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**Preliminary Investigation of Tracer Gas Reaeration
Method for Shallow Bays**

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**PRELIMINARY INVESTIGATION OF TRACER GAS
REGENERATION METHOD FOR SHALLOW BAYS**

by

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Edward R. Holley

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ABSTRACT

Accurate estimates of surface exchange rates for volatile pollutants in bays are needed to allow predictions of pollutant movement and retention time. The same types of estimates can be used to calculate reaeration rates. The tracer gas technique has been used to measure surface gas transfer rates in rivers, and to a lesser extent, in estuaries. Application of the technique to bays would be extremely useful, but it is complicated by differences in the hydrodynamics and the density stratification that can exist due to fresh river water overriding heavier saline ocean water. The objective of this research has been to investigate field procedures for application of the tracer gas technique to shallow bays.

The modified tracer technique was used with propane for the tracer gas and Rhodamine-WT, a fluorescent dye, for the "conservative" tracer. The propane was injected through porous tile diffusers, and the dye was released simultaneously. The propane acts as a model for the surface exchange of other gases and volatile compounds.

Three four-day field trips to Lavaca Bay on the Texas coast of the Gulf of Mexico were made during the course of the study. A variety of experimental techniques was investigated. One was to make a short-duration injection (10-30 minutes) and sample the dye cloud as it moved through the bay. Another was to use a long-duration injection (3 to 4 hours) to obtain quasi-steady conditions. The long injections were discontinued because there appeared to be no practical method of determining the travel time for the samples taken from the tracer plume. Drogues (floats) which are normally used for this purpose consistently drifted downwind from the tracer plumes. Pulses of a second fluorescent dye for determining time of travel became too diffuse to be used for this purpose. The most promising method appears to be the short-duration injection method with a large pulse of the second dye released during the injection to mark the middle of the tracer cloud. A special injection device was designed to prevent mixing of the tracers with heavier saline water near the bed of the bay during injection.

A field fluorometer was used both in the field to track the tracer cloud and in the laboratory to measure dye concentrations in the field samples. Propane concentrations were determined with gas chromatography. The same equipment was used to perform laboratory studies to test performance of the equipment in the field and to aid in understanding field test results.

These were apparently the first tests to be performed using the tracer gas technique in bays. As a result, the emphasis was on the development of techniques rather than on obtaining data. It appears that workable techniques have been developed, but they now need to be tested under a variety of conditions. Also, the preliminary results which were obtained for gas transfer coefficients indicate some anomalous results. After the completion of the project, it was learned that the addition of formalin to the field tracer gas samples may be affecting the samples adversely. Thus, some laboratory tests are now needed to investigate the behavior of tracer gases in bay water. In summary, the method appears to be very promising, but some additional developmental work is required before it can be used on a routine basis.

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CHAPTER 1 INTRODUCTION

1.1 Background

Dissolved oxygen has continued to be an important measure of water quality since the work of Streeter and Phelps (1925), yet surface reaeration, a major source of dissolved oxygen, is difficult to predict. When an oxygen balance is performed on a water body, the reaeration rate is determined from the residual term in which inaccuracies in measurements accrue. In order to avoid this problem, the tracer gas method was developed to directly measure surface gas transfer rates in field studies.

Tracer gas studies have been applied widely to rivers and, to a much lesser extent, estuaries. Although reaeration rates are not as often needed for typically oxygen-rich bays as they are for rivers, tracer gas studies are needed for bays to find surface gas transfer rates for volatile compounds such as benzene, chloroform, methylene chloride, and toluene (Rathbun and Tai, 1981). Even higher molecular weight compounds, including DDT, have been shown to volatilize at appreciable rates (Acree et al., 1963).

1.2 Objectives

The purpose of this project was to investigate field methods for the application of tracer gas studies to shallow bays. It would have been premature to try to actually measure surface transfer rates. Rather, the need was to investigate ways to obtain consistent results from the field tests. In order to better understand the evolution of the field methods over the course of this study, a brief review of the theory and application of the tracer gas method is presented, followed by a description of the laboratory methods employed to test field samples and then the results from laboratory tests performed to aid in data analysis. The field studies are then described, and the data presented and discussed.

CHAPTER 2 LITERATURE REVIEW

2.1 Tracer Gas Concept

Adeney and Becker (1919) were the first to show that reaeration is a first-order process that can be described in a vertically mixed system by

$$\frac{dC}{dt} = K_2 (C_s - C) \quad (2.1)$$

where C_s = saturation concentration of dissolved oxygen at a given temperature and partial pressure, C = dissolved oxygen concentration at a given temperature, and K_2 = reaeration rate coefficient.

The tracer gas method for determining K_2 was developed by Tsivoglou et al. (1965,1968) and involves dissolving a gas tracer in a water body, measuring the rate of the gas desorption, and relating the tracer gas surface transfer coefficient to the gas of interest. Due to the fact that $C_s = 0$ for the tracer, this rate can be expressed for a mixing tank with only surface transfer as

$$\frac{dC_T}{dt} = -K_T C_T \quad (2.2)$$

where sub-T denotes tracer and K_T = the gas tracer desorption coefficient. Solution of Eq. 2.2 for constant K_T yields the expression

$$\frac{C_T}{(C_T)_0} = \exp (-K_T t) \quad (2.3)$$

where $(C_T)_0 = C_T$ at $t = 0$.

To account for the reduction of the gas tracer concentration in a natural water body due to mixing and dilution, a conservative tracer must be released at the same time as the gas. The change in the gas concentration due to desorption will be proportional to the change in the ratio of the two tracers. For a vertically well-mixed water body, Eq. 2.3 then becomes

$$\frac{\left(C_T/C_C \right)_2}{\left(C_T/C_C \right)_1} = \exp [-K_T (t_2 - t_1)] \quad (2.4)$$

where the subscript C denotes the conservative tracer (Tsivoglou et al., 1965; Holley and Yotsukura, 1984). With this equation, K_T can be determined from field tests and then related to K_2 using laboratory mixing tank tests that result in a ratio (R_T) described as

$$R_T = \frac{K_2}{K_T} \quad (2.5)$$

In order to measure surface transfer with the tracer gas method, the gas tracer should not occur naturally in the water body, should have no sources or sinks other than surface desorption, and should be measurable to the microgram per liter range. Furthermore, the gas should have a transfer coefficient that is approximately equal to K_2 and a constant R_T value for all temperatures, hydraulic conditions, and water quality conditions (Holley and Yotsukura, 1984).

2.2 Tracers

Tsivoglou et al. (1968) proposed using krypton-85 as the gas tracer and tritium as the conservative tracer. Krypton is an attractive tracer because it is a noble gas and therefore chemically inert, but licensing and training requirements for handling radioactive materials prompted Rathbun et al. (1975) to develop a modified tracer method. In the modified method, hydrocarbon gas is used instead of krypton, and Rhodamine-WT dye takes the place of tritium as the conservative tracer. In the past, both propane and ethylene have served as gas tracers, but the use of ethylene has been discontinued.

The suitability of hydrocarbon gases as tracers is still under investigation. Rathbun et al. (1978) confirmed that the transfer coefficient ratios of ethylene and propane, R_E and R_P , are constant. Independent laboratory studies by Rainwater and Holley (1983) and Bales and Holley (1986) found ratios which agreed with those of Rathbun et al. (1978). In tests of five different suspended sediments, Rainwater and Holley (1983) also found no adsorption of the hydrocarbon gases onto sediments. However, biological and chemical degradation of the hydrocarbons in natural waters has not been thoroughly tested. Rathbun et al. (1975, 1978) have suggested that the effect of biodegradation is negligible for field tests of duration less than 10 hours, but further investigation of this problem is needed.

A significant possible source of error in the modified tracer technique stems from the fact that Rhodamine-WT is not truly conservative. Tai and Rathbun (1988) reported photolysis rates ranging from $0.000048 \text{ min}^{-1}$ for distilled water to 0.00020 min^{-1} for river water with 46 mg/L of total organic carbon and a pH of 4.8. They found that the photolysis rates increased as the total organic carbon content increased

and as the pH decreased. They also referred to the fact that photolysis rates in laboratory containers may be larger than with a horizontal water surface. Some degree of photochemical decay and adsorption to sediments has also been reported (Smart and Laidlaw, 1977). For tracer tests in rivers, dye concentration-versus-time curves and flow measurements from the upstream and downstream ends of the test reach can be used to estimate dye loss from a mass balance (Rathbun et al., 1975). Dye losses between 5 and 20 percent have generally been reported for tests lasting up to 8 hours (Yotsukura et al., 1983; Rathbun, 1979; Kilpatrick et al., 1967). The corresponding decay rates would be 0.00011 min^{-1} to 0.00046 min^{-1} . Tests have shown varying degrees of reduction of Rhodamine-WT fluorescence in the presence of salts with no explanation for the significant differences in reduction rates reported in different tests (Smart and Laidlaw, 1977).

When analyzing data from the modified tracer method, Eq. 2.4 becomes

$$\frac{\left(C_P/C_R \right)_2}{\left(C_P/C_R \right)_1} = \exp [-(K_P - K_R)(t_2 - t_1)] \quad (2.6)$$

where C_P = propane concentration, C_R = Rhodamine-WT concentration, K_P = propane desorption coefficient, and K_R = Rhodamine-WT decay coefficient (Rathbun et al., 1975), assuming a first-order decay for the Rhodamine.

2.3 Injection and Sampling

Prior to this study, tracer gas techniques had been used primarily for rivers. In rivers, the injection procedures depend on the test type and tracers used. For the radioactive tracer technique, the tracers are frequently dissolved together in a glass container that is broken under water to produce an instantaneous point source release (Tsivoglou et al., 1965). In the modified technique, instantaneous releases normally cannot be obtained, but both short-duration (Rathbun et al., 1975; 1978) and long-duration injections (Yotsukura et al., 1983; 1984) have been used. The short injections give a cloud moving downstream while the objective of the long injections is to obtain steady-state conditions at the measurement stations. Injection is performed by bubbling bottled gas through diffusers that are placed on the river or stream bed. It is estimated that 5 to 20 percent of the injected gas goes into solution (Rathbun, 1979). Because of the low solubility of hydrocarbon gas, the gas tracer must be injected over a period of time sufficient to produce detectable concentrations at the end of the test reach. For river studies, the injection times have varied from 20 minutes to several hours (Holley and Yotsukura, 1984).

In both the original and modified tracer methods, Rhodamine-WT dye is used as a field indicator. The dye is visible at fairly low concentrations and is detectable below $1 \mu\text{g L}^{-1}$ with a field fluorometer. Tracer gas concentrations, however, must be determined in the laboratory, so samples are taken at locations downstream of the injection point. Rathbun and Grant (1978) suggest a displacement-type sampler that flushes the sampling bottle several times before filling it, and they recommend the addition of formalin to the hydrocarbon samples to stop biodegradation. It was found during the course of this study that formalin must not be added to dye samples that are tested in the laboratory for precise concentrations because formalin fluoresces within the same wavelength range as Rhodamine-WT. (See Postscript, Section 5.3.)

2.4 Applications

The modified tracer method has been used on a variety of streams and rivers. Kilpatrick et al. (1987) presented many aspects, both basic and practical, for such applications. When using short-duration injections, the conservative tracer is injected in such a way as to duplicate the gas injection as closely as possible (Rathbun et al., 1975). In rivers, it is necessary to sample the entire Rhodamine-WT cloud as it passes to determine the loss of Rhodamine, but tracer gas samples may be taken only near the peak of the dye cloud. The tracer concentrations are used in Eq. 2.4 to find K_T . Before the equation can be applied, however, a mass balance is performed on the dye. Rhodamine-WT is not truly conservative (Rathbun et al., 1975) and the loss must be taken into account (cf. Eq. 2.6).

In some riverine applications, a long-duration injection is preferred in order to achieve steady-state concentrations at the sampling stations. When hydraulics and gas transfer are expected to be steady during testing, dye injection during the entire gas injection is not necessary; an instantaneous dye release is made at the beginning of a longer gas injection. The tail of the passing dye cloud is used to indicate when the gas concentration will be at steady state at the sampling locations (Yotsukura et al. 1983, 1984). In one-dimensional situations, K_T can be determined directly from the gas concentrations with the equation

$$(C_T Q)_2 = (C_T Q)_1 \exp [-K_T (\bar{t}_2 - \bar{t}_1)] \quad (2.7)$$

where Q is the river flow rate (Yotsukura et al., 1983), which can be determined by stream gaging during the test. The Rhodamine-WT is used for time-of-travel to obtain $(\bar{t}_1 - \bar{t}_2)$.

If transverse uniformity is not present (a two-dimensional situation) the same injection method can be applied, but more data and a modified analysis are required (Yotsukura et al. 1984). Using a streamline coordinate system with transverse coordinate q and longitudinal coordinate x , a mass distribution factor is defined as

$$R(x,q) = \frac{Q}{M_C} \int_0^{\infty} C_C(x,q,t) dt \quad (2.8)$$

where M_C is the mass of dye released (Yotsukura et al., 1984). For a given streamline, then,

$$\left(\frac{C_T Q}{R} \right)_2 = \left(\frac{C_T Q}{R} \right)_1 \exp [-K_T (\bar{t}_2 - \bar{t}_1)] \quad (2.9)$$

where C_T is found for the streamline q (Yotsukura et al., 1984).

One of the main assumptions made in the application of the tracer gas method in rivers is that the tracers are uniformly distributed vertically. In most rivers and streams this is a valid assumption. However, in water bodies where vertical density gradients are found, vertical tracer mixing normally is inhibited. A successful determination of gas desorption rates using the tracer gas method in an estuary has not yet been completed (Bales and Holley, 1987). The tracer gas method of reaeration coefficient determination has not previously been applied to bays.

CHAPTER 3

LABORATORY TECHNIQUES AND TESTING

Field samples taken during tracer gas studies were analyzed for propane and Rhodamine-WT concentrations in the laboratory. One mL of formalin was added to each 40 mL sample bottle for gas analysis (not the Rhodamine samples). The sample bottles were capped with Teflon-coated septa to assure complete sealing and to prevent adsorption of the gas onto the septa. Once filled, the sample bottles were kept on ice in closed containers to minimize possible biological and photochemical degradation of the tracers. The samples were analyzed as soon as possible upon return from the field, typically within five to seven days. It perhaps was not necessary to use both formalin and storage on ice, but both were used to try to be certain of the absence of biological degradation. Also, there was no significant problem with bubble formation in the bottles due to cooling them. (See also Sections 3.2 and 5.3.)

Several laboratory experiments were performed during the course of this study to check for possible tracer adsorption on the flow tubing used in the field and to enhance the understanding of tracer degradation in the field. Laboratory samples were analyzed for gas and dye concentrations in the same manner as the field samples. A description of the laboratory techniques used for sample analysis will be given in this section, followed by a presentation of the results from the laboratory experiments.

3.1 Hydrocarbon Sample Analysis

The amount of propane in field and laboratory test samples was determined with a gas chromatograph (GC). The dissolved gas was stripped from the samples using a purge-and-trap system developed by Swinnerton and Linnenbom (1967) and modified by Shultz et al. (1976). A detailed description of the gas stripping apparatus, with modifications suggested in personal communications with Rathbun and Vaupotic of the U.S. Geological Survey, is presented by Rainwater and Holley (1983). A brief summary of the apparatus and procedure, including changes introduced during this study, will be given here.

3.1.1 Equipment. A schematic diagram of the gas analysis equipment is shown in Figure 3.1. Samples were injected into a Pyrex stripping chamber with a 10 mL gas-tight syringe. Helium was the stripping gas. Flowing at a rate of 18 mL/min. and at a pressure of 50 psi, the helium first passed through a molecular sieve to remove impurities and then bubbled through the water sample in the stripping chamber to remove the dissolved propane from the samples. After 12 minutes of stripping, the water was drained from the chamber.

From the stripping chamber, the helium flow was directed through a Pyrex tube packed with anhydrous calcium sulfate, or Drierite, to remove water vapor that could contaminate the GC column. As

necessary between tests, the Drierite column with helium flowing through it was placed in an oven with the temperature over 100°C until all water was removed from the Drierite.

