191.34 GC RUN #437,EARLY STOP,DROP
183.71 438
183.47 439
185.58 440
185.80 441
185.40 442
182.06 443

SAMPLE NO 59

DESCRIPTION:

HW, 60 CM US, BOT RT, PAIR:50, 10:00

AVG CONC [UG/L] 180.55

UNCERTAINTY 3.51

PERCENT UNC 1.94

INDIVIDUAL G.C. RUNS:

181.34 444
178.95 445
180.72 446
181.20 447
189.07 448,DROP,EARLY STOP INT.(ESI)
187.70 449, DROP

SAMPLE NO 62

DESCRIPTION:

HW, 60 CM US, BOT CTR, PAIR:39, 14:30

AVG CONC [UG/L] 176.22

UNCERTAINTY 6.62

PERCENT UNC 3.76

INDIVIDUAL G.C. RUNS:

173.19 476
177.37 477
174.22 478
178.79 479
177.53 480
183.25 481, DROP

SAMPLE NO 12

DESCRIPTION:

HW, 60 CM US, BOT LT, PAIR:11, 19:00

AVG CONC [UG/L] 179.50

UNCERTAINTY 5.44

PERCENT UNC 3.03

INDIVIDUAL G.C. RUNS:

177.85 457
178.63 458
177.62 459
178.59 460
0 461, BIG MISTAKE, DROP
182.65 462
181.64 463

W2

SAMPLE NO 5
DESCRIPTION:
HW, 60 CM US, CTR, 11 CM BS, PAIR:48, 23:30
AVG CONC [UG/L] 180.17
UNCERTAINTY 4.95
PERCENT UNC 2.75
INDIVIDUAL G.C. RUNS:
176.88 464
178.79 465
181.57 466
180.85 467
181.33 468
181.60 469

SAMPLE NO 10
DESCRIPTION:
TW, .3M US, .3M FR LT, PAIR:1, 34:40
AVG CONC [UG/L] 88.53
UNCERTAINTY 2.80
PERCENT UNC 3.17
INDIVIDUAL G.C. RUNS:
87.92 489
87.16 490
89.13 491
89.73 492
91.73 493, DROP
88.70 494

SAMPLE NO 14
DESCRIPTION:
HW, 60 CM US, RT, 11 CM BS, PAIR:37, 28:00
AVG CONC [UG/L] 178.25
UNCERTAINTY 3.84
PERCENT UNC 2.16
INDIVIDUAL G.C. RUNS:
174.64 470, DROP
176.99 471
176.71 472
178.62 473
178.90 474
180.03 475

SAMPLE NO 1
DESCRIPTION:
TW, .3M US, .3M FR LT, PAIR:10, 34:40
AVG CONC [UG/L] 86.59
UNCERTAINTY 1.58
PERCENT UNC 1.82
INDIVIDUAL G.C. RUNS:
87.27 495
86.42 496
86.06 497
86.08 498
87.10 499
90.42 500, DROP

SAMPLE NO 38
DESCRIPTION:
TW, .3M US, .3M FR RT, PAIR:16, 31:24
AVG CONC [UG/L] 91.32
UNCERTAINTY 3.00
PERCENT UNC 3.28
INDIVIDUAL G.C. RUNS:
90.61 483
90.12 484
90.94 485
91.48 486
91.27 487
93.49 488

SAMPLE NO 39
DESCRIPTION:
HW, 60 CM US, BOT CTR, PAIR:62, 14:30
AVG CONC [UG/L] 219.34
UNCERTAINTY 5.44
PERCENT UNC 2.48
INDIVIDUAL G.C. RUNS:
217.16 450, NOTE HIGH CONCENTRATION
216.40 451, ESI, SAMPLE NOT COUNTED
220.19 452
221.89 453, ESI
227.94 454, ESI, DROP
222.20 455
218.45 456
219.05 482, NOTE LATE GC RUN

W2

SAMPLE NO 45

DESCRIPTION:

TW, .3 M US, CTR, PAIR:44, 37:00

AVG CONC [UG/L] 98.71

UNCERTAINTY 16.35

PERCENT UNC 16.56

INDIVIDUAL G.C. RUNS:

86.48	501, THIS IS ONLY GOOD CHROMATOGRAM
78.50	502-507 ALL ESI, DROP ALL, SAMPLE NOT COUNTED
98.81	503, 502-507 ALL HAD HIGH RET TIMES
101.74	504
98.96	505
104.55	506
101.72	507, LAST SAMPLES NOT ANALYZED: GC PROBLEM

W3

PROPANE WEIR TEST THREE - 2/26/88
NO PROPANE RESPONSE TO TAP OR RIVER WATER
PROPANE SOLUTION FLOW 1 L/30.,32.5,30.7 SEC

HEAD [M] .0674
SPECQ [M³/S/M] .0321
TOTALQ [M³/S] .0291
NOVAK SPECQ [M³/S/M] .0329
TAILWATER DEPTH [M] 1.076
FALL HEIGHT 1.519
WATER TEMPERATURE [°C] 2.6

UPS CONC [UG/L] 72.04
DNS CONC [UG/L] 49.51
TRANSFER EFF, E [-] .313
TOTAL UNC IN E [-] .013
PERCENT UNC [-] 4.137
PREC UNC IN E .00857
WE DUE TO CALIB 0
WE DUE TO FW .00969
BE DUE TO SYR VOL 0
BE DUE TO H .00005

TRANSFER EFF., DEF RATIOS:, OXYGEN AT 20°C

MEASURED E .537 R: 2.16
TOTAL UNC IN E .018 R: .08
AVERY & NOVAK E .632 R: 2.72
NAKASONE E .612 R: 2.57

SAMPLE NO 22

DESCRIPTION:

HW,RT,60 CM US,25 CM AB,PAIR 63,4:00

AVG CONC [UG/L] 69.95

UNCERTAINTY 1.78

PERCENT UNC 2.55

INDIVIDUAL G.C. RUNS:

69.34 GC RUN 553, 3MM BUBBLE
69.81 554
71.32 555
69.84 556
69.77 557
69.62 558

SAMPLE NO 50

DESCRIPTION:

HW,CTR,60 CM US,25 CM AB,PAIR 32,12:00

AVG CONC [UG/L] 71.39

UNCERTAINTY .73

PERCENT UNC 1.02

INDIVIDUAL G.C. RUNS:

69.33 559, DROP
71.52 560
71.78 561
71.16 562
71.29 563
71.19 564

SAMPLE NO 32

DESCRIPTION:

HW,CTR,60 CM US,25 CM AB, PAIR 32,12:00

AVG CONC [UG/L] 71.63

UNCERTAINTY .81

PERCENT UNC 1.13

INDIVIDUAL G.C. RUNS:

70.00 565, DROP
71.28 566
71.43 567
71.66 568
72.03 569
71.76 570

SAMPLE NO 14

DESCRIPTION:

HW,LT,60 CM US,25 CM AB,PAIR 36,20:00

AVG CONC [UG/L] 72.67

UNCERTAINTY 1.77

PERCENT UNC 2.43

INDIVIDUAL G.C. RUNS:

73.65 571
72.11 572
72.26 573
72.56 574
73.39 575
72.06 576

W3

SAMPLE NO 47
DESCRIPTION:
HW,RT,60 CM US,10 CM BS,PAIR 10,28:00
AVG CONC [UG/L] 73.71
UNCERTAINTY 2.35
PERCENT UNC 3.19
INDIVIDUAL G.C. RUNS:
72.57 577
75.09 578
74.40 579
73.68 580
73.01 581
73.52 582

SAMPLE NO 55
DESCRIPTION:
HW,CTR,60 CM US,10 CM BS,PAIR 27,36:00
AVG CONC [UG/L] 72.87
UNCERTAINTY 1.55
PERCENT UNC 2.13
INDIVIDUAL G.C. RUNS:
71.98 583
73.36 584
72.68 585
73.35 586
73.45 587
72.42 588

SAMPLE NO 12
DESCRIPTION:
TW,RT,30 CM US,20 CM BS,PAIR 15,38:04
AVG CONC [UG/L] 48.98
UNCERTAINTY 1.08
PERCENT UNC 2.21
INDIVIDUAL G.C. RUNS:
48.67 589
49.59 590
48.41 591
48.99 592
48.96 593
49.29 594

SAMPLE NO 15
DESCRIPTION:
TW,RT,30 CM US,20 CM BS,PAIR 12,38:04
AVG CONC [UG/L] 49.03
UNCERTAINTY 1.31
PERCENT UNC 2.68
INDIVIDUAL G.C. RUNS:
47.67 595, DROP, POOR INJECTION
48.55 596
49.68 597
48.71 598
49.36 599
48.88 600

SAMPLE NO 56
DESCRIPTION:
TW,.8M FR RT,30 CM US,20 CM BS,PAIR 16,40:10
AVG CONC [UG/L] 50.41
UNCERTAINTY .97
PERCENT UNC 1.93
INDIVIDUAL G.C. RUNS:
49.43 601, DROP
50.69 602
49.98 603
50.08 604
50.55 606
50.73 606

SAMPLE NO 67
DESCRIPTION:
TW,RT,30 CM US,25 CM AB,PAIR 62,42:00
AVG CONC [UG/L] 48.73
UNCERTAINTY 1.20
PERCENT UNC 2.45
INDIVIDUAL G.C. RUNS:
48.07 607
48.61 608
48.69 609
49.28 610
49.25 611
48.50 612

W3

SAMPLE NO 54
DESCRIPTION:
TW,LT,30 CM US,10 CM BS,PAIR 45,44:45
AVG CONC [UG/L] 49.39
UNCERTAINTY .85
PERCENT UNC 1.72
INDIVIDUAL G.C. RUNS:
49.10 613
49.58 614
50.78 615, DROP
49.80 616
49.38 617
49.10 618

SAMPLE NO 26
DESCRIPTION:
TW,.8M FR LT,30 CM US,20 CM BS,PAIR 34,46:56
AVG CONC [UG/L] 50.53
UNCERTAINTY .65
PERCENT UNC 1.29
INDIVIDUAL G.C. RUNS:
49.59 619, DROP
50.89 620
50.42 621
50.56 622
50.71 623
50.40 624
50.17 625

SAMPLE NO 5
DESCRIPTION:
HW,LT,60 CM US,10 CM BS,PAIR 30,50:20,CH K
AVG CONC [UG/L] 71.56
UNCERTAINTY 1.64
PERCENT UNC 2.29
INDIVIDUAL G.C. RUNS:
70.65 626
71.20 627
71.97 628
71.38 629
72.48 630
71.68 631

W4

PROPANE WEIR TEST FOUR - 2/29/88
THE WATER IS NOT AS CLEAR AS IN EARLIER TESTS

HEAD [M] .1049
SPECQ [M³/S/M] .0629
TOTALQ [M³/S] .0571
NOVAK SPECQ [M³/S/M] .0608
TAILWATER DEPTH [M] 1.076
FALL HEIGHT 1.557
WATER TEMPERATURE [°C] 2.5

UPS CONC [UG/L] 32.06
DNS CONC [UG/L] 19.11
TRANSFER EFF, E [-] .404
TOTAL UNC IN E [-] .014
PERCENT UNC [-] 3.460
PREC UNC IN E .01117
WE DUE TO CALIB 0
WE DUE TO FW .00840
BE DUE TO SYR VOL 0
BE DUE TO H -.00003