After passing through the Drierite, the stripping gas flow was directed through a 10-port valve into one of two adsorption/desorption traps made from stainless steel tubing packed with activated alumina. The alumina had been conditioned beforehand by heating the traps to 180°C and allowing the stripping gas to flow for 20 to 30 minutes to remove impurities that might interfere with the GC response. The traps were connected to the 10-port valve with Teflon tubing to allow trap movement.

A cold bath of liquid nitrogen caused the propane to adsorb on the activated alumina as the stripping gas passed through the trap. To remove the adsorbed hydrocarbon after the 12 minutes of stripping and trapping, the trap was placed in a hot water bath kept at a temperature of 85 to 90°C. A carrier gas, again helium, carried the vaporized propane from the trap to the GC column. The carrier gas flowed at a rate of 30 mL/min and a pressure of 50 psi.

The GC used in this study was an HP 5750 with a flame ionization detector. The detector flame burned a mixture of air and chromatographic hydrogen flowing at 300 mL/min and 21 psi, and at 30 mL/min and 16 psig, respectively. The temperature of the detector was set at 320°C and the injection port at 180°C to insure against water vapor condensation in the GC column.

A 6 ft. by 1/8 inch stainless steel column packed with Porapak N, 60/80 mesh served as the GC column. The column oven temperature was held at 80°C for five minutes, during which the propane peak on the GC detector occurred. The oven temperature was then raised automatically at a rate of 50°C/min to 175°C and held there for 4 minutes to flush hydrocarbons with higher boiling points than propane from the column. The GC detector response was typically set at an attenuation of 16 and range of 10 to handle hydrocarbon concentrations in the field samples that were usually on the order of 30 µg/L. Increasing oven temperatures were not used in previous studies.

The GC detector output was connected to an integrating strip chart recorder. As a response from the detector was being registered by one pen, an integrating circuit determined the area under the response curve. The area was represented by a second pen in "counts." The area (A) was defined as

$$A = (\text{Counts} \times \text{Chart Width} \times \text{Chart Paper Speed}) / \text{Count Rate} \quad (3.1)$$

The count rate is a machine setting; the count rate used in this study was 6000 counts/minute. As stated by Shultz et al. (1976), the concentration of the hydrocarbon in the sample (C_H) could then be calculated as

$$C_H = \frac{AS_w}{V_s} \quad (3.2)$$

where S_w is the detector response for that hydrocarbon and V_s is the volume of the sample injected. Because the detector response, sample volume, chart width and rate, and count rate were all constant for each set of samples, the gas concentration was directly proportional to the integrating pen counts. For this study, only the tracer concentrations relative to other samples were needed, so the values used for propane concentrations were the count numbers.

The general functioning and linearity of the GC had to be checked regularly. To do this, propane was bubbled through distilled water to produce a solution that was assigned an arbitrary concentration. The solution was diluted to form six standards of different concentrations. The standards were siphoned into 40 mL sample bottles with 1 mL of formalin added to each bottle to prevent biodegradation and to simulate field procedures, and the bottles were stored in a dark room at 4°C. (See Section 5.3.) The linearity of the GC was checked by analyzing 10 mL of each standard in each trap. If the machine functioned properly, a graph of the integral count versus the assigned standard concentration produced a straight line. The GC response was checked with the standards before, during, and after each day's batch of field or laboratory samples was analyzed.

3.1.2 Gas bubbles in sample bottles. Small air bubbles were trapped or subsequently formed in a very small fraction of the field samples. The air bubbles allowed a portion of the tracer gas in the sample to come out of solution. To correct for this, it was assumed that the gas in the bubble and in solution were in equilibrium. The correction, presented by Rainwater and Holley (1983), combined Henry's and Dalton's Laws resulting in the equation

$$\frac{\Delta C}{C} = \frac{\hat{a}M}{R_g T} \frac{V_b}{V_s} \quad (3.3)$$

where C = mass concentration of gas, ΔC = concentration change due to the bubble, \hat{a} = Henry's Law coefficient, M = molecular weight of gas, R_g = universal gas constant, T = absolute temperature, V_b = bubble volume, and V_s = sample bottle volume. The concentration (C_m) of propane measured with the GC was corrected with the equation

$$C_p = C_m + \Delta C \quad (3.4)$$

where C_p = corrected propane concentration. The bubble size was estimated by turning the sample bottle so that the bubble was on the side of the bottle, measuring the diameter of the bubble on the glass, and then assuming the bubble to be half of a sphere. Samples with bubbles were noted, and the concentrations were corrected according to Eq. 3.3. No consistent deviations were detected between the corrected concentrations and the concentrations from samples with no bubbles.

3.2 Rhodamine-WT Sample Analysis

3.2.1 Equipment. Field and laboratory samples were tested for Rhodamine-WT concentrations using a Turner Design Model 10-005R fluorometer with a standard cuvette testing system. The fluorometer had 8 scales ranging from 0 to 3 ppb to 0 to 10,000 ppb and could be read to 0.05 ppb on the most sensitive scale. Standards made with distilled water and Rhodamine-WT were used to calibrate the fluorometer and construct calibration curves as suggested by Wilson et al. (1986). Prior to the third field test, a data acquisition system was added to the laboratory equipment. Use of this system increased the speed and accuracy of sample analysis.

Dunn and Vaupel (1965) noted, for an earlier model fluorometer, a gradual increase in fluorometer efficiency as the machine warmed up. A test conducted on the Model 10 fluorometer used in this study for 3 hours with 8 samples showed a definite decrease in apparent fluorescence with time after the fluorometer was switched on. This decrease was due to fluorometer, and not sample, heating; the test was conducted with the samples maintained at a constant temperature and then put into the fluorometer immediately before each reading. The results of the test, seen in Figure 3.2, suggested a warm-up time of approximately 3 hours was necessary for consistent readings from the fluorometer used in this study. This type of behavior was observed consistently for this fluorometer. However, the experience of the authors and other investigators has been that Model 10 fluorometers normally have negligibly short warm-up times.

3.2.2 Sample handling. As stated previously (Chapter 3), field samples were kept on ice in the dark in order to slow possible biological and photochemical degradation. In the laboratory the samples were allowed to warm to room temperature immediately before testing. Each sample was tested in a cuvette that had been rinsed thoroughly with tap water. As suggested by Wilson et al. (1986), the cuvette remained in the fluorometer until the dial reading stabilized (approximately 10 seconds) but not long enough for the sample to heat.

Smart and Laidlaw (1977) noted that fluorescence intensity varies inversely with sample temperature and presented a correction formula

$$F = F_0 \exp(nT) \quad (3.5)$$

where F = fluorescence reading at temperature T , T = temperature in $^{\circ}\text{C}$, F_0 = fluorescence at 0°C , and n = temperature coefficient for a given dye. Since the fluorometer was calibrated with standards at room temperature, readings were corrected to 23.3°C (the average laboratory temperature) using

$$F_{23.3} = F \exp [n(23.3 - T)] \quad (3.6)$$

where $F_{23.3}$ = fluorescence at 23.3°C. Smart and Laidlaw (1977) reported a temperature coefficient of $n = -0.027^{\circ}\text{C}^{-1}$ for Rhodamine-WT, but a test run during this study resulted in the use of $n = -0.032^{\circ}\text{C}^{-1}$. The results of this test are shown in Figure 3.3 as a semi-logarithmic graph of F_1/F_2 versus temperature difference ($T_1 - T_2$) in °C.

The field sample readings were also corrected for background fluorescence. During the field tests, background samples were taken daily, but the amount of variation in background readings suggests that samples should be taken more often. Because the fluorometer was calibrated with distilled water and laboratory test samples were prepared with distilled water, the background reading for the laboratory samples was zero.

3.3 Laboratory Testing

3.3.1 Brake hose adsorption. Tests reported by Ward (personal communication) concluded that air brake hose provided the best material for flow tubing for Rhodamine-WT in field systems due to low adsorption. The tests found that standard garden hose had a tendency to adsorb Rhodamine-WT and release it at a later time. Air brake hose was reported not to exhibit this tendency. It was decided during this study to test the air brake hose for propane adsorption and to retest the hose with dye. Parker-Hannifin Corp. air brake hose (SAE J844, Type 3B) with a 3/4 in. outside diameter and 9/16 in. inside diameter was tested.

The same type of solution from which GC standards were made was used in the propane adsorption test. A sample of the solution was mixed into a 100-gallon stainless steel tank. The intake line from the field monitoring system was attached to a bulkhead connector on the bottom front of the tank. The field system consisted of 20 feet of air brake hose used as the intake line attached to a flow-through setup on the fluorometer with 5 more feet of hose providing an outflow line; the same amount of hose and the same flow rate as in the field were used. When the connector on the tank was opened, samples were taken first from inside the tank just upstream of the connector, and then, within a few seconds, from the fluorometer outflow line. Seven sets of samples were taken, each set about 3 minutes apart. The results, shown in Table 3.1, suggest that the brake hose does not adsorb propane, at least for the exposure times typical of these testing procedures. For comparison with the results in Table 3.1, the amount of variation in measurements for replicate propane samples is typically 2% to 5%.

To test for Rhodamine-WT adsorption, a 1 ft. length of hose was used. A sample-bottle septum with a small hole drilled in the center of it was attached to one end of the hose. The hose was then attached, capped end down, to a stand. A batch of Rhodamine-WT diluted with distilled water was divided into two cuvettes: one for a standard and the other for testing. One run of the test consisted of pouring the sample into the hose and letting it drain into a third cuvette. The sample filled approximately 10 inches of the hose

and took about 1 minute to drain. For each run, the standard was also poured into another cuvette to account for dilution that occurs when the dye solution is poured into a cuvette that has been rinsed. Ten runs were made with the same sample and standard. Figure 3.4 shows the percentage of initial concentration graphed against the run number. The results indicate that there might be a small amount of initial adsorption and later release. The amount of adsorption, however, is extremely small. In the field the exposure time of the Rhodamine-WT to the brake hose is much less than in the laboratory tests, and the time allowed for the field fluorometer to stabilize should also be enough time to flush the flow line and stabilize any adsorption/desorption for the sampling site. The amount of adsorption suggested by this experiment is well within the limits of field test accuracy.

3.3.2 Salinity effect. Because Lavaca Bay is brackish, it was necessary to test propane for possible decay due to salinity. Instant Ocean with the trace elements added was used to produce three batches of tap water with salinities of 10, 20, and 30 ppt. In the manner described in Section 3.1.1 for producing standards for the GC, propane was dissolved in the mixtures, eight samples of each batch were taken, and formalin was added to the samples. (See Section 5.3.) A standard batch was also sampled. The samples were tested on the GC over a period of 20 days. The results of the tests are shown in Figure 3.5 as a semilog graph of the propane concentration versus time in days. No decay due to salinity was indicated by this experiment. The greatest amount of decay was seen in the standard sample, suggesting that a saline solution might actually inhibit propane concentration decay compared to fresh water. In any event, all samples from a given field test were analyzed within an elapsed time of no more than 24 hours, so any differential change due to salinity should be negligible.

Rhodamine-WT was also tested for decay due to salinity. Samples were made by dissolving Instant Ocean with trace elements in tap water, pouring the saline solution into cuvettes, adding Rhodamine-WT, and then covering the cuvettes with Parafilm test tube covering. Between tests on the fluorometer, the samples were stored in a dark cabinet. Salinities of 0, 8, 19.2, and 27.2 ppt respectively were contained in samples 1-4, and dye concentrations were on the order of 250 ppb. Samples 5-8, with the same salinities as samples 1-4, had dye concentrations of approximately 25 ppb. Results from the experiment are shown in Figures 3.6 and 3.7. A suppression of fluorescence with increasing salinity, as described by Smart and Laidlaw (1977), can be seen, but decay of fluorescence with time is not indicated.

3.3.3 Bay water effect. The fact that Rhodamine-WT is not conservative in field experiments is well documented (Smart and Laidlaw, 1977). In order to find gas transfer rates from the field data, a decay rate for the dye in Lavaca Bay had to be determined. Three gallons of bay water were collected on the third field trip for use in laboratory tests.

To test for decay in bay water, Rhodamine-WT was used to make four sample batches: two in bay water with concentrations on the order of 600 and 100 ppb, and two in distilled water with concentrations of

approximately 600 and 55 ppb. Three samples of each batch were poured into cuvettes and covered with Parafilm. In order to simulate field conditions, the cuvettes were placed in a constant temperature water bath in sunlight. Concentrations of the samples were tested on a fluorometer at regular intervals for more than 4 hours. An extra cuvette, containing bay water and placed in the bath with the samples, was used for temperature measurement each time the samples were tested. The results of the test are shown in Figures 3.8 and 3.9. The original readings of concentrations were believed to be lowered by sediment that had not yet settled and were excluded when calculating decay rates.

The slopes of the lines in Figures 3.8 and 3.9 were calculated to be used as decay rate coefficients (K_R) in the equation

$$C_{RM} = C_{RC} \exp(-K_R t) \quad (3.7)$$

where C_{RM} is the measured Rhodamine-WT concentration at time t and C_{RC} is the concentration that would exist if decay did not occur. Using linear regression, the coefficient calculated for dye decay in bay water in sunlight was $K_R = 0.00017 \text{ min}^{-1}$ from Figure 3.8 and $K_R = 0.00024 \text{ min}^{-1}$ from Figure 3.9. The decay coefficient for the dye in distilled water was $K_R = 0.00011 \text{ min}^{-1}$ from Figure 3.8 and $K_R = 0.00022 \text{ min}^{-1}$ from Figure 3.9. Using the correlation coefficient (R) for the lines from each graph to find a weighted average, the decay coefficient determined for bay water was $K_R = 0.00021 \text{ min}^{-1}$ and for distilled water was $K_R = 0.00017 \text{ min}^{-1}$, indicating that salinity or some other characteristics of the bay water may cause the decay to be somewhat greater than would exist for distilled water. These rates are compatible with those from the literature in Section 2.2.

The decay factor for bay water calculated in this test was applied to the field data that is presented in Chapter 4, unless otherwise stated.

3.3.4 Decay of Fluorescein. Fluorescein, a fluorescent dye detected in the green wavelength region, was used on the third field trip. A high rate of photochemical decay has been reported for Fluorescein (Smart and Laidlaw, 1977). Although Fluorescein was not used for quantitative measurements in this study, an approximate decay rate was desired to help predict the amount of dye to be used in the field.

Fluorescein, purchased as a powder, was dissolved in six samples of distilled water and placed in cuvettes that were covered with Parafilm. The concentrations, initially ranging from 160 to 260 ppb, were measured with a fluorometer with the appropriate filters as described by Turner Designs.

For the test, two samples were put in sunlight, two were placed in a dark cabinet, and two were kept under the fluorescent laboratory lights. Concentrations were measured periodically for more than 3 hours. The results are shown in Figure 3.10. As described by Smart and Laidlaw (1977), photochemical decay can be described as

$$C = C_0 \exp (-K_f t) \quad (3.8)$$

where C is the concentration at time t , C_0 is the initial concentration, and K_f is the decay coefficient for Fluorescein. Although the trend of the data in Figure 3.10 is curved so that Eq. 3.8 is not applicable for these data, only approximate results were needed, so Eq. 3.8 was assumed to be applicable. Using linear regression and averaging the two results for each case, the decay coefficients found were $K_f = 0.0102 \text{ min}^{-1}$ in sunlight, $K_f = 0.00026 \text{ min}^{-1}$ in darkness, and $K_f = 0.00033 \text{ min}^{-1}$ in fluorescent light.

CHAPTER 4

FIELD TECHNIQUES AND TESTING

The field techniques used in this study were developed from techniques applied to tracer gas studies in rivers. Changes in the techniques and choice of equipment evolved through trial and error and were due mainly to the differences between the river and bay environments.

Three field trips were conducted during this study, each four days long. The same field site and basic equipment were used throughout the study. Descriptions of the site and equipment will be given in this section, along with an explanation of the form in which the data are presented. Accounts of the field trips are then given. Modifications of, and additions to, the injection equipment and sampling procedures are identified in the descriptions of the field tests for which they were made. Within each field trip account, injection and sampling methods and problems encountered in the field will be described, and the resulting data presented.

4.1 Research Plan

4.1.1 Study site. When choosing the bay on the Texas coast for field tests, several factors were considered. The bay had to be large enough to offer more than one test site so that any residual concentrations from a test performed one day would not interfere with a test on the next day. It was necessary for fresh water inflow to be low and the bay to be shallow so that vertically uniform water density could be expected. Also, the amount of recreational and commercial vessel traffic in the bay had to be small; boats passing through a dye cloud shortly after injection tend to disrupt the test (Ward, 1985).

Lavaca Bay was chosen as the test site because it met the aforementioned criteria. The bay was also believed to have fewer hazardous objects, such as piles hidden below the water surface, than some of the nearby bays (Ward, personal communication). Lavaca Bay, shown in Figures 4.1 and 4.2, is the largest secondary bay in the Matagorda Bay system (Armstrong and Yamada, 1982). The bay has an average depth of approximately 1.5 meters. Most of the tests were conducted in the vicinity of the causeway, which is about 2.2 mi. long and runs across the upper part of the bay from Port Lavaca to Point Comfort. The causeway is supported on piers throughout its length so that it causes essentially no interference with the natural circulation. An additional advantage to choosing Lavaca Bay was the existence of a public boat ramp in Port Lavaca that provided almost immediate access from the study area to nearby motels and restaurants.

4.1.2 Injection equipment. For this study, the modified tracer method using propane and Rhodamine-WT dye was chosen as a matter of convenience; both propane and Rhodamine-WT are relatively inexpensive, and commercial grade propane is easily purchased in the field.

Commercial-grade propane, used as the gas tracer, was injected from 40-lb. and 30-lb. bottles controlled by a dual-gauge regulator. The regulator measured the pressure both in the bottle and on the diffuser line in psi. The propane was bubbled through two Wifley-Weber porous tile diffuser strips, each 24 inches long and 2.5 inches wide with an average pore size of 15 microns. A stand approximately 10 inches high and 5 feet long, on which the diffusers were initially mounted, was designed to rest on the bay floor and allow water entrainment from below the diffusers while limiting sediment disturbance. The stand was made of wood and weighted on the bottom with steel angle to keep it on the bed and to keep it upright.

Rhodamine WT fluorescent dye, the "conservative" tracer, was purchased as a 20% solution with a specific gravity of approximately 1.2. The dye was mixed in the laboratory with an equal volume of methanol (specific gravity = 0.8) to promote neutral buoyancy, and the mixture was diluted in the field with surface bay water before the injection. Unless otherwise stated, the volume of dye reported for each injection is the volume of the original 20% solution released. The dye was injected with a positive displacement metering pump that could be set to discharge between 0.3 and 21.4 in³/min. A generator provided AC power for the pump, and dye was pumped from a 5 gallon bottle that had been calibrated in the laboratory so that volume changes could be calculated from measured depth changes in the bottle. The dye pump inflow and outflow lines were 3/16 inch Tygon tubing. In many of the tests, the quantity of Rhodamine released was rather large so that the dye plume would be visible for most of the test. This procedure was a definite aid in locating the tracers in the bay and in selecting measurement locations. Nevertheless, as pointed out later, the concentrations near the ends of some of the tests were so small as to be questionable relative to the background.

Other equipment at the injection site included a marine-band radio for communication with the sampling crew.

4.1.3 Sampling equipment. A 19 ft Ski Barge owned by the University of Texas was the sampling boat used during this study. The boat was rigged with a removable pivoting arm-crossbar assembly designed and described in detail by Bales and Holley (1987), a diagram of which is shown in Figure 4.3. The arm, 15 ft. long and made from steel angle, pivoted from a crossbar mounted near the stern of the boat. Another crossbar near the bow held a winch used to raise and lower the arm. The end of the arm supported a submersible pump rated at 1/6 hp that pumped water through the measurement and sampling setup. The purpose of the arm assembly was to allow sampling at different depths and to enable the pump to be raised out of the water when moving between sampling locations.

The same fluorometer used in the laboratory was converted to field use by installing the flow-through system in place of the cuvette-testing system. Flow was routed from the submersible pump to the fluorometer through the brake hose described in the previous chapter. Brake hose was also used for discharge from the fluorometer.

The DC output from the fluorometer was fed into a dual channel, two pen, variable speed strip chart recorder. When the recorder was used it was only to help locate the center of the dye cloud, not to get quantitative data.

A Honda EM 1600X Portable Generator provided AC power to the pump and chart recorder and recharged the 12-volt battery that powered the fluorometer. The battery provided a more uniform power source than the generator.

Other equipment on the boat included a marine-band radio for weather information and communication with the injection operator, a conductivity-salinity-temperature meter for determining salinity, and a sonar-type recording depth meter. The fluorometer and chart recorder were housed on the boat in a plywood cabinet; the chart recorder compartment had a hinged cover to protect the instrument and charts from spray when not in use. Also placed in the cabinet were the 40 mL sampling bottles and caps and the formalin that was injected into the samples taken for GC analysis. (See Section 5.3.)

4.1.4 Data presentation format. For each sample (or set of samples) taken in the field, the resulting data were Rhodamine-WT concentration (C_R), propane concentration (C_P), and travel time (t). The decay rate for Rhodamine-WT in bay water, presented in Section 3.3.3, was applied to the dye concentrations before the data were analyzed. Eq. 2.7, with the dye decay already taken into account (Eq. 3.7), becomes

$$\frac{\left(\frac{C_P}{C_{RC}}\right)_2}{\left(\frac{C_P}{C_{RC}}\right)_1} = \exp [-K_P (t_2 - t_1)] \quad (4.1)$$

where K_P is the surface transfer rate coefficient for propane. Taking the logarithm of both sides and rearranging, the result is

$$\Delta \ln \left(\frac{C_P}{C_{RC}} \right) = -K_P \Delta t$$

or

$$\Delta \log \left(\frac{C_P}{C_{RC}} \right) = -\frac{1}{2.3} K_P \Delta t \quad (4.2)$$

4.1.5 Estimate of K_P . In order to have an idea of the amount of change in the tracer ratio to expect, a value for K_P was predicted from results of laboratory tests (Figure 4.4) and using values of wind speeds (U_a) = 6.7 m/s (15 mph) and 8.9 m/s (20 mph) and a depth (h) = 5 ft (1.5 m). The oxygen transfer

coefficient (K_L) for the given wind speed was estimated from Figure 4.4 to be 50×10^{-6} m/s for $U_a = 15$ mph and 100×10^{-6} for $U_a = 20$ mph, so the reaeration coefficient (K_2), determined from

$$K_2 = \frac{K_L}{h} \quad (4.3)$$

was approximately $33 \times 10^{-6} \text{ sec}^{-1}$ or 0.002 min^{-1} for the first case, and $67 \times 10^{-6} \text{ sec}^{-1}$ or 0.004 min^{-1} for the second. For propane, the ratio defined in Eq. 2.5 has a value of 1.36 (Rainwater and Holley 1983), resulting in predicted values of $K_p = 0.0015 \text{ min}^{-1}$ and 0.0029 min^{-1} . For a four hour test, the decreases in tracer ratios calculated by these values (Eq. 4.1) are 30% and 50%. Results summarized by MacKay and Yeun (1983) suggest that field surface exchange rates for this velocity range might be about one-third smaller than the laboratory results in Figure 4.4. However, the results of Peng et al. (1979) for gas transfer in the ocean are not inconsistent with Figure 4.4 for a U_a range of 7 to 30 mph.

In considering the research plan, it needs to be remembered that the goal of this research is not to calculate a value for K_p , but to find a way to conduct the experiments and to gather data that will produce reliable results.

4.2 Field Tests: June 17-20, 1986

The goals of this first field trip were to test equipment performance in the field, to determine the feasibility of performing tracer gas studies in bays, and to decide on the type of injection (instantaneous or continuous) to be used in future tests. It is easier to determine travel times for the samples from instantaneous releases, but it was feared that the dye clouds from such injections would be severely sheared out vertically; uniform vertical distribution of the tracers is important in the analysis.

4.2.1 Injections. Two "slug" injections of only dye were made during the first field trip, one on June 17 and one on June 18. The first release was 1 liter of 50% Rhodamine-WT - 50% methanol (no bay water) poured quickly from the side of the sampling boat at 11:45 am on June 17. The purpose of this release was to test the field monitoring equipment and to observe the mechanics of dye dispersion in the bay.

A release of both propane and Rhodamine-WT was attempted on June 17 for the purpose of testing the diffusers and determining how fast the propane could be injected. The Tygon tubing outflow from the dye pump was attached to the middle top of the gas diffuser stand. The diffuser stand with four diffuser strips was lowered over the side of the boat in water five feet deep.

The injection started at 2:40 pm. using the 30-lb. propane bottle and 0.75 gal. of 50% dye- 50% methanol mixture in the 5-gallon bottle. The gas regulator was opened until the maximum obtainable pressure on the diffuser line, 9 psi., was reached. The dye pump was set at 25% flow. A loose connection

on the outflow of the pump stopped the dye release almost immediately after starting, but the propane release continued. Approximately 20 lbs. of propane were injected in 6 minutes. Inspection of the diffusers showed no damage from the high flow rate.

Three continuous injections were made during the trip. Stable injection platforms were provided by concrete beams just above water level and between columns in causeway pier groups. Two diffuser strips were used, and gas injection was monitored with a bathroom scale placed under the propane bottle. The gas regulator was adjusted during the tests to keep the mass flow rate constant based on the time record of the weights of the gas bottle. After the gas in the bottle was about half depleted, there was some ice formation on the outside of the bottle for each day's injection.

The first continuous release was made on June 18 from the ninth causeway pier group west of the navigation channel (pier group #106). The diffuser stand was placed on the floor of the bay between two footings and perpendicular to the current that was moving into the bay. During the test, the weight of the propane bottle and the pressures on the bottle and diffuser line were recorded at 15 minute intervals. Due to problems with the dye pump, the dye injection was made by pouring the dye-methanol mixture diluted with bay water on top of the rising gas bubbles every 5 minutes.

The release lasted 255 minutes during which 26.1 lbs. of propane and 0.84 gallons of Rhodamine-WT (20% solution) were injected. An increase in the concentration of dye in the bottle used for the last 50 minutes of the test resulted in a slightly higher dye injection rate (0.80 in³/min of Rhodamine-WT as opposed to 0.67 in³/min).

In order to find travel times on samples taken, drogues were to be released at the injection point every hour. The drogues, which were available from a previous project, were constructed of two 2 ft. by 10 in. strips of 1/4-inch plywood bolted together in the middle at right angles with sheet-metal fins attached to the bottom by nylon cord and a 4 ft. length of 1/2- inch PVC pipe screwed into the top. The concept was that the plywood should float just below the water surface to minimize wind resistance and the fins should carry the drogue along with the current. The PVC pipe was for spotting in the field. The drogues proved to be unstable due to surface waves. These drogues were not used after the first test.

A second instantaneous release of dye was made on June 18 at 2:42 pm. One gallon of the Rhodamine-WT - methanol mixture (no bay water) was poured into the boat wake (to promote mixing). The injection site was left for 1.5 hours due to a necessary return to the boat dock; upon return, the cloud could not be located.

The second continuous release, made from the eighth causeway pier group west of the channel (group #107) on June 19, started at 11:32 am. The same propane injection method was used. The repaired metering pump was set on 15% flow and used to inject the dye with the outflow hose again attached to the diffuser stand. The height of dye-methanol-bay water mixture in the 5-gallon dye bottle was recorded every

5 or 10 minutes as were the gas tank weight and gas pressures. The release continued for 277 minutes during which 25.0 lbs. of propane and 1.2 gallons of Rhodamine-WT were injected.

On June 20, a continuous release started at 11:00 am using the injection method from the day before. The release was made from the sixth causeway pier group east of the channel (group #122). The east side was chosen because the current had changed and would have carried the dye cloud into the navigation channel (Figure 4.2) if injection sites from earlier tests had been used. During the release, which lasted 250 minutes, 24.5 lbs. of propane and 1.3 gallons of Rhodamine-WT were injected.

Thirty minutes into the release it was noticed that the dye was no longer visible about 30 yards from the injection site, apparently due to sinking of the injected plume. Salinity profiles revealed higher density water near the bottom of the bay with which the dye was apparently mixing. Due to a change in conditions, the sinking stopped an hour later.

Each day, the boats were launched about 8:30 am. The time until the cited beginning time for each injection was required for determining the best injection site for that day, setting up equipment and dealing with unexpected problems with the boat or instruments.

4.2.2 Sampling. The first slug injection was monitored visibly and with the fluorometer. Observations are presented in the next section.

After the short-duration gas and dye injection on June 17, three samples were taken simply to check for the presence of propane. The samples were taken by hand from the side of the boat by placing the sample bottles, mouth down, several inches below the water surface and then turning them over to allow filling. This was a crude method which was acceptable for the purposes of that particular test, but which should not be used to obtain reliable quantitative results. When a bottle was removed from the water, formalin was injected into the sample and the cap was quickly placed on top. The time at which the sample was taken, the sample bottle number, and the simultaneous fluorometer reading were recorded. It was realized afterwards that the fluorometer readings were probably not representative of the samples because the sample bottles were filled on the opposite side of the boat from the fluorometer intake.

For the first continuous release, on June 18, sampling was performed in the same manner as described above except that the samples were taken within a few inches of the fluorometer intake, and replicate samples were taken. Sampling began 2 hours after the injection started and stopped at the end of the injection. In total, 21 samples were collected.

Due to the fact that the drogues proved to be unreliable (those that did not capsize were blown completely off course), travel times for the samples could not be calculated. In order to make some use of the data, distances from the injection site were estimated when sampling. It was assumed that the samples could then be ordered sequentially to see if any trend appeared. Because all sampling took place north of the causeway (Figure 4.2), the power lines that ran across the bay were also used for distance approximations.

Fluctuations in the fluorometer readings when sampling, coupled with the length of the fluorometer intake line (about 25 feet), introduced doubt about the knowledge of the dye concentrations in the samples. For the second continuous release (June 19), sample bottles were filled from the outflow from the fluorometer. The fact that the length of the outflow line was 1/4 that of the intake line suggested that fluorometer readings would more nearly represent sample dye concentrations. Each sample bottle was held in the flow long enough for it to be flushed with at least three bottle volumes before the sample was taken.

During the second continuous release, the current flowed southward. Landmarks south of the causeway (a fishing pier, water tower, and channel marker) were used for distance estimates. Samples were taken on a line, parallel to the causeway, defined by a landmark. Sampling started 100 minutes after the injection began and stopped at the end of the injection. Two background samples and eight samples without replicates were taken. Sampling was limited by a large number of shrimp boats disturbing the dye cloud.

The final continuous release for this trip, on June 20, was sampled in the same manner as the day before. The current first carried the dye plume north of the causeway, but reversed during the test. Sampling distances were estimated on both sides of the causeway. Starting one hour after the injection began, sampling continued for 1.5 hours after the injection ended. In all, 54 samples were taken, 25 of which were replicates.

Use of the fluorometer outflow for filling the samples allowed vertical profiles of dye and gas concentrations to be taken on the last two days. Salinity profiles were also recorded throughout the tests.

4.2.3 Data presentation and analysis. Spreading of the dye cloud after the short-duration release on June 17 did not progress as expected. Within 30 minutes the length of the visible cloud was about one-third of the distance the centroid had traveled, but the dye cloud was only several meters wide. The result was a ribbon-like cloud; attempts to anchor within the cloud for sampling were futile.

A handheld rangefinder was used to estimate the velocity of the centroid of the visible dye cloud; the distances between the release point and two day buoys were measured and the times at which the cloud centroid passed the buoys were recorded. The average velocity over the first 45 minutes was 10.4 fpm. After 90 minutes, the dye was detectable only with the fluorometer. Vertical profiles in the front part of the cloud revealed nonuniform dye distribution with higher concentrations near the surface.