TRANSFER EFF., DEF RATIOS:, OXYGEN AT 20°C

MEASURED E .656 R: 2.91
TOTAL UNC IN E .017 R: .14
AVERY & NOVAK E .586 R: 2.42
NAKASONE E .724 R: 3.62

SAMPLE NO 39
DESCRIPTION:
HW,RT,60 CM US,25 CM AB,PAIR 55,7:00
AVG CONC [UG/L] 31.36
UNCERTAINTY .26
PERCENT UNC .82
INDIVIDUAL G.C. RUNS:
31.39 662
31.38 665
31.25 666
31.48 667
32.14 668, DROP
31.28 669

SAMPLE NO 55
DESCRIPTION:
HW,RT,60 CM US,25 CM AB,PAIR 39,7:00
AVG CONC [UG/L] 31.72
UNCERTAINTY 1.59
PERCENT UNC 5.01
INDIVIDUAL G.C. RUNS:

30.90 670
31.49 671
31.19 672
32.06 673
32.44 674
32.23 675

SAMPLE NO 52
DESCRIPTION:
HW,CTR,60 CM US,25 CM AB,PAIR 67,11:00
AVG CONC [UG/L] 31.92
UNCERTAINTY .56
PERCENT UNC 1.76
INDIVIDUAL G.C. RUNS:

31.70 676
32.01 677
31.71 678
33.06 679, DROP
32.09 680
32.11 681

SAMPLE NO 24
DESCRIPTION:
HW,LT,60 CM US,25 CM AB,PAIR 27,15:00
AVG CONC [UG/L] 31.87
UNCERTAINTY 1.02
PERCENT UNC 3.21
INDIVIDUAL G.C. RUNS:
30.67 682, DROP
31.44 683
31.51 684
32.02 685
32.23 686
32.16 687

W4

SAMPLE NO 38
DESCRIPTION:
HW,RT,60 CM US,10 CM BS,PAIR 25,19:00
AVG CONC [UG/L] 32.65
UNCERTAINTY 1.52
PERCENT UNC 4.64
INDIVIDUAL G.C. RUNS:
32.02 688
33.23 689
32.39 690
33.32 691
32.92 692
32.02 693

SAMPLE NO 45
DESCRIPTION:
HW,CTR,60 CM US,10 CM BS,PAIR 63,23:00
AVG CONC [UG/L] 32.84
UNCERTAINTY 1.18
PERCENT UNC 3.59
INDIVIDUAL G.C. RUNS:
33.02 694
32.36 695,DROP
33.05 696
33.18 697
32.12 698
32.82 699

SAMPLE NO 2
DESCRIPTION:
TW,RT,30 CM US,10 CM BS,PAIR 64,25:02
AVG CONC [UG/L] 19.07
UNCERTAINTY .36
PERCENT UNC 1.90
INDIVIDUAL G.C. RUNS:
18.85 700, 1-2MMBUBBLE
18.40 701, DROP
19.16 702
19.06 703
19.14 704
19.12 705

SAMPLE NO 64
DESCRIPTION:
TW,RT,30 CM US,10 CM BS,PAIR 2,25:02
AVG CONC [UG/L] 18.94
UNCERTAINTY .82
PERCENT UNC 4.34
INDIVIDUAL G.C. RUNS:
18.91 706
18.53 707
18.88 708
18.71 709
19.19 710
19.42 711

SAMPLE NO 12
DESCRIPTION:
TW,CTR,30 CM US,10 CM BS,PAIR 42,27:32
AVG CONC [UG/L] 19.28
UNCERTAINTY .68
PERCENT UNC 3.52
INDIVIDUAL G.C. RUNS:
18.45 712, DROP
19.39 713
18.93 714
19.60 715
19.26 716
19.22 717

SAMPLE NO 36
DESCRIPTION:
TW,LT,30 CM US,10 CM BS,PAIR 18,29:44
AVG CONC [UG/L] 19.14
UNCERTAINTY .70
PERCENT UNC 3.65
INDIVIDUAL G.C. RUNS:
19.39 718
18.99 719
18.87 720
18.84 721
19.39 722
19.38 723

W4

SAMPLE NO 48

DESCRIPTION:

TW,1M FR LT,30 CM US,10 CM BS,PAIR 50,31:59

AVG CONC [UG/L] 18.81

UNCERTAINTY .33

PERCENT UNC 1.73

INDIVIDUAL G.C. RUNS:

18.74	724
18.95	725
18.67	726
18.25	727, DROP
18.91	728
18.80	729

SAMPLE NO 59

DESCRIPTION:

TW,1M FR RT,30 CM US,10 CM BS,PAIR 32,34:18

AVG CONC [UG/L] 19.41

UNCERTAINTY .21

PERCENT UNC 1.08

INDIVIDUAL G.C. RUNS:

18.88	730, DROP, BUBBLE
19.46	731
19.43	732
19.31	733
19.44	734
19.68	735, DROP

SAMPLE NO 10

DESCRIPTION:

HW,CTR,60 CM US,10 CM BS,PAIR:37,36:49, CH K

AVG CONC [UG/L] 31.17

UNCERTAINTY .96

PERCENT UNC 3.06

INDIVIDUAL G.C. RUNS:

31.46	736
30.62	737
31.23	738
30.96	739
31.66	740
31.08	741

W5

PROPANE WEIR TEST FIVE - 3/2/88
INTEGRATOR PROBLEMS IN HEADWATER SAMPLES

HEAD [M] .1046
SPECQ [M³/S/M] .0626
TOTALQ [M³/S] .0569
NOVAK SPECQ [M³/S/M] .0611
TAILWATER DEPTH [M] .646
FALL HEIGHT 1.986
WATER TEMPERATURE [°C] 3.5

UPS CONC [UG/L] 97.64
DNS CONC [UG/L] 49.72
TRANSFER EFF, E [-] .491
TOTAL UNC IN E [-] .009
PERCENT UNC [-] 1.842
PREC UNC IN E .00550
WE DUE TO CALIB 0
WE DUE TO FW .00718
BE DUE TO SYR VOL 0
BE DUE TO H -.00009

TRANSFER EFF., DEF RATIOS:, OXYGEN AT 20°C

MEASURED E .742 R: 3.88
TOTAL UNC IN E .009 R: .14
AVERY & NOVAK E .665 R: 2.98
NAKASONE E .738 R: 3.81

SAMPLE NO 59
DESCRIPTION:
HW,RT,60 CM US,25 CM AB,PAIR 39,4:00
AVG CONC [UG/L] 99.02
UNCERTAINTY 2.17
PERCENT UNC 2.19
INDIVIDUAL G.C. RUNS:
99.07 782
97.49 785
99.52 786, SLOPE SENS. (SS) =>.1
99.43 787
98.73 788
99.86 789, SS=>.2

SAMPLE NO 39
DESCRIPTION:
HW,RT,60 CM US,25 CM AB,PAIR 59,4:00
AVG CONC [UG/L] 98.98
UNCERTAINTY 1.05
PERCENT UNC 1.06
INDIVIDUAL G.C. RUNS:
96.60 790, DROP,SS=>.1
108.32 791,DROP
101.74 792, DROP
98.90 793
99.39 794, SS=>.15
98.60 795, SS=>.20
99.05 796

SAMPLE NO 30
DESCRIPTION:
HW,CTR,60 CM US,25 CM AB,PAIR 62,6:15
AVG CONC [UG/L] 96.69
UNCERTAINTY .95
PERCENT UNC .98
INDIVIDUAL G.C. RUNS:
97.16 797
96.70 798
96.30 799
96.43 800
96.85 801
95.26 802, DROP

SAMPLE NO 2
DESCRIPTION:
HW,LT,60 CM US,25 CM AB,PAIR 48,8:30
AVG CONC [UG/L] 96.86
UNCERTAINTY 4.10
PERCENT UNC 4.23
INDIVIDUAL G.C. RUNS:
95.03 803
98.12 804
95.75 805
105.25 806, DROP, INF 4,5 T=-.82,1.32
112.69 807, DROP
101.10 808, DROP
96.96 809, CHG SEPTA, STOP INF
98.46 810

W5

SAMPLE NO 16
DESCRIPTION:
HW,RT,60 CM US,10 CM BS,PAIR 25,10:45
AVG CONC [UG/L] 97.55
UNCERTAINTY 1.37
PERCENT UNC 1.41
INDIVIDUAL G.C. RUNS:
95.99 811, DROP, ESI
97.36 812, EARLY STOP INT. (ESI)
96.85 813, ESI
97.70 814, ESI
98.19 815, ESI, SS=>.1
97.66 816, ESI

SAMPLE NO 10
DESCRIPTION:
HW,CTR,60 CM US,10 CM BS,PAIR 24,13:00
AVG CONC [UG/L] 96.75
UNCERTAINTY 1.95
PERCENT UNC 2.02
INDIVIDUAL G.C. RUNS:
96.13 817, DROP, ESI
96.32 818, SS=>.2
97.33 819
96.81 820, ESI
95.81 821
97.50 822, ESI

SAMPLE NO 38
DESCRIPTION:
TW,RT,30 CM US,10 CM BS,PAIR 32,14:53
AVG CONC [UG/L] 50.29
UNCERTAINTY .77
PERCENT UNC 1.53
INDIVIDUAL G.C. RUNS:
51.61 823, 2MM BUBBLE, DROP
50.41 824
50.62 825
49.89 826
50.16 827
50.39 828

SAMPLE NO 42
DESCRIPTION:
TW,CTR,30 CM US,10 CM BS,PAIR 63,16:15
AVG CONC [UG/L] 49.75
UNCERTAINTY 1.13
PERCENT UNC 2.28
INDIVIDUAL G.C. RUNS:
50.01 829
49.08 830
50.38 831
49.77 832
49.51 833
49.74 834

SAMPLE NO 12
DESCRIPTION:
TW,LT,30 CM US,10 CM BS,PAIR 55,17:54
AVG CONC [UG/L] 49.03
UNCERTAINTY .52
PERCENT UNC 1.07
INDIVIDUAL G.C. RUNS:
49.13 835
49.22 836
49.16 837
48.93 838
49.07 839
48.67 840

SAMPLE NO 27
DESCRIPTION:
TW,1M FR RT,30 CM US,10 CM BS,PAIR 34,19:15
AVG CONC [UG/L] 50.08
UNCERTAINTY .13
PERCENT UNC .27
INDIVIDUAL G.C. RUNS:
49.63 841, DROP
50.02 842
50.06 843
50.15 844
50.10 845
50.08 846

W5

SAMPLE NO 34

DESCRIPTION:

TW, 1M FR RT, 30 CM US, 10 CM BS, PR 27, 19:15

AVG CONC [UG/L] 49.62

UNCERTAINTY .36

PERCENT UNC .72

INDIVIDUAL G.C. RUNS:

49.33	847, DROP
49.60	848
49.69	849
49.73	850
49.66	851
49.41	852

SAMPLE NO 56

DESCRIPTION:

TW, 1M FR LT, 30 CM US, 10 CM BS, PAIR 15, 20:40

AVG CONC [UG/L] 49.52

UNCERTAINTY .71

PERCENT UNC 1.44

INDIVIDUAL G.C. RUNS:

49.05	853, DROP
49.70	854
49.79	855
49.32	856
49.60	857
49.19	858

SAMPLE NO 14

DESCRIPTION:

HW, CTR, 60 CM US, 10 CM BS, PAIR 44, 22:45, CH K

AVG CONC [UG/L] 92.08

UNCERTAINTY 1.19

PERCENT UNC 1.30

INDIVIDUAL G.C. RUNS:

91.89	859
91.79	860
93.58	861, DROP
92.02	862
95.97	863
92.62	864

W6

PROPANE WEIR TEST SIX - 3/9/88
DUPLICATE TO RUN #5: SPECQ=.0626, TW=.646,
T=3.5, D=-.475, +/- .015

HEAD [M] .1058
SPECQ [M³/S/M] .0637
TOTALQ [M³/S] .0579
NOVAK SPECQ [M³/S/M] .0622
TAILWATER DEPTH [M] .651
FALL HEIGHT 1.983
WATER TEMPERATURE [°C] 5.8

UPS CONC [UG/L] 53.20
DNS CONC [UG/L] 26.63
TRANSFER EFF, E [-] .499
TOTAL UNC IN E [-] .010
PERCENT UNC [-] 2.068
PREC UNC IN E .00754
WE DUE TO CALIB 0
WE DUE TO FW .00706
BE DUE TO SYR VOL 0
BE DUE TO H -.00003

TRANSFER EFF., DEF RATIOS:, OXYGEN AT 20°C

MEASURED E .731 R: 3.71
TOTAL UNC IN E .011 R: .15
AVERY & NOVAK E .663 R: 2.97
NAKASONE E .741 R: 3.85

SAMPLE NO 34
DESCRIPTION:
HW,RT,60 CM US,25 CM AB,PAIR 34,2:00
AVG CONC [UG/L] 53.04
UNCERTAINTY .34
PERCENT UNC .64
INDIVIDUAL G.C. RUNS:
49.37 882,DROP
53.02 883
53.09 884
54.29 885, DROP
52.91 886
53.16 887

SAMPLE NO 39
DESCRIPTION:
HW,CTR,60 CM US,25 CM AB,PAIR 39,4:15
AVG CONC [UG/L] 52.97
UNCERTAINTY .73
PERCENT UNC 1.38
INDIVIDUAL G.C. RUNS:

52.98 888
52.92 889
53.13 890
52.78 891
52.61 892
53.43 893

SAMPLE NO 47
DESCRIPTION:
HW,LT,60 CM US,25 CM AB,PAIR 57,6:30
AVG CONC [UG/L] 52.42
UNCERTAINTY 1.54
PERCENT UNC 2.94
INDIVIDUAL G.C. RUNS:

51.80 900
52.85 901
53.31 902
52.38 903
52.40 904
51.77 905

SAMPLE NO 45
DESCRIPTION:
HW,RT,60 CM US,10 CM BS,PAIR 1,7:44
AVG CONC [UG/L] 53.16
UNCERTAINTY .91
PERCENT UNC 1.71
INDIVIDUAL G.C. RUNS:

52.60 906
53.56 907
53.11 908
53.03 909
53.13 910
53.52 911

W6

SAMPLE NO 54
DESCRIPTION:
HW,LT,60 CM US,10 CM BS,PAIR 54,8:50
AVG CONC [UG/L] 54.31
UNCERTAINTY 1.43
PERCENT UNC 2.64
INDIVIDUAL G.C. RUNS:
54.04 912
54.43 913
53.40 914
54.48 915
55.09 916
54.43 917

SAMPLE NO 66
DESCRIPTION:
HW,CTR,60 CM US,10 CM BS,PAIR 63,11:00
AVG CONC [UG/L] 53.29
UNCERTAINTY 1.15
PERCENT UNC 2.16
INDIVIDUAL G.C. RUNS:
52.92 918, CHANGE SEPTA
53.97 919, STRANGE BASELINE
52.89 920
53.49 921
53.53 922
52.91 923

SAMPLE NO 18
DESCRIPTION:
TW,RT,30 CM US,10 CM BS,PAIR 62,12:40
AVG CONC [UG/L] 26.46
UNCERTAINTY .92
PERCENT UNC 3.47
INDIVIDUAL G.C. RUNS:
25.93 924
26.56 925
26.52 926
26.57 927
26.98 928
26.20 929

SAMPLE NO 55
DESCRIPTION:
TW,CTR,30 CM US,10 CM BS,PAIR 48,13:55
AVG CONC [UG/L] 27.12
UNCERTAINTY .89
PERCENT UNC 3.28
INDIVIDUAL G.C. RUNS:
26.64 936
27.42 937
27.61 938
27.05 939
27.07 940
26.93 941

SAMPLE NO 12
DESCRIPTION:
TW,LT,30 CM US,10 CM BS,PAIR 24,15:10
AVG CONC [UG/L] 26.91
UNCERTAINTY .85
PERCENT UNC 3.15
INDIVIDUAL G.C. RUNS:
26.43 942
27.29 943
26.70 944
26.97 945
26.85 946
27.26 947

SAMPLE NO 2
DESCRIPTION:
TW,80 CM FROM RT,30 CM US,10 CM BS,PAIR 14,16
AVG CONC [UG/L] 25.98
UNCERTAINTY .45
PERCENT UNC 1.74
INDIVIDUAL G.C. RUNS:
25.78 948,3MM BUBBLE,
26.12 949
26.03 950
26.12 951
25.83 952
26.64 953, DROP

W6

SAMPLE NO 26
DESCRIPTION:
TW, .8M FR LT, 30 CM US, 10 CM BS, PR 59, 17:48
AVG CONC [UG/L] 26.67
UNCERTAINTY .46
PERCENT UNC 1.72
INDIVIDUAL G.C. RUNS:
26.02 954 DROP
26.92 955
26.46 956
26.67 957
26.69 958
26.64 959

SAMPLE NO 44
DESCRIPTION:
HW, CTR, 60 CM US, 10 CM BS, PR 64, 19:46, CH K
AVG CONC [UG/L] 51.98
UNCERTAINTY 1.15
PERCENT UNC 2.22
INDIVIDUAL G.C. RUNS:
52.51 961
51.96 962
51.67 963
52.30 964
52.16 965
51.27 967

SAMPLE NO 30
DESCRIPTION:
HW, CTR, 60 CM US, 25 CM AB, PR 39, 4:15, CH P
AVG CONC [UG/L] 53.36
UNCERTAINTY .37
PERCENT UNC .70
INDIVIDUAL G.C. RUNS:
53.39 894
53.22 895
53.43 896
53.36 897
53.57 898
53.17 899

SAMPLE NO 32
DESCRIPTION:
TW, RT, 30 CM US, 10 CM BS, PR 18, 12:40, CH P
AVG CONC [UG/L] 26.80
UNCERTAINTY .77
PERCENT UNC 2.86
INDIVIDUAL G.C. RUNS:
26.58 930
26.45 931
26.69 932
26.80 933
27.28 934
26.98 935

W7

PROPANE WEIR TEST SEVEN - 3/14/88
NAPPE WIDTH IS 91.5 CM AT POINT OF IMPACT
NAPPE WAS NOT BURSTING, SOME AIR IN PIPE

HEAD [M] .0402
SPECQ [M³/S/M] .0147
TOTALQ [M³/S] .0134
NOVAK SPECQ [M³/S/M] .0178
TAILWATER DEPTH [M] .276
FALL HEIGHT 2.292
WATER TEMPERATURE [°C] 3.2

UPS CONC [UG/L] 272.62
DNS CONC [UG/L] 128.15
TRANSFER EFF, E [-] .530
TOTAL UNC IN E [-] .009
PERCENT UNC [-] 1.743
PREC UNC IN E .00642
WE DUE TO CALIB 0
WE DUE TO FW .00663
BE DUE TO SYR VOL 0
BE DUE TO H .00032

TRANSFER EFF., DEF RATIOS:, OXYGEN AT 20°C

MEASURED E .783 R: 4.62
TOTAL UNC IN E .009 R: .18
AVERY & NOVAK E .795 R: 4.88
NAKASONE E .463 R: 1.86

SAMPLE NO 44
DESCRIPTION:
HW,RT,1.2 M US,25 CM AB,PAIR 2,6.30
AVG CONC [UG/L] 279.65
UNCERTAINTY 7.87
PERCENT UNC 2.82
INDIVIDUAL G.C. RUNS:
274.62 990
278.16 991
279.70 992
280.41 993
281.35 994
283.64 995

SAMPLE NO 54
DESCRIPTION:
HW,CTR,1.2 M US,25 CM AB,PAIR 45,9.00
AVG CONC [UG/L] 277.29
UNCERTAINTY 5.20
PERCENT UNC 1.88
INDIVIDUAL G.C. RUNS:

277.18 1012
275.62 1013
274.40 1014
278.48 1015
278.11 1016
279.98 1017

SAMPLE NO 18
DESCRIPTION:
HW,LT,1.2 M US,25 CM AB,PAIR 57,11:30
AVG CONC [UG/L] 274.28
UNCERTAINTY 5.49
PERCENT UNC 2.00
INDIVIDUAL G.C. RUNS:

267.90 1018, DROP
267.50 1019, DROP
273.75 1020
272.38 1021
272.96 1022
274.94 1023
277.37 1024

SAMPLE NO 34
DESCRIPTION:
HW,RT,1.2 M US,10 CM BS,PAIR 30,16:00
AVG CONC [UG/L] 273.37
UNCERTAINTY 10.06
PERCENT UNC 3.68
INDIVIDUAL G.C. RUNS:
268.73 1025
269.54 1026
272.04 1027
276.42 1028
274.91 1029
278.56 1032

W7

SAMPLE NO 12
DESCRIPTION:
HW,CTR,1.2 M US,10 CM BS,PAIR 26,20:30
AVG CONC [UG/L] 269.37
UNCERTAINTY 2.63
PERCENT UNC .98
INDIVIDUAL G.C. RUNS:
265.03 1030, DROP
268.15 1031
268.73 1033
270.60 1034
269.72 1035
269.64 1036

SAMPLE NO 55
DESCRIPTION:
HW,LT,1.2 M US,10 CM BS,PAIR 63,27:00
AVG CONC [UG/L] 261.74
UNCERTAINTY 6.80
PERCENT UNC 2.60
INDIVIDUAL G.C. RUNS:
258.13 1037, 2MM BUBBLE
260.26 1038
261.40 1039
261.11 1040
264.13 1041
265.43 1042

SAMPLE NO 39
DESCRIPTION:
TW,RT,30 CM US,2 CM BS,PAIR 50,29:29
AVG CONC [UG/L] 128.72
UNCERTAINTY 2.19
PERCENT UNC 1.70
INDIVIDUAL G.C. RUNS:
127.66 1043
128.38 1044
128.99 1045
128.75 1046
129.81 1047

SAMPLE NO 64
DESCRIPTION:
TW,CTR,30 CM US,2 CM BS,PAIR 47,31:00
AVG CONC [UG/L] 127.97
UNCERTAINTY 2.56
PERCENT UNC 2.00
INDIVIDUAL G.C. RUNS:
125.15 1057, DROP
126.68 1058
127.39 1059
128.74 1060
128.82 1061
128.25 1062

SAMPLE NO 27
DESCRIPTION:
TW,LT,30 CM US,2 CM BS,PAIR 1,32:30
AVG CONC [UG/L] 129.32
UNCERTAINTY 1.88
PERCENT UNC 1.46
INDIVIDUAL G.C. RUNS:
127.06 1063, DROP
128.76 1064
128.61 1065
130.31 1066
129.55 1067
129.37 1068

SAMPLE NO 38
DESCRIPTION:
TW,.8M FROM RT,30 CM US,2 CM BS,PAIR 16,33:48
AVG CONC [UG/L] 127.49
UNCERTAINTY 2.19
PERCENT UNC 1.72
INDIVIDUAL G.C. RUNS:
126.26 1074
126.92 1075
127.46 1076
127.69 1077
127.82 1078
128.77 1079