Samples taken following the instantaneous gas release on June 17 did contain sufficient propane for reliable concentration measurement. As was explained in the previous section, the samples could not be used for quantitative analysis, but did prove that sufficient propane for testing could be injected with a short-duration release.

Data from the first two continuous releases are not presented here. Although the tests were invaluable as field experience, the data proved to be of little analytical use. The dye injection method of the

continuous release on June 18, when dye was poured onto the gas bubbles at 5 minute intervals, produced a patchy cloud with variable dye concentrations. The tracer plume from the second release was drastically disturbed by shrimp boats. Numerous trails of laterally entrained water due to boat wakes were visible throughout the plume by the end of the test.

Figure 4.5 is a semilog graph of the data from the continuous release on June 20. The horizontal axis is the estimated distance of the sampling location from the injection site on the vertical axis, C_p is the propane concentration and C_R is the Rhodamine-WT concentration. Since travel times could not be measured for these samples, the estimated dye decay factor discussed in Chapter 3 could not be included.

Figure 4.6 is the comparison of gas and dye concentrations from two sampling sites on June 20 with salinity profiles taken at the same locations. The graphs suggest that the salinity gradient inhibited vertical mixing of the tracers.

Although the data from this field test could not be used to calculate a gas transfer coefficient, the fact that the values found for C_p/C_R in the last test could be determined and had scatter which was within a reasonable range (Figure 4.5) suggested that, with improved methodology, tracer-gas studies could be applied to bays.

4.2.4 Evaluation. Two problems with the injection method were discovered on the first field trip. It had been believed that the scale would provide a reliable, direct method of monitoring propane injection. However, towards the middle of each injection, ice began to form on the outside of the propane bottle, increasing the apparent tank weight. The amount of decrease this caused in the gas flow rate is not known. It was decided that a gas flow metering device would provide better flow rate monitoring.

The second injection problem was indicated by field results. It is possible that some of the variation in C_p/C_R could have been caused by the point source of the dye release. The initial dye plume was very thin and concentrated. While turbulent eddies could be expected to cause patchiness on the edges of the cloud, they were instead disturbing the entire plume. Samples from different lateral points in the plume could not, therefore, be compared. The possible solution selected was to design a line source release for dye so that more initial mixing would occur during dye injection.

There were also two major sampling problems to be addressed. The first, discovered through both field and laboratory observations, involved using field fluorometer readings as data for dye concentrations. Throughout the tests, the tracer plumes continued to be laterally thinner than was originally expected. A constant fluorometer reading during the flushing and filling of the sample bottle, as necessary to insure knowledge of the sample dye concentration, was almost impossible to obtain; the sampling boat would have had to be held in one spot against wind and waves. (The idea of anchoring in the plume had to be abandoned because of the difficulty and time involved.) Often, an average fluorometer reading over the filling time was estimated.

Laboratory information increased the level of uncertainty about dye concentrations. As discussed in Chapter 3, it was discovered that the warmup time for the fluorometer was longer than originally thought. A three hour warmup period was difficult to insure in the field because the sampling crew was usually busy helping to setup the injection at the start of the test, leaving no one to monitor the sampling equipment. To correct this problem in future tests, two samples would be taken simultaneously: one treated with formalin and kept for gas analysis, and the other held for dye concentration analysis in the laboratory after the trip.

The second sampling problem involved travel time measurement. Tidal control of current speeds prohibited the use of distances for time estimates. It was decided that, if an improved drogue design could be found, the drogue concept should be applied again before more complicated travel time measurement methods were considered.

4.3 Field Tests: July 29 - August 1, 1986.

4.3.1 Injections. Continuous tracer releases were made during the second field trip. A gas flowmeter with a built-in flow control valve was installed in the propane line near the tank to insure a constant gas flow rate. With the flowmeter valve left open, the dual-gauge tank regulator was again used to adjust the flow. The flowmeter was bolted to a 1 ft. by 2 ft. plywood base for stability.

A line source for the dye was provided by a dye diffuser constructed from a five foot length of 1/2-inch diameter PVC pipe. The dye diffuser was clamped to the propane diffuser stand 3 inches above and directly over the gas diffusers. Ten 1/16 -inch diameter holes were spaced five inches apart along the pipe over the gas diffuser strips, and a tee connection in the middle provided the dye inflow point. Both ends of the pipe were capped.

New drogues were constructed. The design, from Ward (personal communication), consisted of four parts (the body, handle, and two fins) that could be quickly assembled in the field. The drogue float was made from a 2 ft by 2 ft piece of 1/2 inch plywood painted fluorescent orange to enhance sighting in the bay. The plywood had a 1 inch hole drilled in the middle. To assure buoyancy, two strips of Styro-foam 12" x 3.25" x 1" were clamped to the top of each drogue.

The drogue handle was a 3.25 inch square of plywood with a metal drawer handle bolted to one side. A nylon cord was threaded through the center of the drogue handle and had a metal clip tied to the far end. The cord length could be changed in the field, raising or lowering the fins. The fins were two pieces of sheet metal 24 inches long and 8.25 inches wide, constructed as shown in Figure 4.7.

To assemble a drogue, the fins were slipped together. The clip from the handle was run through the hole in the center of the body and clipped to the hole in the top of the angles on the fin set. Two orange surveying flags (approximately 2.5 inches square) were stuck into small holes on the top of the float

with the wire "poles" for the flags crimped to hold the flags about 18 inches above the top of the float. The whole assembly was tossed into the water. When retrieved, the entire drogue could be lifted into the boat by the handle and disassembled in just a minute or two. The increased size of the drogues made them stable in the bay waves; they were used for the duration of this second field trip.

Causeway pier group bases were again used for injection platforms. The first release was made on July 29 from the eighth causeway pier group east of the navigation channel (pier group #124). The injection started at 10:00 am and lasted 310 minutes during which 2.8 lbs of propane and 0.8 gallons of Rhodamine-WT (20% solution) were released. Less than the desired amount of propane was released because of an underestimation of the flow rate to be maintained on the flowmeter.

Two hours into the injection, it became evident that the dye cloud was sinking 20 to 30 yards from the injection point. Salinity profiles revealed higher density water near the bottom of the bay with which it was believed the gas and dye were mixing upon release. In an attempt to correct the problem, the diffuser stand was raised to a depth of 3 feet and suspended from the base of the injection platform at 12:30. This maneuver did appear to at least partially correct the problem.

The second release on July 30, also from pier group #124, began at 8:35 am. Over the 228 minute duration, 7.1 lbs of propane and 1.4 gallons of Rhodamine-WT were released. The diffuser stand was suspended at a depth of 3 feet; one end was tied to the injection platform and the other was tied to an improvised anchored buoy. The buoy was made of several empty 1-gallon plastic bottles tied together and anchored with cinder blocks. Use of the buoy made it possible to again place the diffusers perpendicular to the current direction.

The third release, started with the diffuser stand again at a depth of 3 feet, was made on July 31 from the seventh pier group west of the navigation channel (pier group #108). The injection started at 11:10 am and lasted 290 minutes during which 30.9 lbs. of propane and 1.1 gallons of Rhodamine-WT were released. The initial propane release rate had to be decreased after nearly half of the gas supply was depleted in the first hour. The diffuser stand was raised to a depth of 2 feet 90 minutes after the start of the injection because the dye-plume was again sinking. The decreased diffuser depth greatly increased the visible dye plume length.

On August 1 the fourth release was made from pier group #108 with the diffuser stand at a depth of 3 feet. The injection began at 9:00 am and lasted 268 minutes during which 13.2 lbs of propane and 0.5 gallons of Rhodamine-WT were released. Sinking of the dye plume was again observed, but the problem was obscured by others described in the following section.

During all four releases, drogues were released at the rate of one every half-hour. The tops of the fins were initially set at a depth of 3 feet. The drogues were stable but were not following the visible part of the dye plume and occasionally became snagged on oyster beds. During the third release the fins were

raised as high as possible so that the tops of the fins were just below the drogue floats. The drogues then seemed to stay closer to the dye plume, but they were obviously drifting downwind from the dye.

4.3.2 Sampling. The only change made in the sampling equipment was an alteration of the fluorometer outflow line. Two holes, two inches apart, were drilled in the brake hose one foot from the outflow end. Eight-inch lengths of 3/16 -inch diameter Tygon tubing were inserted two inches into the hose through the holes and pointed upstream. The outflow from the tubing was used to fill the sample bottles.

Addition of the Tygon tubing allowed two samples to be taken simultaneously so that the dye concentration in one sample was believed to represent the dye concentration in the duplicate sample that was analyzed for propane content. To take the samples, two bottles were held so that the tubing ends were inside the bottles just above the bottom. The bottles were filled and allowed to flush several times and were then slowly removed from the tubes to allow time for filling the space in the bottles being vacated by the tubes. One sample, taken for gas analysis, was treated with formalin. Caps were quickly placed on both bottles and the sample numbers were recorded along with the time, fluorometer reading, and sample depth. The samples were then handled in the same manner as described for the previous trip.

The drogues were used as travel time indicators for the samples. Whenever possible, the sampling boat was anchored in the dye cloud downdrift of a drogue. Samples were taken and the time at which the drogue passed the fluorometer intake pump was recorded. On several occasions the bay was too rough or the dye plume was too thin to use this method, so samples were taken while the motor was used to hold the boat near a drogue.

On July 29, sampling started 90 minutes after the injection began and continued until the end of the release. In all, 24 sets of duplicate samples were taken. The salinity difference between the bay surface and bottom was measured three times during the sampling period. Throughout the day, severe patchiness of the dye plume was observed.

Sampling on July 30 began 60 minutes after the start of the release and continued for 30 minutes after the injection was stopped. Twenty-eight sample sets were taken and four salinity measurements were made. Three of the salinity measurements were profiles at 1 or 1.5 foot intervals over the depth.

Sinking of the dye plume was discovered when dye appeared in the boat wake in apparently clear areas. Dye trails were also seen behind causeway piers several hours after the dye plume had moved past those piers during a current reversal.

On July 31, sampling began 110 minutes after the start of the injection. Thirty-five sets of samples were collected and 7 salinity profiles were taken. Wind and waves higher than on previous days caused the sampling to be discontinued at the end of the release; injection equipment had to be loaded onto the sampling boat while it was still possible to dock near the causeway piers without damaging the boat.

The higher wind on July 31 also produced circulating cells of water, known as Langmuir cells, evidenced by the parallel foam lines that form at the cell boundaries. The cells were spotted throughout the day and could have been responsible for the lower salinity differences between the surface and bottom of the bay measured on that day.

The wind increased again on August 1 gusting over 20 mph according to a handheld Wind Wizard meter. Early in the release, waves were estimated to be over 1 ft in height. Sampling started 60 minutes after the beginning of the injection and continued until 30 minutes after the injection ended. Twenty-three sets of samples were taken along with 7 salinity profiles.

Sampling was interrupted on August 1 by the appearance of a very distinct foam line sometime near 12:30 pm. The line, indicating a front, was at least 300 yards long. Numerous studies on the cause of fronts in estuarine environments are being performed (McClimans, 1986), but the origin of this front was unknown. The foam line ran approximately 10 degrees southwest of perpendicular to the causeway and crossed under the causeway three pier groups east of the injection site. At the time that the front was observed, the dye plume was moving toward the front in a line almost parallel to and just south of the causeway. When the plume reached the front, it turned at an angle greater than 90 degrees to run south along the west side of the foam line. Forty or fifty yards past the turn, the dye plume disappeared. A drogoue released at 12:10 pm followed the plume along the foam line until it neared the point where the plume could not be seen. The drogoue then crossed the foam and reversed direction, traveling north along the east side of the line at a greatly increased speed.

Attempts to take samples in the afternoon were hindered by the appearance of jellyfish in the bay on the west side of the front. The jellyfish were so abundant near the foam line that the fluorometer intake pump could not be operated just west of the foam line. Although the drogues were moving north along the east side of the foam line, only trace amounts of the dye were found in the area. Salinity profiles revealed identical salinities with no vertical gradient within 30 yards on each side of the front.

4.3.3 Data presentation and analysis. The graph in Figure 4.8 is a semilog plot of the data collected on July 29 with dye decay corrections included. In the middle of the injection the diffuser stand was raised to a depth of 3 feet. The only samples taken at a depth of five feet were from parts of the plume released after this change; propane to dye concentration ratios were lower in these samples than in the others. The data from July 30, seen in Figure 4.9, show wide variation, yet less difference between extreme values than seen in the previous day. The injection rates were held steady on July 30, but patches were observed in the dye plume. Figure 4.10 shows the data graphed separately for four drogues followed during the test. In most cases, somewhat less variation is seen when comparing samples taken in approximately the same section of the plume. Unfortunately, there were not enough samples taken at any one drogoue to provide a meaningful analysis.

The release on July 31, the data from which is shown in Figure 4.11, was extremely unsteady. Even more variation in the data was expected than was seen. Two sets of data points with the lowest concentration ratios (at travel times of 74 and 150 minutes) were from samples collected at the same drogue and were the only samples taken at that drogue.

The graph in Figure 4.12 is a semilog plot of the data from August 1. The release was steady and the bay was well-mixed, but the amount of Rhodamine-WT injected was much too small. The problem with low dye concentrations stems from not knowing the actual background concentration for each sample; the fluorescence from one background sample was used to correct the concentrations for all of the samples taken on that day. It is believed, however, that the background fluorescence varied within the sampling areas. With dye concentrations as low as those seen on August 1, the data could be biased by this fact.

The salinity measurements from the second trip are given in Tables 4.1, 4.2 and 4.3, and salinity profiles taken on July 30 through August 1 are shown in Figures 4.13 - 4.15 as measured salinity versus depth. In these figures, zero depth corresponds to the water surface and the lowest depth measurement in each figure was at the bed. As the wind speed steadily increased each day, the salinity gradient decreased until the gradient was almost nonexistent on August 1.

4.3.4 Evaluation. One of the most important results of the second trip was that even the greatest amount of variation in the data for each test was less than the amount of variation seen in the data from the first trip.

One of the major problems discovered during the second trip had to do with determining travel time for the samples. Although the new drogues performed better than the original ones, they still tended to drift downwind of the dye plume. Their original positions in the plume could be estimated by starting at the drogues in the sampling boat and heading into the wind until dye was encountered, but the continuous variation in wind speed and direction caused confidence in the estimates of travel time to be low. It was decided to try a procedure using a second fluorescent dye, which would not interfere with the measurement of Rhodamine-WT concentrations, with pulses of this dye being released at intervals in the tracer plume to use as a travel-time indicator.

Another major problem was the sinking of the dye plume. For the second trip, the dye-methanol mixture had been carefully prepared in the laboratory so that the density of the mixture was essentially that of water. If anything, the mixture should have risen to the surface when introduced into the saline bay water. It had to be assumed that the injection was entraining the higher salinity water from the bottom of the bay causing the plume to be heavier than the surface water. It also had to be assumed that the vertical salinity gradient would exist frequently enough that it could not be neglected. A new injection procedure that would overcome this problem was needed.

The gas flowmeter that had been added to the injection equipment required alteration. The flowmeter provided an easy method for monitoring the gas flow rate to keep it steady, but the valve in the flowmeter caused so much head loss that the desired flow rates could not be maintained after only about a half of the gas in the bottle had been used. The result was smaller quantities of injected propane than desired.

Another problem encountered was interference with the dye plume from the causeway piers. Some of the tracers, trapped in the wake of the piers, could be released back into the plume at a later time. This would produce false travel time calculations if a patch of the older dye and gas was sampled. A search of Lavaca Bay and several nearby bays did not reveal any other structure suitable to use as an injection platform. It was decided that future releases should be made from a boat.

4.4 Field Tests: April 1-4, 1987.

4.4.1 Injections. Several changes were made in the injection equipment and planned procedure in order to correct the problems discussed in the previous section. A second fluorescent dye, Fluorescein, was purchased. As described by Smart and Laidlaw (1977), Fluorescein and Rhodamine-WT can be used in combination because they fluoresce at different wavelengths; Rhodamine-WT is a red dye and Fluorescein fluoresces green. The fact that Fluorescein decays quickly in sunlight, as the experiment described in Section 3.3.4 verified, prevents the dye from being used for quantitative field measurements during tests in open waters. The plan, however, was to use the dye only as a travel time indicator; small amounts of Fluorescein were to be released from the injection site every hour.

An injection box was designed to overcome the problem of the sinking tracer plume. The box was made from 1/4 -inch exterior plywood following the plans shown in Figure 4.16. Rising bubbles from the gas diffuser, placed 8 inches above the bottom on the outflow side of the box, pulled water under the dividing plate from the intake side. The opening on the intake side allowed water in from only the top 10 inches. Styrofoam strips were attached to the outside top, and the box was anchored by tethering the bottom to concrete blocks. The anchor lines were tightened until the top of the injection box was level with the bay surface. The two gas diffuser strips were placed beside each other, 4 inches apart, and a new dye diffuser was installed 4 inches above the strips. The dye diffuser was constructed from two pieces of 1/2-inch diameter PVC connected by elbows and a tee at one end; the ports were the same as on the original diffuser. This arrangement assured complete mixing of the Rhodamine and the propane in the water before it left the injection box.

The head loss through the gas flowmeter was decreased by drilling out the internal valve orifice and filing the end of the needle valve. Gas flow could still be monitored with the flowmeter and controlled with the propane tank regulator. The pressure on the low side of the two-stage regulator was decreased from

over 40 psi for the desired flow rate to 6 psi for the same flowmeter setting. Thus, a larger percentage of the gas in the bottle could be used.

A second 19 ft. Ski Barge, owned by the University of Texas, was taken on the third trip to be used as the injection platform. The sampling boat could not be used for injecting; limited space did not allow room for the injection box and, if the planned continuous releases were made, the boats would be used simultaneously for part of the test.

The first release, on April 1, was made mainly to test the new injection equipment. The injection boat was anchored 200 yards from the west shore and approximately one-third of the distance from the causeway to the north end of the bay. The injection box was placed in 4.5 feet of water. Due to movement caused by surface waves, the box had to be held away from the boat with a paddle during the injection.

The injection began at 11:00 am and continued for 190 minutes during which 20.8 lbs of propane and 0.8 gallons of Rhodamine-WT (20% solution) were released. Once an hour, 0.2 lb pulses of Fluorescein powder dissolved in tap water were poured into the plume at the outflow of the injection box. Two drogues were placed in each Fluorescein cloud.

Problems with the dye pump connections and an initial overestimation of the necessary dye pump setting resulted in an unsteady injection rate. Furthermore, the Fluorescein pulses did not remain in the plume (possibly caused by poor initial placement). For these reasons, the injection was not sampled.

Several problems arose before and during the first release. Unusually low tides due partially to northerly winds made it difficult to get the boats out of and into the launch area. The decrease in depth in the bay also made finding a place deep enough to accommodate the injection box difficult. The injection box itself turned out to be more cumbersome than expected, and the vertical salinity gradient that prompted the use of the box in the first place was not observed on April 1. Most importantly, the Fluorescein pulses had not performed as was hoped. It was decided to try a different approach to injecting for the second release.

The second injection, on April 2, was a short-duration release made with the original diffuser stand. The injection was made from the sampling boat at approximately the same spot that was used the day before. Because the dye was diluted less than usual, the dye pump clogged causing two false injection starts. The injection finally started at 9:09 am and was planned to last for 20 minutes, but the propane bottle was emptied in 6 minutes. During this time, 23.6 lbs of propane and 0.1 gallons of Rhodamine-WT were released. Drogues were used to mark the cloud.

Another short-duration release was performed on April 3. The sampling boat was anchored on the east side of the bay north of the causeway and used for injection (since the injection box was not being used). The dye-methanol mixture was not diluted and the dye pump was set at 100%. With the gas flow rate decreased, the injection started at 1:45 pm and continued for 25 minutes during which 24.2 lbs of

propane and 1.2 gallons of Rhodamine-WT were released. A drogue was released 15 minutes into the injection.

On April 4 the injection method from the day before was used except that a large slug of Fluorescein was released during the injection to mark the approximate center of the cloud. The injection began at 8:45 am on the east side of the upper bay and continued for 29 minutes during which 10.8 lbs of propane and 1.4 gallons of Rhodamine-WT were released. Eleven minutes into the injection, 1.2 lbs of Fluorescein dissolved in water were poured onto the rising gas bubbles. A drogue was used to mark the Fluorescein cloud.

4.4.2 Sampling. A second fluorometer was installed on the sampling boat. With the appropriate filters, as described by Turner Designs, the fluorometer was used to detect Fluorescein and was placed inline between the intake pump and the original fluorometer to minimize the flow time from the measuring of the Rhodamine-WT to the tubes for filling the sample bottles.

One of the reasons air bubbles had previously been trapped in the samples was that the person taking the samples had to lean over the side of the boat to reach the outflow tubing and then return to the fluorometer cabinet for the formalin and bottle caps. Portions of some of the samples were spilled during this time. To correct the problem, the outflow line was altered by installing the device shown in Figure 4.17, to allow sampling near the fluorometers. A plastic one-gallon jug with the bottom and front face cut out was nailed upside down to a plywood panel. The mouth of the bottle pointed into a funnel which was also nailed to the panel, and a rubber drain hose was attached to the bottom of the funnel. The hose ran to the side of the boat. Three feet from the fluorometer outflow, a tee was installed in the brake hose to which were attached the two Tygon tubes used to fill the sample bottles. The brake hose ran over the top of the plastic bottle and to the side of the boat. The Tygon tubes were held inside the bottle and, when samples were not being taken, the flow from the tubes exited the boat through the funnel and rubber hose. The panel was bolted to the top front of the fluorometer cabinet. With this alteration, the person taking samples could remain seated in front of the cabinet. This meant not only faster capping of the samples and fewer air bubbles, but also that the person taking the samples could watch the fluorometer to decide when the reading was steady enough to collect the samples.

A small battery-operated trolling motor was added to be used when sampling. The boat could be held in place with less disturbance to the dye plume than was caused with the larger motor and with finer control.

For reasons stated in the previous section, no samples were taken on April 1. Sampling on April 2 started one hour after the injection; 31 sets of samples were taken. Drogues were placed in the approximate center of the cloud several times throughout the test. Due to the small amount of dye released, the highest field readings three hours into the sampling were only 1.5 times background on the fluorometer.

Sampling continued, however, for another hour. A sudden frontal passage producing large waves ended the test at 2:00 pm.

The injection was delayed on April 3 because low tide prevented boat launching until after noon. Sampling time was limited by the appearance of the typical late afternoon increase in wave height. Between 3:15 and 6:20 pm, 35 sets of samples were taken. Salinity profiles revealed well-mixed conditions throughout the test. Several drogues were repositioned in the cloud as necessary to correct for wind-induced drift out of the cloud; during sampling, the boat was not anchored, but rather was held near a drogue using the trolling motor. Occasionally, the drogues drifted out of the dye cloud just during the sampling time.

On April 4, sampling began 45 minutes after the end of the injection and continued for 4.3 hours during which 45 sets of samples were taken. A steady wind produced choppy waves throughout the day and kept the bay well-mixed vertically. The Fluorescein pulse indicated sample location in the dye cloud; drogues were again used as a reference point to hold the boat in place while sampling.

Halfway through the test on April 4 a gap appeared in the dye cloud just downdrift from the Fluorescein pulse. Both parts of the cloud were sampled. Travel times were estimated by comparing the distance from the Fluorescein to the sampling location to the distance from the Fluorescein to the leading or trailing edge of the Rhodamine cloud at the time of sampling. After 3 hours the Fluorescein was barely detectable, so the gap in the cloud was used as the reference point.

During the second half of the test, the dye cloud was in water less than 3 feet deep. This could account for the fact that the Rhodamine was still highly visible when the test ended.

4.4.3 Data presentation and analysis. Figures 4.18 through 4.20 are semi-logarithmic graphs of the concentration ratios versus travel time for the data from April 2, 3, and 4. The data from April 2 (Figure 4.18) are not considered reliable because of the low dye concentrations. A change in background concentration of 1 ppb would produce very different results. The data from April 3 and 4 should be more accurate. The variation in concentration ratios seen on April 3 could be due in part to not having a location indicator within the cloud; some samples could have come from the cloud edges that were produced before the injection rates stabilized or at the end of the injection. The data from April 4, seen in Figure 4.20, result in a graph that gives the best definition of a straight line of any of the experiments in the entire study.

The fact that the data from the final two injections seem to be more reliable than any collected earlier in this study suggests that the short-duration injection method used both days is the method best suited to the bay environment, at least when the water is shallow enough that the cloud does not become significantly sheared by the vertical distribution of velocity. The injection box, however, is probably still necessary in deeper or stratified water.

4.4.4 Evaluation. The large Fluorescein pulse used on April 4 appeared to be extremely useful in determining sampling locations. The pulse, however, did not last long because of the rapid rate of Fluorescein decay in sunlight. It is suggested that another pulse could be injected as the Fluorescein concentration approaches background. This would probably require a release of Fluorescein once every two or three hours.

A major problem is indicated by the small slope on the graphs of the data. Using linear regression, the slope of the graph of the data from April 4 is $-0.00033 \text{ min}^{-1}$. This is 51% of the slope for $U_a = 6.7 \text{ m/s}$ (15 mph) and 26% of the slope for $U_a = 8.9 \text{ m/s}$ (20 mph) predicted in Section 4.1.4. (Although the wind speed on April 4 was not being monitored, it was at least 20 mph for most of the test.) It should not be inferred that these data give accurate K_2 values. Any, or all, of several factors could be responsible for the small observed slope. The predicted Rhodamine-WT decay rate, which accounts for 28% of the slope (Eq. 2.6), could be inaccurate. A decay rate should be determined with tests in the field. It could also be possible that the saline water inhibits the surface exchange of propane, or that other chemical or biological inhibitors are present in the bay water. This possibility should be explored in the laboratory before further field testing is performed. It is also probable that the formalin interfered with the sample concentration. (See Section 5.3.)

Nevertheless, if the surface exchange rate for propane in the bay is as small as that suggested by the data from this study, much longer tests will be required to accurately measure the rate. In order to lengthen the tests, the problem of an increase in scatter of the data with time, seen in the results from this trip, will have to be overcome. It is believed that most of the scatter results from low dye concentrations in the samples taken near the end of the tests. To lessen this effect, more Rhodamine-WT should be injected, which would require a larger dye pump than the one used in this study.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Laboratory Results

Laboratory experiments were performed during this study to help predict and understand field results. The necessity of testing field samples for Rhodamine-WT concentrations in the laboratory was revealed. A temperature correction factor for Rhodamine-WT samples was evaluated; the correction factor from Eq. 3.5 for the fluorometer used in this study was found to be $n = -0.032^{\circ}\text{C}$ instead of $n = -0.027^{\circ}\text{C}$ as was reported in the literature. It was also found that a warm up time for the fluorometer on the order of three hours was required.

Tests on air brake hose verified reports that it was an appropriate material to use for flow tubing for the field system. The hose exhibited no tendency to adsorb propane, and the amount of initial adsorption and later release of Rhodamine-WT was not large enough to effect field measurements.

Experiments run with saline water revealed no increase of decay rates for propane or Rhodamine-WT with increasing salinity. Tests run on Rhodamine-WT samples in sunlight, however, did show a slight increase in rate of decay for samples in bay water as compared to those in distilled water. The coefficients found for Eq. 3.7 were $K_R = 0.00021 \text{ min}^{-1}$ for bay water and $K_R = 0.00017 \text{ min}^{-1}$ for distilled water.

The high rate of decay of Fluorescein in sunlight was confirmed. Although the trend of the data could not actually be defined by Eq. 3.8, approximate decay coefficients were calculated to be $K_f = 0.0102 \text{ min}^{-1}$ for samples in sunlight, $K_f = 0.00026 \text{ min}^{-1}$ for samples in darkness, and $K_f = 0.00033 \text{ min}^{-1}$ for samples in fluorescent light.

5.2 Field Results

The primary purpose of this study was to investigate field methods for the application of tracer gas studies to shallow bays. The tests that yielded the most consistent results were short-duration injections lasting approximately 25 minutes. Two major problems prevented successful use of continuous injections: maintaining constant tracer injection rates for several hours and determining accurate travel times for samples.

A large pulse of Fluorescein released during the injection proved useful in locating the center of the tracer cloud during sampling and in determining travel times for the samples from various parts of the cloud. In the future, it would be advisable to replenish the pulse periodically because of the rapid decay of Fluorescein in sunlight.

It was not possible to use the drogues for travel time determination with the continuous injections, as was hoped, but they were useful as reference points when sampling from several depths at one location.

They were also used to help locate the tracer cloud from a distance after anchoring for repairs or between sampling times.

The injection box described in Sec. 4.4.1 was not used for the final two injections because the vertical salinity gradient often seen was not present. It is believed that the box would be necessary in water deeper than that tested or when the salinity gradient is present. A salinity profile should be taken before the injection equipment is set up.

Before the last set of field experiments, it had been assumed that the lack of a significant slope of the semilog graph of C_p/C_{RC} versus t for the previous studies was due to experimental difficulties. In retrospect, this was apparently not the case. Essentially the same trend of little or no slope, as seen in the most reliable data (April 4), can be seen in most of the previous studies also. Thus, it was concluded that the situation needs to be addressed at a more fundamental level. One possible source of problems is the decay of the Rhodamine. When the testing was started, it was assumed from information in the literature that the decay of the Rhodamine would be much slower than the surface exchange of the propane. However, this apparently was not the case. For the data from April 4, the Rhodamine decay rate evaluated from laboratory tests accounted for 28% of the small slope of the C_p/C_{RC} data versus time. If Rhodamine is used as one of the tracers, it will be essential to determine the actual decay rate in the field rather than using laboratory estimates. Since it is impractical to do a mass balance for the Rhodamine, some indirect approach such as use of submerged, closed, transparent containers of Rhodamine needs to be investigated. Another possible problem is that the salinity or some other constituent of the bay water may interfere with surface exchange of the propane. This possibility needs to be addressed in laboratory mixing tank tests.

If the gas exchange is indeed as slow as indicated by the April 4 test, then the field tests need to be longer than the four hours typical of these tests. One of the problems to be solved before the tests can be lengthened is the increase in the scatter of the data with time. It is believed that most of the scatter in this study resulted from low dye concentrations; as dye concentration decreases, the importance of background fluorescence increases. The amount of injected dye needs to be increased considerably. Also, in future tracer gas studies in bays, more attention should be given to background fluorescence variation so that more accurate dye concentrations can be determined. Background samples should be taken periodically throughout the sampling time at different locations. It is believed that vertical profiles of background fluorescence would be helpful.

5.3 Postscript

After this study was completed and the report written, it was learned (H. J. Liljestrang, personal communication) that formalin may polymerize, and that the tendency toward polymerization increases as the salinity of a water sample increases. The degree of polymerization in river waters is unknown, but the

polymer formation (a whitish precipitate) has been visually observed in laboratory samples prepared with instant ocean (30 ppt). The polymers apparently form potential adsorption sites for the dissolved propane and thereby change the concentration in the sample from its original value. In addition to visually observing the polymers, their effects are also seen in the measurements from replicate laboratory standards. Replicate samples of propane in distilled water, either with or without formalin added to the sample bottle, regularly vary by no more than 5%. Samples of saline water (10 ppt to 30 ppt) with identical procedures regularly vary by at least 25% and sometimes more. Laboratory work is continuing to study the effects of inorganic biocides to eliminate the polymer problem.