W7

SAMPLE NO	24	SAMPLE NO	25
DESCRIPTION:		DESCRIPTION:	
TW, .8M FROM LT, 30 CM US, 2 CM BS, PAIR 10, 35:23		HW, CTR, 1.2 M US, 10 CM BS, PAIR 37, 37:32, CH K	
AVG CONC [UG/L]	127.24	AVG CONC [UG/L]	235.92
UNCERTAINTY	3.87	UNCERTAINTY	4.79
PERCENT UNC	3.04	PERCENT UNC	2.03
INDIVIDUAL G.C. RUNS:		INDIVIDUAL G.C. RUNS:	
124.77	1080	233.93	1086, LG. BUBBLE 5MM
126.24	1081	234.10	1087
127.17	1082	234.69	1088
128.40	1083	237.86	1089
128.35	1084	237.60	1090
128.53	1085	237.33	1091
SAMPLE NO	2	SAMPLE NO	11
DESCRIPTION:		DESCRIPTION:	
HW, RT, 1.2 M US, 25 CM AB, PAIR 44, 6:30, CH P		LOD SAMPLE ADD 250 uL 99.7 PPM PROP. SHK	
AVG CONC [UG/L]	279.12	AVG CONC [UG/L]	2.00
UNCERTAINTY	5.98	UNCERTAINTY	.72
PERCENT UNC	2.14	PERCENT UNC	36.10
INDIVIDUAL G.C. RUNS:		INDIVIDUAL G.C. RUNS:	
275.92	1006	2.75	1098
277.67	1007	1.90	1099
277.67	1008	1.89	1100
280.88	1009	1.90	1101
281.05	1010	1.90	1102
281.53	1011	1.92	1103
		1.86	1104
SAMPLE NO	50	1.85	1105
DESCRIPTION:		SAMPLE NO	5
TW, RT, 30 CM US, 2 CM BS, PAIR 39, 29:29, CH P		DESCRIPTION:	
AVG CONC [UG/L]	131.92	LOD, ADD 100uL 99.7 PPM PROP., SHAKE	
UNCERTAINTY	3.06	AVG CONC [UG/L]	.69
PERCENT UNC	2.32	UNCERTAINTY	.09
INDIVIDUAL G.C. RUNS:		PERCENT UNC	12.45
128.02	1050, DROP	INDIVIDUAL G.C. RUNS:	
130.37	1051	.69	1106
133.59	1052, REPLACE SEPTA, ESI, DROP	.71	1107
132.57	1053	.77	1108
133.06	1054, REPLACE SEPTA	.69	1109
132.39	1055	.65	1110
131.20	1056	.69	1111
		.66	1112
		.67	1113
		.64	1114

WB

PROPANE WIER TEST EIGHT - 3/17/88
MAXIMUM DISCHARGE, MINIMUM TAILWATER DEPTH

HEAD [M] .1064
SPECQ [M³/S/M] .0643
TOTALQ [M³/S] .0584
NOVAK SPECQ [M³/S/M] .0635
TAILWATER DEPTH [M] .353
FALL HEIGHT 2.281
WATER TEMPERATURE [°C] 4.0

UPS CONC [UG/L] 84.03
DNS CONC [UG/L] 47.15
TRANSFER EFF, E [-] .439
TOTAL UNC IN E [-] .011
PERCENT UNC [-] 2.508
PREC UNC IN E .00766
WE DUE TO CALIB 0
WE DUE TO FW .00791
BE DUE TO SYR VOL 0
BE DUE TO H .00005

TRANSFER EFF., DEF RATIOS:, OXYGEN AT 20°C

MEASURED E .682 R: 3.14
TOTAL UNC IN E .012 R: .12
AVERY & NOVAK E .704 R: 3.38
NAKASONE E .715 R: 3.51

SAMPLE NO 18
DESCRIPTION:
HW,RT,60 CM US,25 CM AB,PAIR 24,2:00
AVG CONC [UG/L] 83.10
UNCERTAINTY 1.31
PERCENT UNC 1.58
INDIVIDUAL G.C. RUNS:
82.49 1126
82.54 1127
83.11 1128
83.52 1129
83.75 1130
83.20 1131

SAMPLE NO 44
DESCRIPTION:
HW,CTR,60 CM US,25 CM AB,PAIR 63,3:31
AVG CONC [UG/L] 82.93
UNCERTAINTY 1.71
PERCENT UNC 2.07
INDIVIDUAL G.C. RUNS:
82.24 1132
83.23 1133
82.12 1134
83.67 1135
83.57 1136
82.76 1137

SAMPLE NO 16
DESCRIPTION:
HW,LT,60 CM US,25 CM AB,PAIR 1,5:00
AVG CONC [UG/L] 83.57
UNCERTAINTY 1.46
PERCENT UNC 1.74
INDIVIDUAL G.C. RUNS:
82.58 1138,BAD SEPTA
83.71 1139,BAD SEPTA,LEAKED
83.28 1140,REPLACED SEPTA
84.07 1141
83.74 1142
84.06 1143

SAMPLE NO 32
DESCRIPTION:
HW,RT,60 CM US,10 CM BS,PAIR 66,6:33
AVG CONC [UG/L] 86.12
UNCERTAINTY 2.33
PERCENT UNC 2.71
INDIVIDUAL G.C. RUNS:
74.21 1150, DROP, POOR INJ.,2MM BUBBLE
76.80 1151, DROP, POOR INJ.
85.11 1152
85.75 1153
85.03 1154
87.26 1155
87.23 1156
85.69 1157
86.74 1158

W8

SAMPLE NO 39
DESCRIPTION:
HW,CTR,60 CM US,10 CM BS,PAIR 11,8:02
AVG CONC [UG/L] 83.91
UNCERTAINTY 2.47
PERCENT UNC 2.95
INDIVIDUAL G.C. RUNS:
84.94 1159
84.94 1160
83.71 1161
83.82 1162
82.36 1163
83.67 1164

SAMPLE NO 48
DESCRIPTION:
HW,LT,60 CM US,10 CM BS,PAIR 45,9:36
AVG CONC [UG/L] 84.57
UNCERTAINTY .59
PERCENT UNC .69
INDIVIDUAL G.C. RUNS:
78.83 1174,DROP
79.92 1175,DROP
79.82 1176,DROP
84.12 1177
84.60 1178,CLEAN PLUNGER TIP
84.69 1179
84.75 1180
84.64 1181
84.61 1182

SAMPLE NO 47
DESCRIPTION:
TW,RT,30 CM US,10 CM BS,PAIR 59,11:27
AVG CONC [UG/L] 47.14
UNCERTAINTY .88
PERCENT UNC 1.87
INDIVIDUAL G.C. RUNS:
46.69 1183
47.19 1184
47.00 1185
47.35 1186
47.67 1187
46.92 1188

SAMPLE NO 38
DESCRIPTION:
TW,CTR,30 CM US,10 CM BS,PAIR 64,13:02
AVG CONC [UG/L] 47.38
UNCERTAINTY 1.21
PERCENT UNC 2.55
INDIVIDUAL G.C. RUNS:
46.65 1189,
47.12 1190
47.35 1191
47.40 1192
47.93 1193
47.83 1194

SAMPLE NO 27
DESCRIPTION:
TW,LT,30 CM US,10 CM BS,PAIR 57,14:19
AVG CONC [UG/L] 46.44
UNCERTAINTY 1.38
PERCENT UNC 2.97
INDIVIDUAL G.C. RUNS:
45.73 1195
45.89 1196
46.52 1197
46.63 1198
46.66 1199
47.18 1200

SAMPLE NO 42
DESCRIPTION:
TW,.8M FR RT,30 CM US,10 CM BS,PAIR 62,15:50
AVG CONC [UG/L] 47.95
UNCERTAINTY 1.06
PERCENT UNC 2.20
INDIVIDUAL G.C. RUNS:
47.58 1201
48.00 1202
47.55 1203
48.34 1204
48.30 1205
49.08 1206, DROP

W8

SAMPLE NO 2
DESCRIPTION:
TW, .8M FR LT, 30 CM US, 10 CM BS, PAIR 37, 17:10
AVG CONC [UG/L] 46.83
UNCERTAINTY 1.01
PERCENT UNC 2.15
INDIVIDUAL G.C. RUNS:
46.33 1207
46.49 1208
47.31 1209
46.70 1210
46.95 1211
47.20 1212

SAMPLE NO 30
DESCRIPTION:
HW, CTR, 60 CM US, 10 CM BS, PAIR 34, 19:00, CH K
AVG CONC [UG/L] 82.10
UNCERTAINTY 3.45
PERCENT UNC 4.20
INDIVIDUAL G.C. RUNS:
80.44 1219,
82.18 1220
82.25 1221
80.66 1222,
83.50 1223
83.58 1224

SAMPLE NO 45
DESCRIPTION:
HW, LT, 60 CM US, 10 CM BS, PAIR 48, 9:36, CH P
AVG CONC [UG/L] 82.89
UNCERTAINTY 3.61
PERCENT UNC 4.36
INDIVIDUAL G.C. RUNS:
79.11 1165, DROP
82.65 1166
83.10 1167
78.80 1168, DROP
84.86 1169
80.72 1170
81.59 1171
84.52 1172
82.78 1173

SAMPLE NO 37
DESCRIPTION:
TW, .8M FR LT, 30 CM US, 10 CM BS, PAIR 2, 17:17, CH P
AVG CONC [UG/L] 45.84
UNCERTAINTY .89
PERCENT UNC 1.94
INDIVIDUAL G.C. RUNS:
45.86 1213
46.06 1214
45.44 1215
46.22 1216
46.96 1217, DROP
45.60 1218

W9

PROPANE WEIR TEST NINE - 3/21/88
MIN DISCHARGE, MAX TW
NOTE CONTRACTION OF NAPPE AT LOWER FLOWS

HEAD [M] .0399
SPECQ [M³/S/M] .0145
TOTALQ [M³/S] .0132
NOVAK SPECQ [M³/S/M] .0163
TAILWATER DEPTH [M] 1.073
FALL HEIGHT 1.495
WATER TEMPERATURE [°C] 3.4

UPS CONC [UG/L] 81.81
DNS CONC [UG/L] 60.60
TRANSFER EFF, E [-] .259
TOTAL UNC IN E [-] .014
PERCENT UNC [-] 5.414
PREC UNC IN E .00938
WE DUE TO CALIB 0
WE DUE TO FW .01044
BE DUE TO SYR VOL 0
BE DUE TO H .00011

TRANSFER EFF., DEF RATIOS:, OXYGEN AT 20°C

MEASURED E .454 R: 1.83
TOTAL UNC IN E .021 R: .07
AVERY & NOVAK E .687 R: 3.19
NAKASONE E .486 R: 1.94

SAMPLE NO 67

DESCRIPTION:

HW,RT,60 CM US,25 CM AB,PAIR 35,5:00

AVG CONC [UG/L] 82.06

UNCERTAINTY 1.21

PERCENT UNC 1.47

INDIVIDUAL G.C. RUNS:

210.79 GC RUN NUMBER 1235,DROP
80.29 1236 , DROP
82.10 1237
81.68 1238
82.58 1239
81.36 1240
82.14 1241
82.50 1242

SAMPLE NO 50

DESCRIPTION:

HW,CTR,60 CM US,25 CM AB,PAIR 56,21:16

AVG CONC [UG/L] 82.84

UNCERTAINTY 1.57

PERCENT UNC 1.90

INDIVIDUAL G.C. RUNS:

82.38 1262
82.27 1263
84.23 1264, DROP
82.88 1265
83.69 1266
82.99 1267

SAMPLE NO 2

DESCRIPION:

HW,LT,60 CM US,25 CM AB,PAIR 10,37:00

AVG CONC [UG/L] 81.45

UNCERTAINTY 2.22

PERCENT UNC 2.72

INDIVIDUAL G.C. RUNS:

80.49 1274
80.93 1275
81.29 1276
82.14 1277
82.39 1278
83.34 1279, DROP

SAMPLE NO 32

DESCRIPTION:

HW,RT,60 CM US,10 CM BS,PAIR 37,53:00

AVG CONC [UG/L] 80.22

UNCERTAINTY 2.52

PERCENT UNC 3.15

INDIVIDUAL G.C. RUNS:

78.68 1280
79.17 1281
79.94 1282
80.40 1283
81.33 1284
80.58 1285
81.41 1286

W9

SAMPLE NO 52
DESCRIPTION:
HW,CTR,60 CM US,10 CM BS,PAIR 22,54:45
AVG CONC [UG/L] 82.68
UNCERTAINTY 2.30
PERCENT UNC 2.78
INDIVIDUAL G.C. RUNS:
81.92 1287
82.18 1288
81.76 1289
82.75 1290
83.84 1291
83.66 1292

SAMPLE NO 55
DESCRIPTION:
HW,LT,60 CM US,10 CM BS,PAIR 25,69:30
AVG CONC [UG/L] 81.61
UNCERTAINTY 1.62
PERCENT UNC 1.98
INDIVIDUAL G.C. RUNS:
81.06 1293
80.36 1294, DROP
81.21 1295
81.49 1296
81.77 1297
82.53 1298

SAMPLE NO 5
DESCRIPTION:
TW,RT,30 CM US,10 CM BS,PAIR 16,71:30
AVG CONC [UG/L] 59.97
UNCERTAINTY 1.22
PERCENT UNC 2.04
INDIVIDUAL G.C. RUNS:
59.53 1299, ~2MM BUBBLE
59.51 1300
59.92 1301
59.80 1302
60.37 1303
60.70 1304

SAMPLE NO 27
DESCRIPTION:
TW,CTR,30 CM US,10 CM BS,PAIR 47,73:17
AVG CONC [UG/L] 60.45
UNCERTAINTY .96
PERCENT UNC 1.59
INDIVIDUAL G.C. RUNS:
60.29 1305
60.28 1306
60.33 1307
60.91 1308
61.96 1309, DROP
62.40 1310, DROP

SAMPLE NO 15
DESCRIPTION:
TW,LT,30 CM US,10 CM BS,PAIR 36,75:00
AVG CONC [UG/L] 60.25
UNCERTAINTY 1.29
PERCENT UNC 2.13
INDIVIDUAL G.C. RUNS:
59.75 1311
59.58 1312
60.25 1313
60.41 1314
60.80 1315
60.72 1316

SAMPLE NO 62
DESCRIPTION:
TW,.8M FR RT,30 CM US,10 CM BS,PAIR 63,76:30
AVG CONC [UG/L] 59.75
UNCERTAINTY 1.16
PERCENT UNC 1.94
INDIVIDUAL G.C. RUNS:
58.98 1324
59.61 1325
59.84 1326
59.69 1327
60.17 1328
60.22 1329

W9

SAMPLE NO 59

DESCRIPTION:

TW, .8 FROM LT, 30 CM US, 10 CM BS, PAIR 24, 78:26

AVG CONC [UG/L] 62.57

UNCERTAINTY .70

PERCENT UNC 1.11

INDIVIDUAL G.C. RUNS:

62.21	1330
61.67	1331, DROP
62.50	1332
62.55	1333
62.74	1334
62.86	1335

SAMPLE NO 44

DESCRIPTION:

HW, CTR, 60 CM US, 10 CM BS, PAIR 1, 80:01, CH K

AVG CONC [UG/L] 80.33

UNCERTAINTY 2.57

PERCENT UNC 3.21

INDIVIDUAL G.C. RUNS:

79.45	1336
79.40	1337
79.39	1338
81.39	1339
81.24	1340
81.08	1341

SAMPLE NO 56

DESCRIPTION:

HW, CTR, 60 CM US, 25 CM AB, PAIR 50, 21:16, CH PR

AVG CONC [UG/L] 82.88

UNCERTAINTY 1.14

PERCENT UNC 1.38

INDIVIDUAL G.C. RUNS:

81.00	1268, DROP
82.17	1269
83.03	1270
82.96	1271
83.03	1272
83.23	1273

SAMPLE NO 47

DESCRIPTION:

TW, CTR, 30 CM US, 10 CM BS, PAIR 27, 73:17, CH PR

AVG CONC [UG/L] 59.91

UNCERTAINTY 1.15

PERCENT UNC 1.91

INDIVIDUAL G.C. RUNS:

59.35	1317, BUBBLE-RECAP
59.90	1319
59.49	1320
60.54	1321
60.23	1322
59.97	1323

W10

PROPANE WEIR TRACER TEST TEN - MAR 24, 1988
WATER IS MUCH DIRTIER FOR THIS LAST TEST
DISCHARGE IN RIVER HAS INCREASED

HEAD [M] .0701
SPECQ [M³/S/M] .0341
TOTALQ [M³/S] .0310
NOVAK SPECQ [M³/S/M] .0364
TAILWATER DEPTH [M] .314
FALL HEIGHT 2.284
WATER TEMPERATURE [°C] 5.3

UPS CONC [UG/L] 128.89
DNS CONC [UG/L] 70.45
TRANSFER EFF, E [-] .453
TOTAL UNC IN E [-] .012
PERCENT UNC [-] 2.700
PREC UNC IN E .00951
WE DUE TO CALIB 0
WE DUE TO FW .00771
BE DUE TO SYR VOL 0
BE DUE TO H .00018

TRANSFER EFF., DEF RATIOS:, OXYGEN AT 20°C

MEASURED E .687 R: 3.19
TOTAL UNC IN E .013 R: .14
AVERY & NOVAK E .746 R: 3.94
NAKASONE E .603 R: 2.52

SAMPLE NO 36
DESCRIPTION:
HW, RT, 60 CM US, 25 CM AB, PAIR:66, T=2:00
AVG CONC [UG/L] 126.54
UNCERTAINTY 5.63
PERCENT UNC 4.45
INDIVIDUAL G.C. RUNS:

123.41 GC RUN NUMBER:1391
128.23 1392
124.43 1393
125.80 1394
128.14 1395
125.88 1396
129.87 1397

SAMPLE NO 42
DESCRIPTION:
HW, CTR, 60 CM US, 25 CM AB, PAIR:66, T=4:15
AVG CONC [UG/L] 132.00
UNCERTAINTY 3.54
PERCENT UNC 2.68
INDIVIDUAL G.C. RUNS:

129.81 1398
130.98 1399
131.01 1400
133.08 1401
132.16 1402
133.29 1403
133.69 1404

SAMPLE NO 45
DESCRIPTION:
HW, LT, 60 CM US, 25 CM AB, PAIR:18, T=6:30
AVG CONC [UG/L] 131.52
UNCERTAINTY 3.46
PERCENT UNC 2.63
INDIVIDUAL G.C. RUNS:

129.76 1405
126.45 1406, DROP
127.91 1407, DROP, ESI
131.83 1408
133.24 1409
133.03 1410
132.21 1411
130.14 1412
130.44 1413

SAMPLE NO 11
DESCRIPTION:
HW, RT, 60 CM US, 10 CM BS, PAIR:48, T=8:00
AVG CONC [UG/L] 128.25
UNCERTAINTY 2.28
PERCENT UNC 1.77
INDIVIDUAL G.C. RUNS:
127.47 1422
127.25 1423
127.65 1425
128.94 1425
128.99 1426
129.21 1427

W10

SAMPLE NO 24
DESCRIPTION:
HW, CTR, 60 CM US, 10 CM BS, PAIR:30, T=9:00
AVG CONC [UG/L] 127.55
UNCERTAINTY 1.99
PERCENT UNC 1.56
INDIVIDUAL G.C. RUNS:
127.86 1428
127.96 1429
126.09 1430
128.29 1431
127.41 1432
127.71 1433

SAMPLE NO 39
DESCRIPTION:
HW, LT, 60 CM US, 10 CM BS, PAIR:38, T=11:00
AVG CONC [UG/L] 127.50
UNCERTAINTY 3.98
PERCENT UNC 3.12
INDIVIDUAL G.C. RUNS:
124.47 1434 BAD INJECTION ?, DROP
126.19 1435
127.62 1436
126.49 1437
129.90 1438
126.07 1439
128.71 1440

SAMPLE NO 12
DESCRIPTION:
TW, RT, BOTTOM, PAIR:54, T=14:45
AVG CONC [UG/L] 69.25
UNCERTAINTY 2.10
PERCENT UNC 3.03
INDIVIDUAL G.C. RUNS:
68.57 1448
68.02 1449
69.85 1450
69.34 1451
70.21 1452
53.70 1453 POOR INJECTION, DROP
69.54 1454

SAMPLE NO 34
DESCRIPTION:
TW, CTR, BOTTOM, PAIR:54, T=14:45
AVG CONC [UG/L] 72.29
UNCERTAINTY 2.35
PERCENT UNC 3.24
INDIVIDUAL G.C. RUNS:
71.15 1456
71.57 1457
71.73 1458
73.19 1459
73.20 1460
72.92 1461

SAMPLE NO 5
DESCRIPTION:
TW, LT BOTTOM, PAIR:63, T=16:18
AVG CONC [UG/L] 70.20
UNCERTAINTY 2.17
PERCENT UNC 3.08
INDIVIDUAL G.C. RUNS:
69.63 1462
68.98 1463
69.87 1464
68.23 1465 DROP
70.90 1466
70.72 1467
71.12 1468

SAMPLE NO 1
DESCRIPTION:
TW, 0.8M FROM RT, BOTTOM, PAIR:16, T=17:45
AVG CONC [UG/L] 69.81
UNCERTAINTY 1.02
PERCENT UNC 1.46
INDIVIDUAL G.C. RUNS:
67.87 1469, DROP
69.57 1470
69.33 1471
67.93 1472 DROP
69.92 1473
69.94 1474
70.29 1475

W10

SAMPLE NO 44
DESCRIPTION:
TW, 0.8M FROM LT, BOTTOM, PAIR:62, T=19:10
AVG CONC [UG/L] 70.67
UNCERTAINTY 2.26
PERCENT UNC 3.20
INDIVIDUAL G.C. RUNS:
69.75 1476
70.01 1477
69.88 1478
71.51 1479
71.67 1480
71.19 1481

SAMPLE NO 48
DESCRIPTION:
HW, RT, 60 CM US, 10 CM BS, PAIR:11, CH PR
AVG CONC [UG/L] 129.48
UNCERTAINTY 3.27
PERCENT UNC 2.53
INDIVIDUAL G.C. RUNS:
73.89 1414 , POOR INJ, DROP
128.36 1415
125.40 1416 , DROP
128.11 1417
130.81 1418
130.07 1419
130.04 1420
125.55 1421 , DROP

SAMPLE NO 26
DESCRIPTION:
TW, RT BOTTOM, PAIR:12, CHECK PAIR!
AVG CONC [UG/L] 69.25
UNCERTAINTY 3.17
PERCENT UNC 4.58
INDIVIDUAL G.C. RUNS:
67.38 1441
69.40 1442
70.32 1443
68.28 1444
70.66 1445
38.79 1446 , POOR INJECTION, DROP
69.45 1447

SAMPLE NO 62
DESCRIPTION:
TW, .8M FROM LT, BOTTOM, PAIR:44, TWIG IN VIAL
AVG CONC [UG/L] 69.17
UNCERTAINTY 3.07
PERCENT UNC 4.44
INDIVIDUAL G.C. RUNS:
67.49 1482
68.41 1483
68.61 1484
69.62 1485
70.37 1486
70.49 1487

SAMPLE NO 56
DESCRIPTION:
HW, CTR, 60 CM US, 10 CM BS, PAIR:25, T=22:00
AVG CONC [UG/L] 129.59
UNCERTAINTY 3.69
PERCENT UNC 2.85
INDIVIDUAL G.C. RUNS:
128.36 1488
128.56 1489
128.22 1490
129.82 1491
131.25 1492
131.34 1493

HSC2

LISTING OF PROGRAM HSC2 WHICH:
COMPUTES CONCENTRATIONS FROM HEADSPACE ANALYSIS AND
TRANSFER EFFICIENCY AND UNCERTAINTY IN EFFICIENCY

00010 PROGRAM HSC2(INPUT,OUTPUT,BODAT,EXPDAT,EXPRES,
00020+ TAPE1=BODAT,TAPE2=EXPDAT,TAPE3=EXPRES)
00030C
00040C THIS PROGRAM COMPUTES THE ORIGINAL WATER CONCENTRATIONS FOR
00050C PROPANE ANALYZED BY THE HEADSPACE GAS CHROMATOGRAPHIC TECHNIQUE
00060C ADDITIONALLY IT COMPUTES THE TRANSFER NUMBER, D, AND
00070C THE UNCERTAINTY ASSOCIATED WITH THAT NUMBER
00080C FILES NEEDED:
00090C THIS FILE = HSC2 (OLD,HSC2)
00100C BODAT (GET,BODAT) THE NUMBER OF BOTTLES, THE WIEGHT OF THE
00110C BOTTLES (GM) AND THEIR VOLUMES (ML)
00120C EXPDAT (GET,EXPDAT=FILENAME) WHERE FN IS THE NAME OF A FILE
00130C WITH THE NUMBER OF SAMPLES, THE SAMPLING AND ANALYSIS
00140C THE BOTTLE NUMBER, THE MASS WITH H.S. (GM), THE G.C.
00150C TEMPERATURES(^C), THE SLOPE(UL/AREA) THEN, PER SAMPLE:
00160C AREA COUNTS, THE VOLUME INJECTED (UL), AND A 25 SYMBOL
00170C DESCRIPTION IN QUOTES EX: 'UPSTREAM,12:15,6/25/87'
00180C
00190 PARAMETER(NB=70,MAXINJ=10)
00200 DIMENSION TSCORE(15),BOWT(NB),BOVOL(NB),VW(NB),WWHS(NB),VH(NB),
00210+ NOTINC(NB),WCP(NB),NINJ(NB),CAVG(NB),X(25),Y(25),C(25),
00220+ PERWCP(NB),AREA(NB,MAXINJ),VINJ(NB,MAXINJ),CENV(NB,MAXINJ),
00230+ INCLUD(NB,MAXINJ)
00240 CHARACTER DESC(NB)*60,GCNOTE(NB,MAXINJ)*45,TESTD(3)*60
00250 INTEGER BOTN(NB)
00260 REAL MPROP,MWATER,MCAP,MSEPTA,NAPPEW
00270 PARAMETER (MPROP=44.0616, MWATER=18.0152, RUNIV=0.082057,
00280+ YINT=0, WEIRL=.9083, WEIRW=.518, HO=1.497, CRATIO=1.383,
00290+ TKO=273.15, MCAP=3.036, MSEPTA=1.166, SLFACT=.0054448)
00300 TSCORE(1)=12.706
00310 TSCORE(2)=4.303
00320 TSCORE(3)=3.182
00330 TSCORE(4)=2.776
00340 TSCORE(5)=2.571
00350 TSCORE(6)=2.447
00360 TSCORE(7)=2.365
00370 TSCORE(8)=2.306
00380 TSCORE(9)=2.262
00390 TSCORE(10)=2.228
00400 TSCORE(11)=2.201
00410 TSCORE(12)=2.179
00420 TSCORE(13)=2.160
00430 TSCORE(14)=2.145
00440 TSCORE(15)=2.131
00450C
00460C MOLAR MASS, CAP AND SEPTA MASS IN GRAMS
00470C
00480 REWIND 1
00490 REWIND 2
00500 REWIND 3

HSC2

```
00510 READ(1,*)NOBOT
00520 READ(1,*)(BOWT(1),BOVOL(1),I=1,NOBOT)
00530 READ(2,*)(TESTD(1),I=1,3)
00540 READ(2,*)NCAL,NSAMP,NUPS,NDNS
00550 READ(2,*)TENV,TLAB,PRESS,POINTH,TAILWH,NAPPEW
00560 READ(2,*)(X(1),Y(1),C(1),I=1,NCAL)
00570C
00580C ** X IS AREA COUNTS & Y VOLUME [UL] & C IS IN PPM **
00590C
00600 DO 200 I=1,NSAMP
00610 READ(2,*)BOTN(I),WWHS(I),NINJ(I),DESC(I)
00620 DO 100 J=1,NINJ(I)
00630 READ(2,*) AREA(I,J),VINJ(I,J),INCLUD(I,J),GCNOTE(I,J)
00640 100 CONTINUE
00650 200 CONTINUE
00660C
00670 TENV=TENV+TKO
00680 TLAB=TLAB+TKO
00690 RHOLAB=RHO(TLAB)
00700 RHOENV=RHO(TENV)
00710C
00720C *****
00730C ** CALCULATE A BEST FIT CALIBRATION LINE **
00740C *****
00750C
00760 XSUM=0
00770 YSUM=0
00780 X2SUM=0
00790 XYSUM=0
00800 SLFAC=MPROP*PRESS/760/RUNIV/TLAB/1000000
00810 DO 300 I=1,NCAL
00820 Y(I)=Y(I)*SLFAC*C(I)
00830C ** Y(I) IS NOW IN UG ( Y(I) WAS IN UL AND C(I) IN PPM )*
00840 XYSUM=X(I)*Y(I) + XYSUM
00850 X2SUM=X(I)**2 + X2SUM
00860 XSUM=X(I) + XSUM
00870 YSUM=Y(I) + YSUM
00880 300 CONTINUE
00890 SLOPE=XYSUM/X2SUM
00910C
00920C *****
00930C ** CALCULATE C(I,J), CAVG(I), AND WCP(I) **
00940C *****
00950C
00960C COMPUTE H IN ATM*L/G, NOTE RTOMPH IS UNITLESS
00970C
00980 HC=HENRY(TLAB,RHOLAB)
00990 RTOMPH=(RUNIV*TLAB)/(MPROP*HC)
01000C
01010C COMPUTE VOLUMES IN LITERS
01020C COMPUTE CONCENTRATION IN MICROGRAMS PER LITER
01030C
01040 DO 700 I=1,NSAMP
```

HSC2

```
01050      VW(I)=(WVHS(I)-BOWT(BOTN(I))-MCAP-MSEPTA)/RHOLAB
01060      VH(I)=BOVOL(BOTN(I))/1000-VW(I)
01070      DILFAC=1.0
01080      CSUM=0
01090      CSUM2=0
01100      NOTINC(I)=NINJ(I)
01110      DO 500 J=1, NINJ(I)
01120          DILFAC=DILFAC*(1+VINJ(I,J)/(VH(I)*1000000))
01130          CSYR =(AREA(I,J)*SLOPE)/VINJ(I,J)
01140          CHSI=CSYR*DILFAC*1000000
01150          CLAB=CHSI*(RTOMPH+VH(I)/VW(I))
01160          CENV(I,J)=CLAB*RHOLAB/RHOENV
01170          CSUM=CSUM+INCLUD(I,J)*CENV(I,J)
01180          CSUM2=CSUM2+INCLUD(I,J)*CENV(I,J)**2
01190          NOTINC(I)=NOTINC(I)-INCLUD(I,J)
01200      500 CONTINUE
01210      NINC=NINJ(I)-NOTINC(I)
01220      CAVG(I)=CSUM/NINC
01230C
01240      SDCI=((CSUM2-CSUM**2/NINC)/(NINC-1))**0.5
01250      WCP(I) = SDCI*TSCORE(NINC-1)
01260      PERWCP(I) = 100*WCP(I)/CAVG(I)
01270      700 CONTINUE
01280C
01290C *****
01300C ** COMPUTE PREC UNC'S: WCUP, WCDP, WDP IN CU, CD, D **
01310C *****
01320C
01330      WSUM=0
01340      CSUM=0
01350      DO 800 I=1,NUPS
01360          CSUM=CSUM+CAVG(I)
01370          WSUM=WSUM+WCP(I)**2
01380      800 CONTINUE
01390      CU=CSUM/NUPS
01400      WCUP=WSUM**(0.5)/NUPS
01410C
01420C
01430      CSUM=0
01440      WSUM=0
01450      DO 900 I=NUPS+1,NUPS+NDNS
01460          CSUM=CSUM+CAVG(I)
01470          WSUM=WSUM+WCP(I)**2
01480      900 CONTINUE
01490      CD=CSUM/NDNS
01500      WCDP=WSUM**(0.5)/NDNS
01510C
01520      D=1-CD/CU
01530C
01540      WDP=((- WCDP/CU)**2+(CD*WCUP/CU**2)**2)**0.5
```

HSC2

```
01550C
01560C *****
01570C ** COMPUTE WYO, WCY(I,J), WCY(I), WCUY, WCDY AND WDY **
01580C ** WDY IS THE UNC IN D DUE TO AN UNC IN THE Y-INT **
01590C *****
01600C
01610     WYOS2=0
01620     DO 920 I=1,NCAL
01630         WYOS2=(Y(I)-X(I)*SLOPE)**2 + WYOS2
01640     920 CONTINUE
01650     WYO=(WYOS2/(NCAL-1))**0.5
01660     IF((NCAL-1).LE.15) THEN
01670         WYO=WYO*TSORE(NCAL-1)
01680     ELSE
01690         WYO=WYO*2.1
01700     END IF
01710C
01720     WCIYS2=0
01730     DO 960 I=1,NUPS+NDNS
01740         FW=(RTOMPH + VH(I)/VW(I))
01750         DILFAC=1.0
01760         WCJYS2=0
01770         DO 940 J=1,NINJ(I)
01780             DILFAC=DILFAC*(1+VINJ(I,J)/(VH(I)*1000000))
01790             WCJY=(FW*DILFAC*WYO/VINJ(I,J))*1000000
01800             WCJYS2=WCJYS2+(WCJY**2)*INCLUD(I,J)
01810         940 CONTINUE
01820         WCIY=(WCJYS2/(NINJ(I)-NOTINC(I))**(2))**0.5
01830         WCIYS2=WCIYS2+WCIY**2
01840         IF (I.EQ.NUPS) THEN
01850             WCUY=WCIYS2**0.5/NUPS
01860             WCIYS2=0
01870         END IF
01880     960 CONTINUE
01890     WCDY=WCIYS2**0.5/NDNS
01900C
01910     WDY=((CD/CU/CU*WCUY)**2 + (WCDY/CU)**2)**0.5
01920C
01930C *****
01940C ** COMPUTE BDVSYR: THE BIAS IN D DUE TO A BIAS **
01950C **             SYRINGE VOLUME **
01960C *****
01970C
01980     BDVSYR=0.02*CD/CU
01990C
02000C *****
02010C ** COMPUTE WDFW: THE UNCERTAINTY DUE TO THE TERM **
02020C **             FW=(RTOMPH + VH(I)/VW(I)) **
02030C *****
02040C
02050     WDFW=0.0141*CD/CU
```