REFERENCES

- Acree, F., Jr., Beroza, M., and Bowman, M. 1963. "Codistillation of DDT with water," Journal of Agricultural and Food Chemistry, Vol. 11, No. 4, pp. 278-280.
- Adeney, W.E. and Becker, H.G. 1919. "The determination of the rate of solution of atmospheric nitrogen and oxygen by water," Philosophical Magazine, Vol. 38, p. 317.
- Armstrong, N.E. and Yamada, S.H. 1982. "A statistical methodology for predicting salinity in Upper Lavaca Bay," CRWR Tech. Report #191, Center for Research in Water Resources, Bureau of Engineering Research, The University of Texas at Austin, Austin, Texas, 122 p.
- Bales, J. and Holley, E.R. 1987. "Field and numerical studies of tracer gas transport and surface gas transfer in laterally uniform, partially stratified estuaries," Tech. Report, Center for Research in Water Resources, Bureau of Engineering Research, The University of Texas at Austin, Austin, Texas.
- Downing, A.L. and Truesdale, G.A. 1955. "Some factors affecting the rate of solution of oxygen in water," Journal of Applied Chemistry, Vol. 5, pp. 570-581.
- Dunn, B. and Vaupel, D.E. 1965. "Effect of sample and fluorometer compartment temperatures on fluorometer readings," U. S. Geological Survey, Prof. Paper 525D, pp. 225-227.
- Eloubaidy, A.F. and Plate, E.J. 1972 "Wind shear-turbulence and reaeration coefficient," Journal of the Hydraulics Div., American Society of Civil Engineers, Vol. 98, No. HY1, pp. 153-170.
- Holley, E.R. and Yotsukura, N. 1984. "Field techniques for reaeration measurements in rivers," in Gas Transfer at Water Surfaces, Brutsaert, W., and Jirka, G.H., eds., Reidel Publishing Co., Dordrecht, Holland, pp. 381-401.
- Hoover, T.E. and Berkshire, D.C. 1969. "Effects of hydration on carbon dioxide exchange across an air-water interface," Journal of Geophysical Research, Vol. 74, No. 2, pp 456-464.
- Kanwisher, J. 1963. "On the exchange of gases between the atmosphere and the sea," Deep-Sea Research, Vol. 10, pp.195-207.
- Kilpatrick, F.A., Rathbun, R.E., Yotsukura, N., Parker, G.W., and DeLong, L.L. 1987. "Determination of stream reaeration coefficients by use of tracers," U. S. Geological Survey, Open-File Report 87-245, Denver, CO, USA, 84 p.
- Kilpatrick, F.A., Sayre, W.W., and Richardson, E.V. 1967. Discussion of "Flow measurements with fluorescent tracers," Journal of the Environmental Engineering Div., American Society of Civil Engineers, Vol. 93, No. HY4, pp. 298-308.
- Kim, J.H., and Holley, E.R. 1988. "Literature survey on reaeration in estuaries," Report presented to Pate Engineers, Inc. and Espey, Huston and Associates; Technical Memorandum 88-1, Center for Research in Water Resources, The University of Texas at Austin, Austin, Texas.
- Liss, P.S. 1973. "Processes of gas exchange across an air-water interface," Deep-Sea Research, Vol. 20, No. 3, pp. 221-238.

- Mackay, D. and Yeun, T.K. 1983. "Mass transfer coefficient correlations for volatilization of organic solutes from water," Env. Science and Technology, Vol. 17, No. 4, pp. 211-217.
- Mattingly, G.E. 1977. "Experimental study of wind effects on aeration," Journal of the Environmental Engineering Div., American Society of Civil Engineers, Vol.103, No. HY3, pp. 311-323.
- McClimans, T.A. 1986. "Estuarine fronts and river plumes," presented at International Symposium. Physical Processes in Estuaries, Sept. 9-12, Delft Hydraulics Laboratory, Delft, The Netherlands.
- Peng, T.-H., Broecker, W.S., Mathieu, G.G., Li, Y.-H., and Bainbridge, A.E. 1979. "Radon evasion rates in the Atlantic and Pacific Oceans as determined during the Geosecs Program," Journal of Geophysical Research, Vol. 84, No. C5, pp. 2471-2486.
- Rainwater, K.A. and Holley, E.R. 1983. "Laboratory studies on the hydrocarbon gas tracer technique for reaeration measurement," CRWR Tech. Report #189, Center for Research in Water Resources, Bureau of Engineering Research, The University of Texas at Austin, Austin, Texas, 114 p.
- Rathbun, R.E., Schultz, D.J., and Stephens, D.W. 1975. "Preliminary experiments with a modified tracer technique for measuring stream reaeration coefficients," U. S. Geological Survey, Open-File Report 75-256, Bay St. Louis, Mississippi, USA, 36 p.
- Rathbun, R.E. and Grant, R.S. 1978. "Comparison of the radioactive and modified techniques for measurement of stream reaeration coefficients," Water Resources Investigations 78-68, U. S. Geological Survey, NSTL Station, Mississippi, USA, 57 p.
- Rathbun, R.E., Stephens, D.W., and Tai, D.Y. 1978. "Laboratory studies of tracers for reaeration," Journal of the Environmental Engineering Div., American Society of Civil Engineers, Vol.106, No. EE3, pp. 663-670.
- Rathbun, R.E. 1979. "Estimating the gas and dye quantities for modified tracer technique measurements of stream reaeration coefficients," Water Resources Investigations 79-27, U. S. Geological Survey, NSTL Station, Mississippi, USA, 42 p.
- Rathbun, R.E. and Tai, D.Y. 1981. "Technique for determining the volatilization coefficients of priority pollutants in streams," Water Research, Vol. 15, pp. 243-250.
- Schultz, D.J., Pankow, J.F., Tai, D.Y., Stephens, D.W., and Rathbun, R.E. 1976. "Determination, storage, and preservation of low molecular weight hydrocarbon gases in aqueous solution," U. S. Geological Survey Journal of Research, Vol. 4, No. 2, pp. 247-251.
- Smart, P.L. and Laidlaw, I.M.S. 1977. "An evaluation of some fluorescent dyes for water tracing," Water Resources Research, American Geophysical Union, Vol. 13, No 1, pp. 15-33.
- Streeter, H.W. and Phelps, E.B. 1925. "A study of the pollution and natural purification of the Ohio River," Public Health Bulletin No.146, U. S. Public Health Service, Washington, DC.
- Swinnerton, J.W. and Linnenbom, V.J. 1967. "Determination of the C₁ to C₄ hydrocarbons in sea water by gas chromatography," Journal of Gas Chromatography, Vol. 5, pp. 570-573.
- Tai, D.Y. and Rathbun, R.E. 1988. "Photolysis of Rhodamine-WT Dye," Chemosphere, Vol. 17, No. 3, pp. 559-573.

- Tsivoglou, E.C., O'Connell, R.L., Walter, C.M., Godsil, P.J., and Logsdon, G.S. 1965. "Tracer measurements of atmospheric reaeration; I: Laboratory studies," Journal of the Water Pollution Control Federation, Vol. 37, No. 10, pp. 1343-1362.
- Tsivoglou, E.C., Cohen, J.B., Shearer, S.D., and Godsil, P.J. 1968. "Tracer measurements of stream reaeration; II: Field studies," Journal of the Water Pollution Control Federation, Vol. 40, No. 2-Part 2, pp. 285-305.
- Ward, G.H., Jr. 1985. "Dye diffusion experience in the Texas bays: low-wave conditions," Journal of Geophysical Research, Vol. 90, No. C3, pp. 4959-4968.
- Wilson, J.F., Jr., Cobb, E.D., and Kilpatrick, F.A. 1986. "Fluoremetric procedures for dye tracing," in Techniques of Water-Resources Investigations of the United States Geological Survey, Vol. 3, U. S. Geological Survey, Washington, D.C., 34 p.
- Yotsukura, N., Steadfast, D.A., Draper, R., and Brutsaert, W.H. 1983. "An assessment of steady-state propane gas tracer method for reaeration, the Coweselon Creek, New York," U. S. Geological Survey, Open-File Report, Reston, VA, 88 p.
- Yotsukura, N., Steadfast, D.A., and Jirka, G.H. 1984. "Assessment of a steady-state propane-gas tracer method for determining reaeration coefficients, Chenango River, New York," Water Resources Investigations, 84-4368, U. S. Geological Survey, 69 p.

APPENDIX A

TABLES

TABLE 3.1 - TEST FOR PROPANE ADSORPTION TO BRAKE HOSE
 (Values are integrator counts at range 10, attenuation 64)

BEFORE PUMP	AFTER PUMP	DIFFERENCE (%)
1305	1295	-0.7
1290	1315	1.9
1290	1315	1.9
1300	1293	-0.5
1355	1290	-4.8
1315	1170	-11.0
1290	1300	0.8

TABLE 4.1 - SALINITY DATA

July 29, 1986

Salinity (ppt)			
Time	11:38	12:01	13:50
Depth			
Surface	12.4	11.0	10.0
Bottom	16.0	15.5	13.5
Bottom Depth (ft)	6	6	5.5

July 30, 1986

Salinity (ppt)			
Time	9:54	11:25	12:55
Depth (ft)			
0	12.9	11.6	12.2
1.5		12.8	12.2
3	13.1	16.0	15.8
4	15.0		
4.5		17.0	17.5
5	17.5		
6	17.9*	17.4	17.5*
7		17.4*	

*Bottom

TABLE 4.2 - SALINITY DATA

July 31, 1986

		Salinity (ppt)					
Time	9:35	10:00	10:30	11:20	12:30	14:06	14:30
Depth (ft)							
0			11.8				
1	11.8	11.7	12.5	11.7	12.3	13.1	12.9
2	12.6	12.4	12.9	11.8	12.4	12.8	12.3
3	13.3	12.8	13.0	12.4	12.0	12.8	12.3
4	13.4	13.0	13.2	12.7	13.4	13.8	12.3
5	13.2	13.3	13.2	13.1	14.1	14.1	12.3
5.5						12.8*	
6	13.2*	13.4	13.3	13.6	14.1		14.2*
6.5					14.1*		
7		13.4*	13.3*	13.7*			

*Bottom

TABLE 4.3 - SALINITY DATA

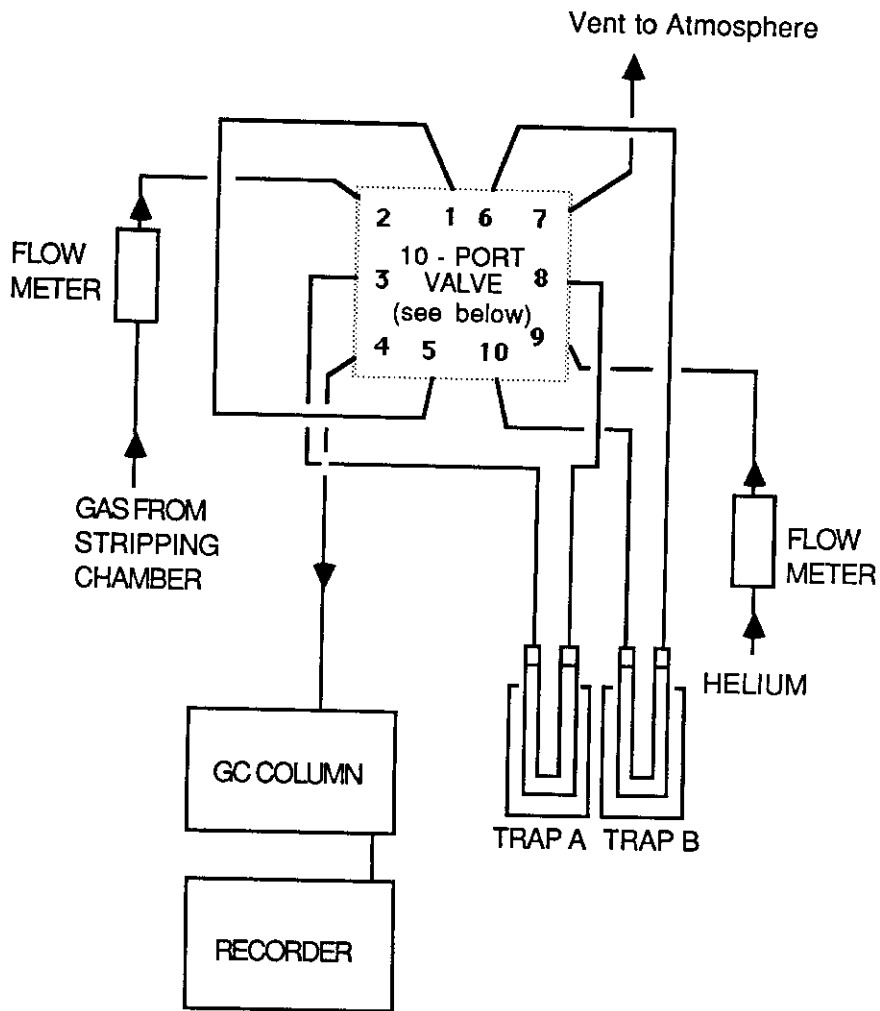
August 1, 1986

		Salinity (ppt)			
Time	7:55	9:06	11:20	13:30	
Depth (ft)				(E. of Front)	(W. of Front)
1	14.8	14.3	15.2	15.0	15.0
2	14.9	14.3	15.4		
3	14.8	14.3	15.5	15.2	15.1
4	14.8	14.4	15.6		
5	14.7	14.5	15.7	15.2*	15.2*
6	14.7*	14.3*	16.0*		