HSC2

```
02060C
02070C *****
02080C ** COMPUTE BDH: THE BIAS IN D DUE TO BIAS IN H **
02090C *****
02100C
02110     BCHS=0
02120     DO 1000 I=1,NUPS
02130         CHS=CAVG(I)/(RTOMPH+VH(I)/VW(I))
02140         BCH=CHS*RTOMPH*0.098
02150         BCHS=BCHS+BCH
02160     1000 CONTINUE
02170     BCUH=BCHS/NUPS
02180C
02190     BCHS=0
02200     DO 1100 I=NUPS+1,NUPS+NDNS
02210         CHS=CAVG(I)/(RTOMPH+VH(I)/VW(I))
02220         BCH=CHS*RTOMPH*0.098
02230         BCHS=BCHS+BCH
02240     1100 CONTINUE
02250     BCDH=BCHS/NDNS
02260C
02270     BDH=-BCDH/CU + BCUH*CD/CU**2
02280C
02290C *****
02300C ** COMBINE WDP, WDY, WDFW, BDVSYR AND BDH TO GIVE **
02310C **           THE TOTAL UNCERTAINTY IN D = UD           **
02320C *****
02330C
02332 WDY=0
02334 BDVSYR=0
02340     UD2=(WDP**2+WDY**2+WDFW**2+(BDVSYR+BDH)**2)
02350     UD=UD2**0.5
02360C
02370C *****
02380C ** COMPUTE DISCHARGE **
02390C *****
02400C
02410     HEADM=(POINTH-H0)/3.28
02420     CCD=0.611 + (HEADM/WEIRW)*0.08
02430     SPECQ=2.0/3.0*CCD*4.427*HEADM**1.5
02440     TOTALQ=SPECQ*WEIRL
02450     TAILWH=TAILWH/3.28
02460C
02470C *****
02480C ** COMPUTE D @ 20C BY NAKASONE, AVERY & NOVAK **
02490C *****
02500C
02510     FALLH=HEADM+2.528-TAILWH
02512     SQNAP=TOTALQ/NAPPEW
02520     RAN=(1 + 0.245*FALLH**1.34*SQNAP**(-.36) )**1.1087
02530     DAN=1.0 - 1.0/RAN
02540     SQHOUR=3600*SPECQ
```

HSC2

```
02550      IF(FALLH.LE.(1.2) .AND. SQHOUR.LE.(235))
02560+     RNAK=EXP(.0785*FALLH**1.31*SQHOUR**.428*TAILWH**.310)
02570      IF(FALLH.GT.(1.2) .AND. SQHOUR.LE.(235))
02580+     RNAK=EXP(.0861*FALLH**.816*SQHOUR**.428*TAILWH**.310)
02590      IF(FALLH.LE.(1.2) .AND. SQHOUR.GT.(235))
02600+     RNAK=EXP(5.39*FALLH**1.31*SQHOUR**(-.363)*TAILWH**.310)
02610      IF(FALLH.GT.(1.2) .AND. SQHOUR.GT.(235))
02620+     RNAK=EXP(5.92*FALLH**.816*SQHOUR**(-.363)*TAILWH**.310)
02630      DNAK=1.0-1.0/RNAK
02640C *****
02650C ** CONVERT D(P,TENV) TO D(02,20^C) **
02660C *****
02670      RP=1.0/(1.0-D)
02680      URP=UD*(1.0-D)**(-2)
02690      CORRF= (CRATIO*(293.15/TENV)**0.5*
02700+         (RMHU(TENV)/RMHU(293.15))**0.75*
02710+         (RHO(293.15)/RHO(TENV))**0.25)
02730      ROX=RP**CORRF
02740      UROX=URP*CORRF*RP**(CORRF-1.0)
02750      DOX=1.0-1.0/ROX
02760      UDOX=UROX/(ROX**2.0)
02770C
02780C *****
02790C ** OUTPUT CU, CD, D, UD AND THE COMPONENT WD'S. **
02800C *****
02810C
02820      WRITE(3,1800)
02830      WRITE(3,1900)(TESTD(I),I=1,3)
02840      WRITE(3,1800)
02850      WRITE(3,1910)HEADM
02860      WRITE(3,1920)SPECQ
02870      WRITE(3,1930)TOTALQ
02874      WRITE(3,1934)SQNAP
02880      WRITE(3,1940)TAILWH
02884      WRITE(3,1944)FALLH
02890      WRITE(3,1950)(TENV-TK0)
02900      WRITE(3,2000)CU
02910      WRITE(3,2020)CD
02920      WRITE(3,2100)D
02930      WRITE(3,2120)UD
02940      WRITE(3,2140)100*UD/D
02950      WRITE(3,2200)WDP
02960      WRITE(3,2300)WDY
02970      WRITE(3,2400)WDFW
02980      WRITE(3,2500)BDVSYR
02990      WRITE(3,2600)BDH
03000      WRITE(3,2625)
03010      WRITE(3,2650)DOX,ROX
03020      WRITE(3,2700)UDOX,UROX
03030      WRITE(3,2750)DAN,RAN
03040      WRITE(3,2800)DNAK,RNAK
03050C
```

HSC2

```
03060C *****
03070C ** OUTPUT INDIVIDUAL CONCENTRATIONS AND WCP(1) **
03080C *****
03090C
03100 WRITE(*,2900)
03110 READ(*,*)YORN
03120 IF (YORN.EQ.0) GOTO 1400
03130 DO 1300 I=1,NSAMP
03140 WRITE(3,3000)BOTN(I)
03150 WRITE(3,3020)DESC(I)
03160 WRITE(3,3100)CAVG(I)
03170 WRITE(3,3110)WCP(I)
03180 WRITE(3,3120)PERWCP(I)
03190 WRITE(3,3150)
03200 WRITE(3,3200)(CENV(I,J),GCNOTE(I,J),J=1,NINJ(I))
03210 1300 CONTINUE
03220 1400 CONTINUE
03230C
03240 1800 FORMAT(/)
03250 1900 FORMAT(A60)
03260 1910 FORMAT('HEAD [M] ',F12.4)
03270 1920 FORMAT('SPECQ [M^3/S/M] ',F12.4)
03280 1930 FORMAT('TOTALQ [M^3/S] ',F12.4)
03284 1934 FORMAT('NOVAK SPECQ [M^3/S/M] ',F11.4)
03290 1940 FORMAT('TAILWATER DEPTH [M] ',F11.3)
03294 1944 FORMAT('FALL HEIGHT ',F11.3)
03300 1950 FORMAT('WATER TEMPERATURE [^C]',F7.1)
03310 2000 FORMAT('/'UPS CONC [UG/L] ',F10.2)
03320 2020 FORMAT('DNS CONC [UG/L] ',F10.2)
03330 2100 FORMAT('TRANSFER #, D [-] ',F13.3)
03340 2120 FORMAT('TOTAL UNC IN D [-]',F13.3)
03350 2140 FORMAT('PERCENT UNC [-] ',F13.3)
03360 2200 FORMAT('PREC UNC IN D ',F15.5)
03370 2300 FORMAT('WD DUE TO CALIB. ',F15.5)
03380 2400 FORMAT('WD DUE TO FW ',F15.5)
03390 2500 FORMAT('BD DUE TO SYR VOL ',F15.5)
03400 2600 FORMAT('BD DUE TO H ',F15.5)
03410 2625 FORMAT('/'TRANSFER EFF., DEF RATIOS:, OXYGEN AT 20^C')
03420 2650 FORMAT('/MEASURED D ',F13.3,' R: ',F6.2)
03430 2700 FORMAT('TOTAL UNC IN D ',F13.3,' R: ',F6.2)
03440 2750 FORMAT('AVERY & NOVAK D ',F13.3,' R: ',F6.2)
03450 2800 FORMAT('NAKASONE D ',F13.3,' R: ',F6.2)
03460 2900 FORMAT('OUTPUT INDIVIDUAL CONCENTRATIONS? 1:Y, 0:N')
03470 3000 FORMAT('/SAMPLE NO ',I2)
03480 3020 FORMAT('DESCRIPTION ',A45)
03490 3100 FORMAT('AVG CONC [UG/L]',F7.2)
03500 3110 FORMAT('UNCERTAINTY ',F6.2)
03510 3120 FORMAT('PERCENT UNC ',F6.2)
03520 3150 FORMAT('INDIVIDUAL G.C. RUNS:')
03530 3200 FORMAT(3X,F6.2,8X,A45)
03540C
03550C
03560 END
```


HSC2

```
03570C *****
03580C ** FUNCTIONS **
03590C *****
03600     FUNCTION HENRY(T,R)
03610C
03620C HENRY'S CONST. HAS UNITS OF LITER*ATMOSPHERE/GRAM
03630C MOLE FRACTION (MFRAC) IS UNITLESS
03640C
03650     REAL MP,MWATER,MFRAC
03660     PARAMETER (MP=44.0616, MWATER=18.0152)
03670     PARAMETER (A=-628.866, B=31638.4, C=88.0808, RR=1.9872)
03680     MFRAC=EXP((A+B/T+C*LOG(T))/RR)
03690     CS=MFRAC*MP*R/MWATER
03700     HENRY=1/CS
03710     END
03720C
03730C
03740     FUNCTION RHO(T)
03750C
03760C RHO IS DENSITY IN G/L, GIVEN BY EQUATION FROM HENDERSON-SELLERS
03770C
03780     PARAMETER (AA=999.9726, BB=0.00009297173, CC=277.029325,
03790+         DD=1.894816)
03800     RHO=AA*(1-BB*(ABS(T-CC))**DD)
03810C RHO IS ACCURATE TO WITHIN 0.00035
03820     END
03830C
03840C
03850     FUNCTION RMHU(T)
03860C
03870C     RMHU IS DYNAMIC VISCOSITY IN POISE: E. C. BINGHAM
03880C     RMHU IS ACCURATE WITHIN .4 FROM 0 TO 30^C
03890C
03900     PARAMETER(AAA=.021482, BBB=8.435, CCC=16.87,
03910+         DDD=8149.5492, EEE=1.2)
03915     TM=T-273.15
03920     RMHU=0.01/(AAA*(TM-BBB+(TM**2.0-CCC*TM+DDD)**0.5)-EEE)
03930     END
```

APPENDIX B. DATA FROM NAKASONE (1987) AND PREDICTED EFFICIENCIES

The data which were used for the evaluation and development of the equations in Section V are reported herein. Most of the data given are from Nakasone [1987] and are indicated by the symbol "●" here and in Figs. V-3 through V-6. The remaining data is from this study and is indicated by a number 2 through 10. These numbers are also used as symbols in Figs. V-3 through V-6. The C_s values are taken from *Standard Methods* [American Public Health Association et al., 1980] and the efficiencies at 15 and 20°C are adjusted from the given temperature by Eq. II-8. The efficiencies computed by the evaluated equations are listed under the appropriate equation number.