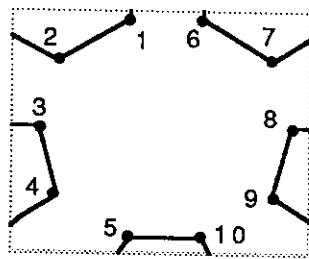
*Bottom

APPENDIX B

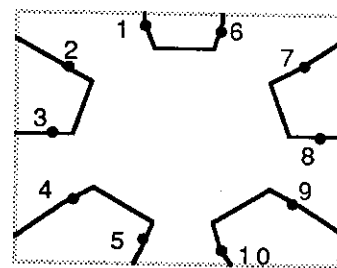
FIGURES



10-PORT VALVE



POSITION 1
TRAP A: Desorbing
TRAP B: Trapping



POSITION 2:
TRAP A: Trapping
TRAP B: Desorbing

FIGURE 3.1 - SCHEMATIC OF GAS ANALYSIS EQUIPMENT

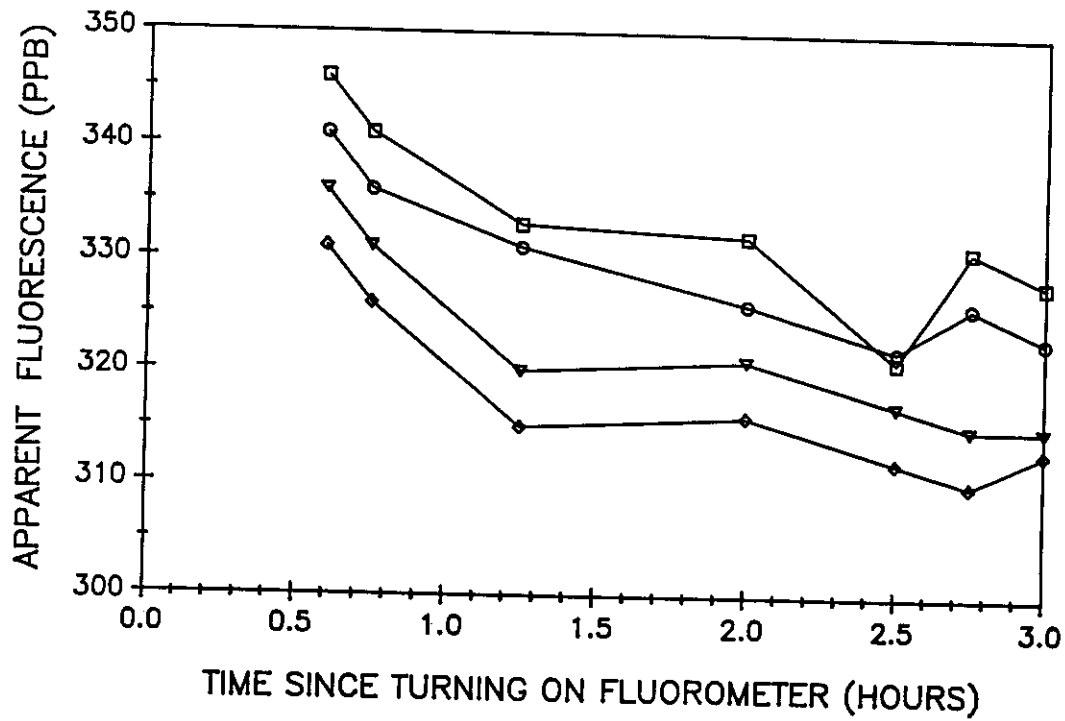


FIGURE 3.2 - FLUOROMETER WARMUP TIME

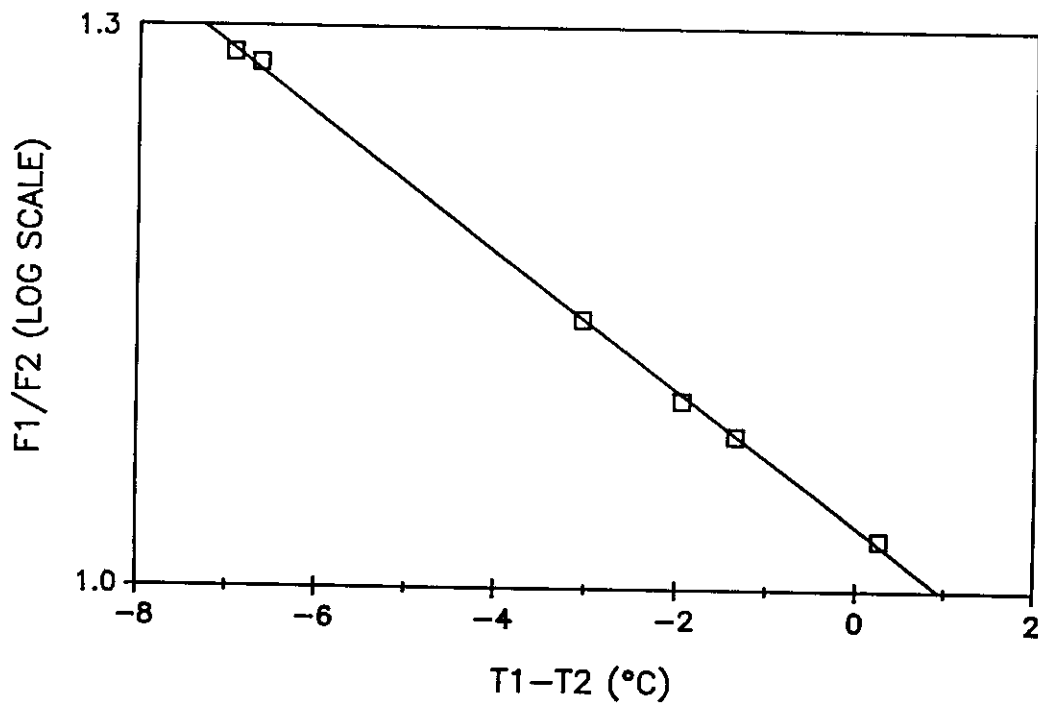


FIGURE 3.3 - TEMPERATURE EFFECT ON FLUORESCENCE

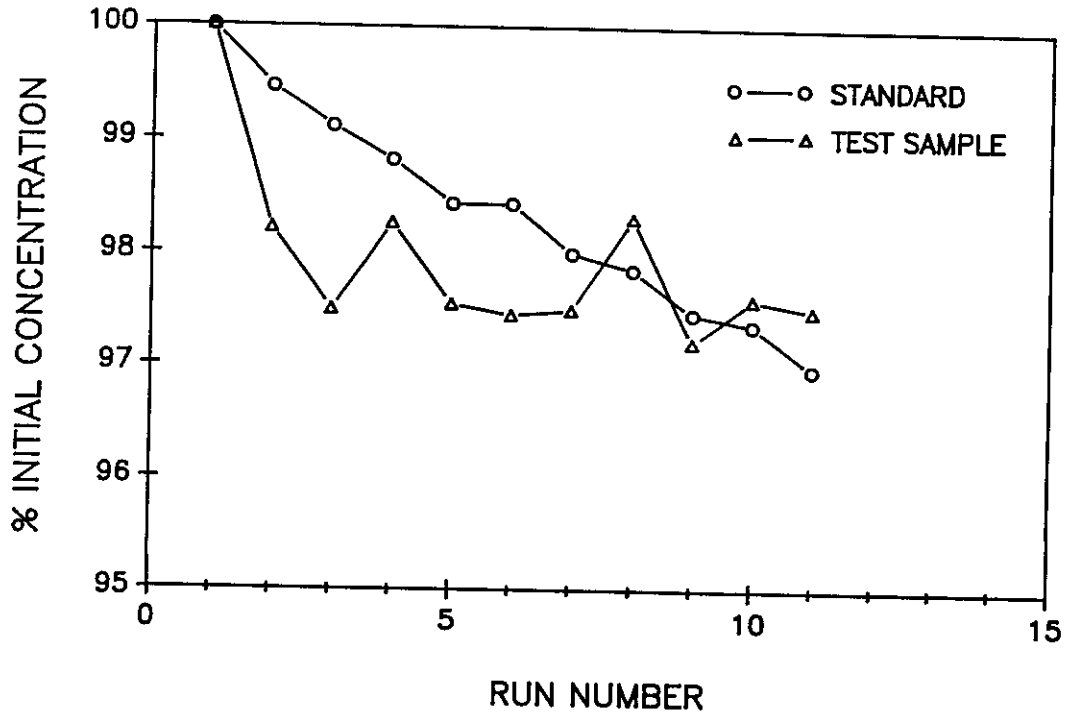


FIGURE 3.4 - BRAKE HOSE ADSORPTION TEST

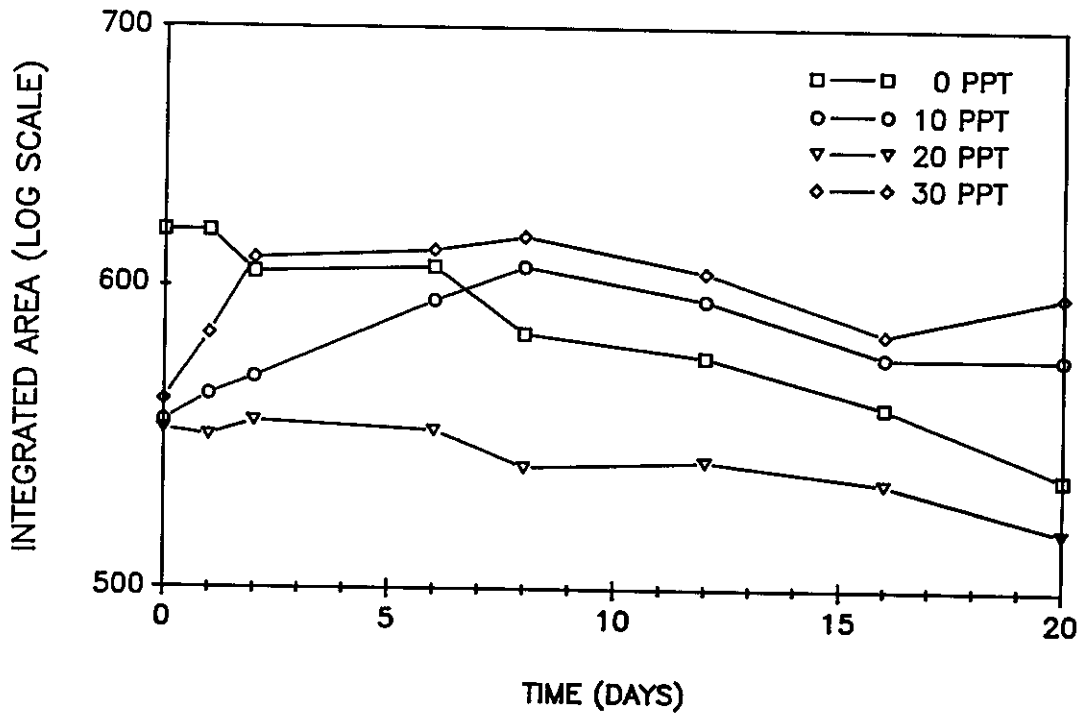


FIGURE 3.5 - SALINITY EFFECT ON PROPANE

FIGURE 3.7 - SALINITY EFFECT ON RHODAMINE
(SAMPLES 5-8)

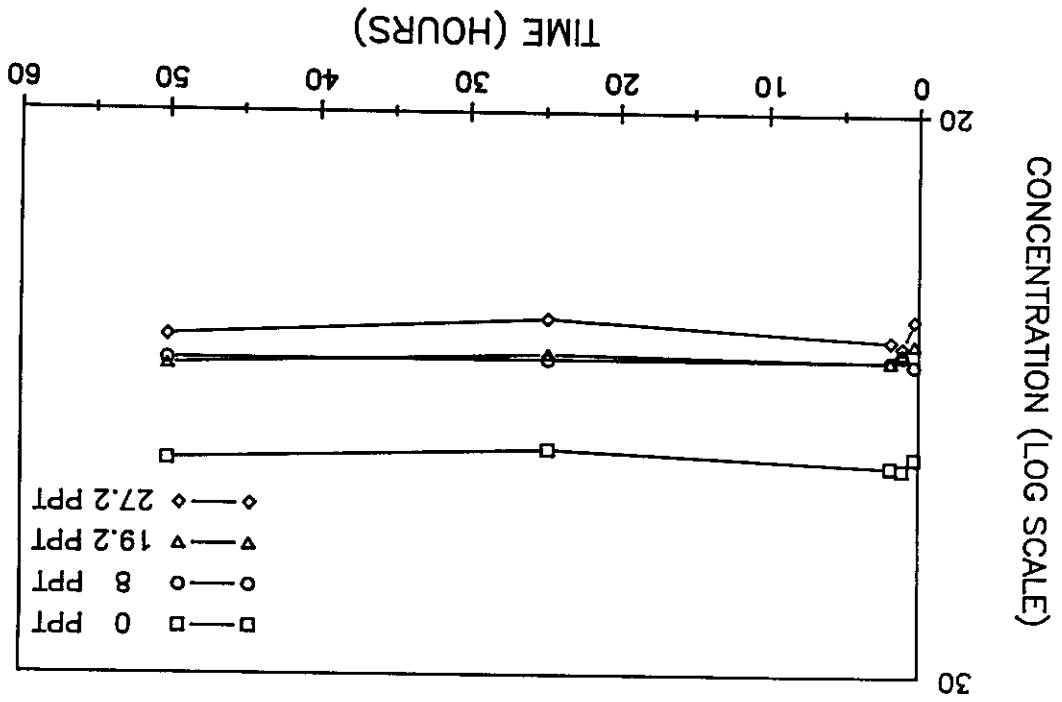
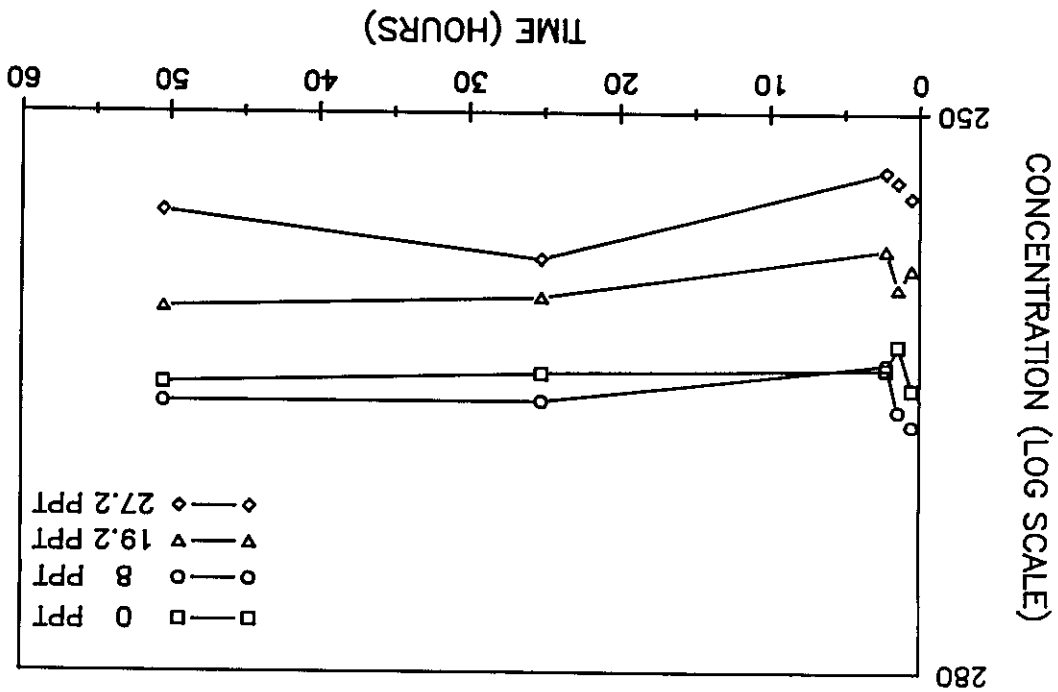


FIGURE 3.6 - SALINITY EFFECT ON RHODAMINE
(SAMPLES 1-4)



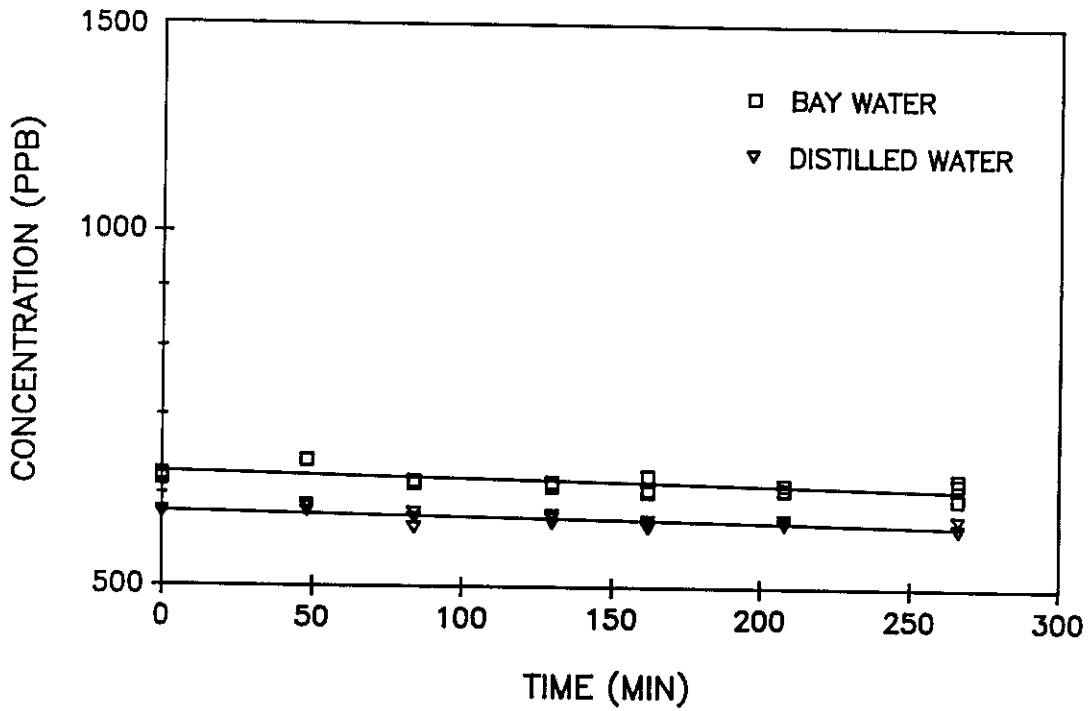


FIGURE 3.8 - RHODAMINE IN BAY WATER
(SAMPLES 1-3)