Data Used for Evaluation of Predictive Equations

Symbols:

- : Data of Nakasone (1987)
- 2-10: Data of this study

T	Cs	Cu	Cd	q	h	H	E(T)	E(15)	E(20)	E(15)	E(20)	E(15)	E(20)
[C]	[mg/L]	[mg/L]	[mg/L]	[m ² /s]	[m]	[m]	meas	meas	meas	Eq. II-5	II-6	V-5	V-15
● 21.0	8.90	5.38	7.81	1.04	5.03	0.67	0.690	0.645	0.683	0.678	0.627	0.571	0.573
● 19.0	9.26	5.41	8.11	1.54	5.00	0.85	0.701	0.671	0.708	0.644	0.600	0.546	0.522
● 6.0	12.43	9.89	10.85	1.32	4.89	1.01	0.378	0.442	0.477	0.650	0.633	0.568	0.534
● 18.0	9.45	6.89	8.26	2.33	4.44	1.51	0.535	0.513	0.550	0.571	0.575	0.508	0.436
● 19.0	9.26	6.22	7.12	1.89	4.75	0.96	0.296	0.276	0.301	0.611	0.571	0.518	0.481
● 15.0	10.07	6.15	8.78	1.01	4.66	1.07	0.671	0.671	0.708	0.657	0.661	0.584	0.550
● 12.0	10.76	7.20	9.39	0.70	4.90	0.79	0.615	0.639	0.677	0.701	0.690	0.613	0.613
● 20.0	9.07	6.10	7.96	0.93	4.90	1.54	0.626	0.588	0.626	0.679	0.728	0.631	0.578
● 20.0	9.07	5.13	7.87	0.81	4.78	0.90	0.695	0.658	0.695	0.683	0.678	0.601	0.586
● 12.0	10.76	5.42	9.28	0.25	5.55	0.45	0.723	0.746	0.781	0.800	0.795	0.709	0.782
● 12.0	10.76	5.11	9.07	0.23	5.63	0.26	0.701	0.724	0.760	0.808	0.752	0.696	0.796
● 12.0	10.76	8.66	9.39	2.81	4.09	1.71	0.348	0.366	0.397	0.527	0.540	0.469	0.392
● 20.0	9.07	6.01	7.87	1.32	4.84	1.06	0.608	0.570	0.608	0.647	0.636	0.568	0.530
● 19.0	9.26	5.14	7.57	3.00	4.69	0.89	0.590	0.560	0.597	0.567	0.499	0.461	0.425
● 18.5	9.36	6.01	8.10	1.09	5.21	0.71	0.624	0.597	0.635	0.684	0.638	0.581	0.579
● 11.0	11.01	6.83	9.28	0.39	5.38	0.48	0.586	0.619	0.656	0.766	0.738	0.664	0.719
● 21.5	8.81	5.42	7.66	0.33	5.71	0.34	0.661	0.612	0.650	0.790	0.739	0.680	0.759
● 19.0	9.26	4.96	8.11	0.52	5.41	0.45	0.733	0.703	0.740	0.749	0.696	0.636	0.685
● 18.5	9.36	5.82	7.83	0.56	5.35	0.60	0.568	0.541	0.579	0.741	0.715	0.642	0.672
● 15.5	9.96	5.60	8.31	0.67	5.27	0.67	0.622	0.618	0.656	0.724	0.699	0.628	0.644
● 21.0	8.90	5.03	7.81	1.04	4.97	0.92	0.718	0.674	0.711	0.674	0.659	0.590	0.569
● 11.0	11.01	6.94	9.50	0.68	5.25	0.68	0.629	0.662	0.699	0.722	0.698	0.626	0.641
● 11.0	11.01	7.26	9.40	1.17	4.78	0.95	0.571	0.603	0.641	0.653	0.636	0.568	0.541
● 9.0	11.55	7.94	9.85	1.48	4.66	1.11	0.529	0.578	0.615	0.626	0.614	0.548	0.504
● 17.0	9.65	5.53	8.34	0.83	4.96	0.75	0.682	0.667	0.704	0.691	0.666	0.597	0.596
● 17.0	9.65	6.28	8.43	1.55	4.46	1.14	0.638	0.622	0.660	0.608	0.598	0.531	0.484
● 24.0	8.40	4.37	7.18	0.52	5.29	0.56	0.697	0.631	0.669	0.743	0.713	0.642	0.677
● 21.0	8.90	5.38	7.38	0.57	5.19	0.59	0.568	0.524	0.561	0.731	0.702	0.631	0.659
● 12.0	10.76	6.05	8.55	0.51	5.17	0.55	0.531	0.554	0.592	0.738	0.707	0.636	0.672
● 26.8	7.98	7.21	7.33	0.0114	0.54	0.25	0.156	0.126	0.138	0.349	0.106	0.269	0.428
● 28.1	7.80	6.58	6.81	0.7410	0.82	1.06	0.189	0.149	0.164	0.173	0.215	0.125	0.170
● 24.3	8.35	7.73	7.83	0.1330	0.86	0.34	0.161	0.136	0.149	0.293	0.286	0.211	0.294
● 31.2	7.38	8.15	7.72	0.0769	1.00	0.63	0.558	0.450	0.485	0.381	0.455	0.317	0.380
● 24.3	8.35	7.50	7.83	0.1450	1.98	0.41	0.388	0.335	0.364	0.551	0.555	0.442	0.504
● 25.7	8.19	7.10	7.17	0.0894	0.24	0.40	0.064	0.052	0.058	0.079	0.074	0.048	0.150
● 32.0	7.28	1.87	4.43	0.8400	1.53	0.15	0.473	0.371	0.402	0.315	0.224	0.173	0.263
● 9.0	11.55	8.84	9.06	7.83	1.52	7.48	0.081	0.092	0.102	0.689	0.314	0.619	0.131
● 13.0	10.52	6.22	6.63	6.01	1.73	6.90	0.095	0.099	0.110	0.595	0.362	0.561	0.159
2	2.8			0.0325	2.09	0.50	0.506	0.728	0.764	0.549	0.623	0.508	0.700
3	2.6			0.0321	1.52	1.08	0.313	0.501	0.537	0.627	0.612	0.563	0.601
4	2.5	Concentrations		0.0629	1.56	1.08	0.414	0.618	0.656	0.625	0.724	0.562	0.533
5	3.5	given in		0.0626	1.99	0.65	0.491	0.706	0.742	0.760	0.738	0.667	0.611
6	5.8	Appendix A,		0.0637	1.98	0.65	0.499	0.694	0.731	0.666	0.741	0.560	0.608
7	3.2	Cs=0		0.0147	2.29	0.28	0.530	0.748	0.783	0.649	0.463	0.625	0.806
8	4.0			0.0643	2.28	0.35	0.439	0.644	0.681	0.710	0.715	0.607	0.653
9	3.4			0.0145	1.50	1.07	0.259	0.420	0.453	0.170	0.485	0.125	0.684
10	5.3			0.0341	2.28	0.31	0.453	0.649	0.686	0.211	0.603	0.163	0.722

ERRATA

for

University of Minnesota
St. Anthony Falls Hydraulic Laboratory
Project Report No. 273

GAS TRANSFER AT WEIRS USING THE HYDROCARBON GAS TRACER METHOD WITH HEADSPACE ANALYSIS

by

John R. Thene

and

John S. Gulliver

May, 1989

SAFHL Project Report No. 273 has previously been published as a thesis under the same title by John R. Thene in partial fulfillment of the requirements of the degree of Master of Science in Civil Engineering from the University of Minnesota.

ERRATA

Equation I-3 (page 2) should read:

$$E = 1 - \frac{1}{r} = \frac{C_d - C_u}{C_s - C_u} \quad (\text{I-3})$$

Equation II-7 (page 8) is adjusted from 15°C as in Gameson et al. [1958] to 20°C and should read [Daniil and Gulliver, 1989]:

$$\ln r_T = \ln r_{20} [1 + 0.0165(T-20)] \quad (\text{II-7})$$

The density (ρ) relation on page 11 is incorrect, the correct relation is given in Eq. III-23 on page 40.

Omit last sentence on page 12. Replace with: Bales and Holley [1986] did not examine the constancy of R with temperature; Rainwater and Holley [1983] had already verified it. Bales and Holley [1986] determined that R was independent of mixing intensity.

In Eq. II-20 (page 18), R_m should be equal to 1.14

On pages 20 and 21 and in the references (page 93), Bales and Holley [1984] should read: Holley and Bales [1984].

Eq. III-13 (page 38) should read:

$$s^2 = \frac{1}{n_i-1} \sum_{j=1}^{n_i} (C_{i,j} - \bar{C}_i)^2 \quad (\text{III-13})$$

Equation III-14 gives the 95% confidence interval (which is used to determine if a value of $C_{i,j}$ is an outlier) correctly, but incorrectly calls it $W_{\bar{C}_i}$, which is the precision uncertainty in \bar{C}_i . $W_{\bar{C}_i}$ is given by:

$$W_{\bar{C}_i} = \frac{t(n_i-1) \sigma}{\sqrt{n_i}}$$

On page 41, $W_{M_{CAP}}$ should be 0.0751g and $W_{M_{SEPTA}}$ should be 0.0213g.

On page 43, Eq. III-31 should read:

$$W_{R_u T / M_p H}^2 = \left[\frac{\partial R_u T}{\partial M_p H} W_T \right]^2 = \left[\frac{R_u}{M_p H} \left[\frac{T}{H} \frac{\partial H}{\partial T} - 1 \right] \right]^2 W_T^2 \quad (\text{III-31})$$

And Eq. III-32 was derived for $R_v = 1.0$. The uncertainty of 1% in \bar{C}_i due to F_w should have been propagated through the C_u and C_d values such that Eq. III-33 would read:

$$W_{EF}^2 = \left[-\frac{C_d}{C_u^2} \frac{0.01}{\sqrt{n_u}} C_u \right]^2 + \left[\frac{1}{C_u} \frac{0.01}{\sqrt{n_d}} C_d \right]^2 \quad (\text{III-33})$$

If $n_u = 6$ and $n_d = 5$ as in this study, W_{EF} is given as:

$$W_{EF} = 0.006 \frac{C_d}{C_u}$$

Henry's Law constant for propane was determined using 25 points not 15 (page 43) and Eq. III-35 should read:

$$B_H = \frac{0.046 H t(25-1)}{\sqrt{25}} = 0.019 H \quad (\text{III-35})$$

and B_{CH} should be given by:

$$B_{CH} = C_{HS} \frac{R_u T}{M_p H} 0.019 \quad (\text{III-37})$$

On page 44, Eqs. III-38 and III-39 should read:

$$B_{EH}^2 = \left[\frac{\partial E}{\partial C_u} B_{C_u} + \frac{\partial E}{\partial C_d} B_{C_d} \right]^2 \quad (\text{III-38})$$

$$B_{EH}^2 = \left[\frac{C_d}{C_u^2} B_{C_u} - \frac{1}{C_u} B_{C_d} \right]^2 \quad (\text{III-39})$$

The correction of the above equations leads to a reduction in the uncertainties so that the total uncertainties in E , U_E , given in Tables IV-2 and IV-3 and in Appendix A are high and the uncertainties in the individual sample concentrations are actually the 95% confidence intervals or $\sqrt{n_i} W_{C_i}$. For this reason the corrected uncertainties in E are given in Table E-1 below.

Table E-1. Uncertainties in Propane Gas Transfer Measurements

Test	E	W_{EP}	W_{EF}	B_{EH}	U_E
W2	0.506	0.00422	0.00349	0.00001	0.0055
W3	0.313	0.00360	0.00397	0.00001	0.0054
W4	0.404	0.00474	0.00344	0.00001	0.0059
W5	0.491	0.00241	0.00294	0.00002	0.0038
W6	0.499	0.00311	0.00303	0.00000	0.0043
W7	0.530	0.00269	0.00285	0.00005	0.0039
W8	0.439	0.00313	0.00340	0.00001	0.0046
W9	0.259	0.00395	0.00449	0.00002	0.0060
W10	0.453	0.00381	0.00331	0.00003	0.0050

Figs. V-1, V-3, V-4 are given at 15°C, others in Section V are at 20°C.

Reference

Daniil, E. and J. S. Gulliver, 1989. "Temperature dependence of liquid film coefficient for gas transfer," Journal of Environmental Engineering, ASCE, Vol. 114, No. 5, pp. 1224-1229.