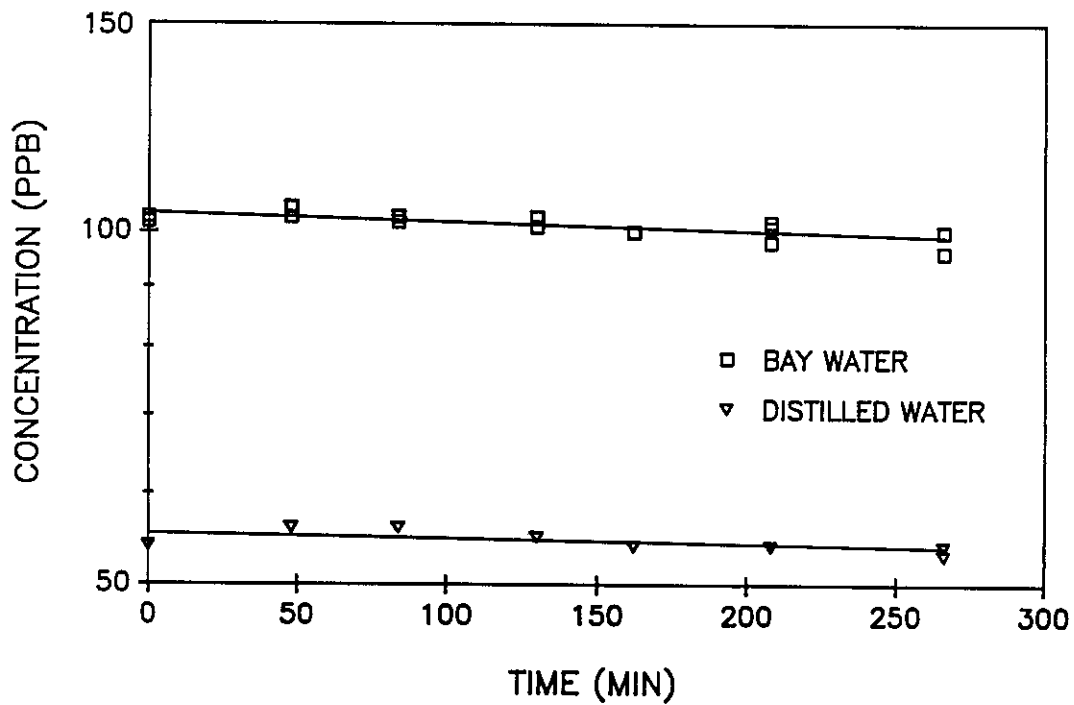


FIGURE 3.9 - RHODAMINE IN BAY WATER
(SAMPLES 4-6)

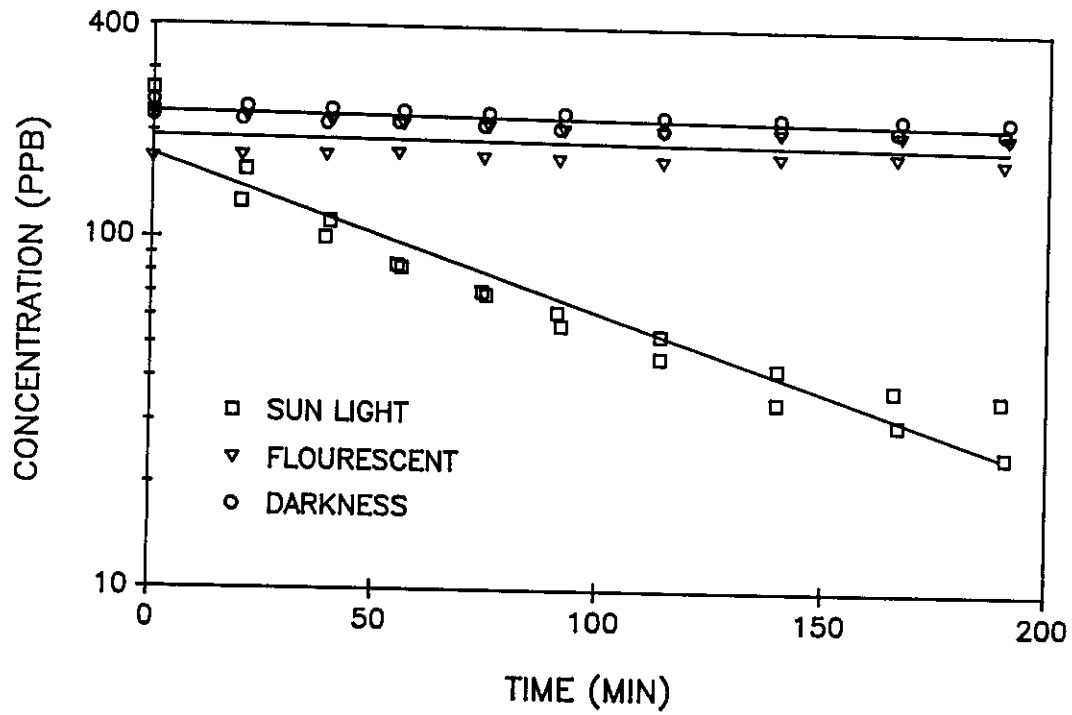


FIGURE 3.10 - FLUORESCEIN DECAY TEST

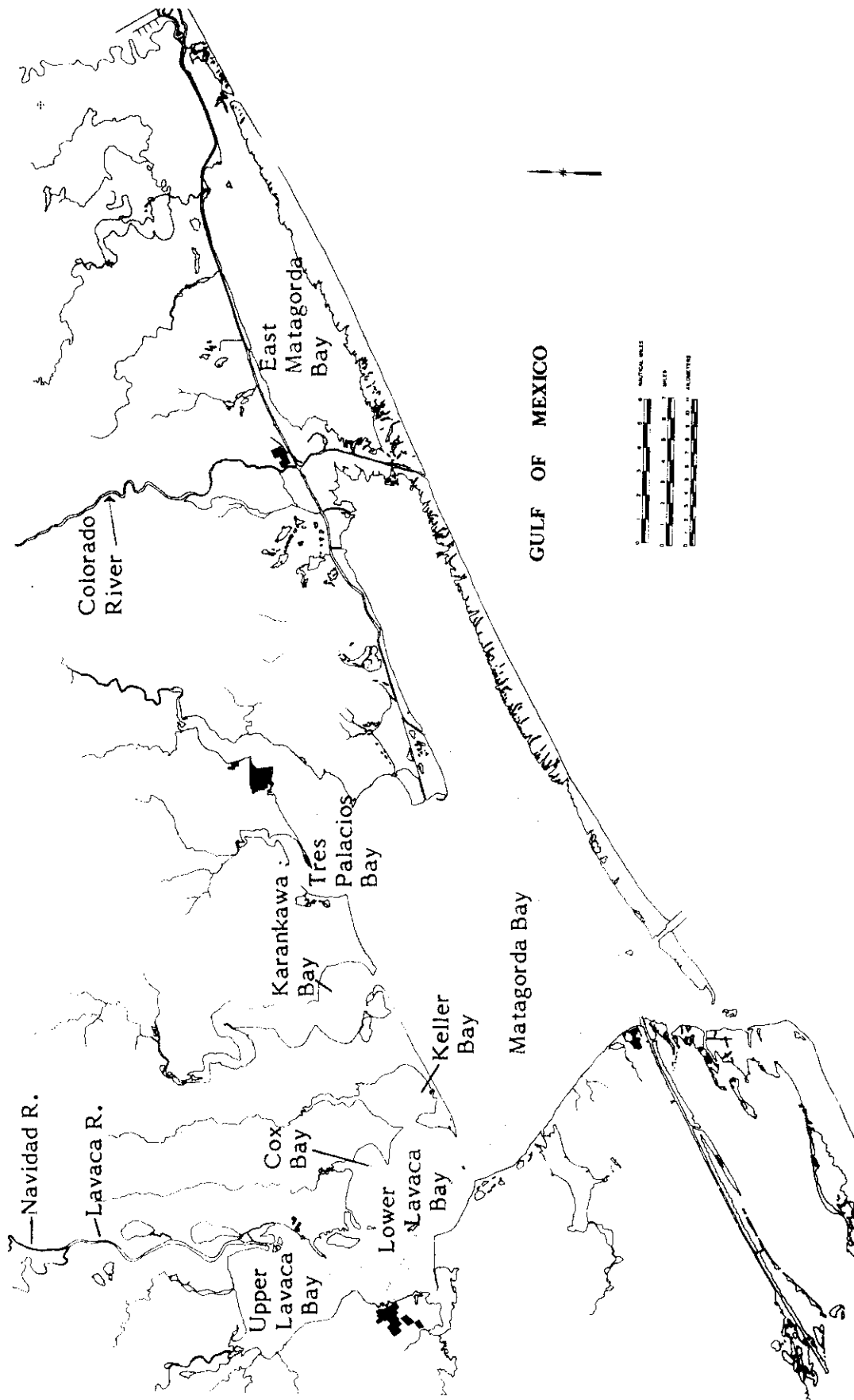


FIGURE 4.1 - MATAGORDA BAY SYSTEM

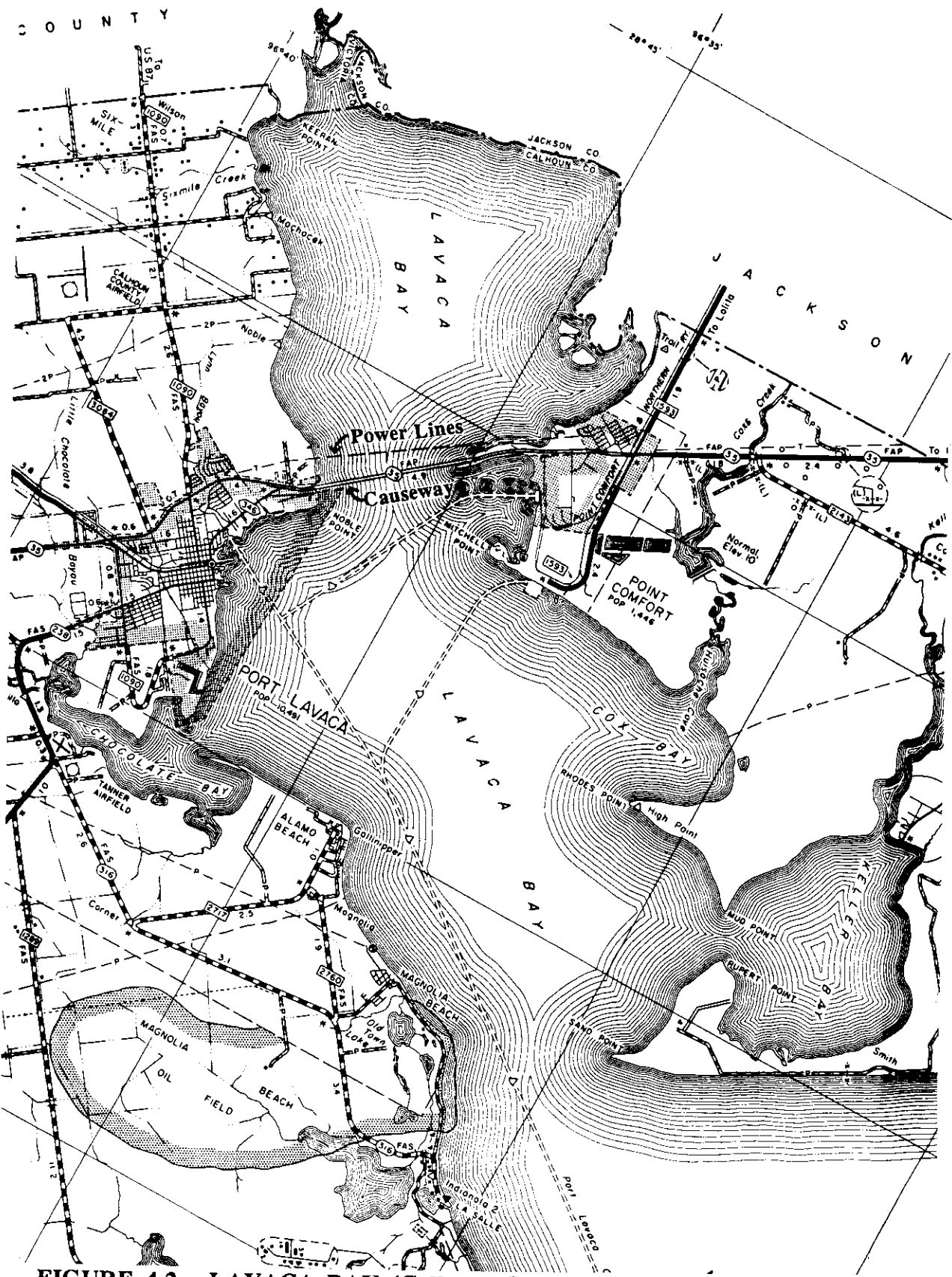


FIGURE 4.2 - LAVACA BAY (Calhoun County Map, Texas State Highway Department, 1972)

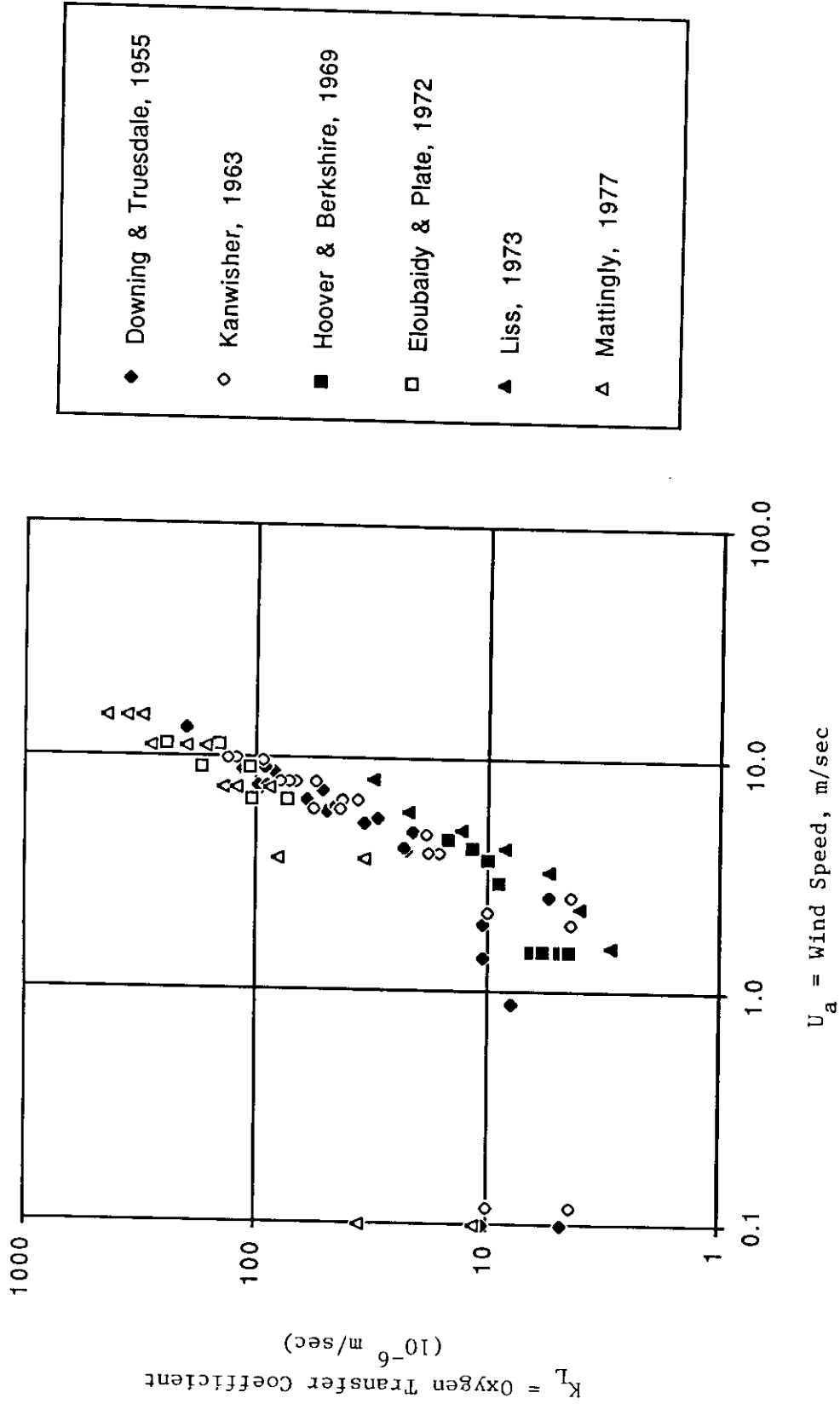
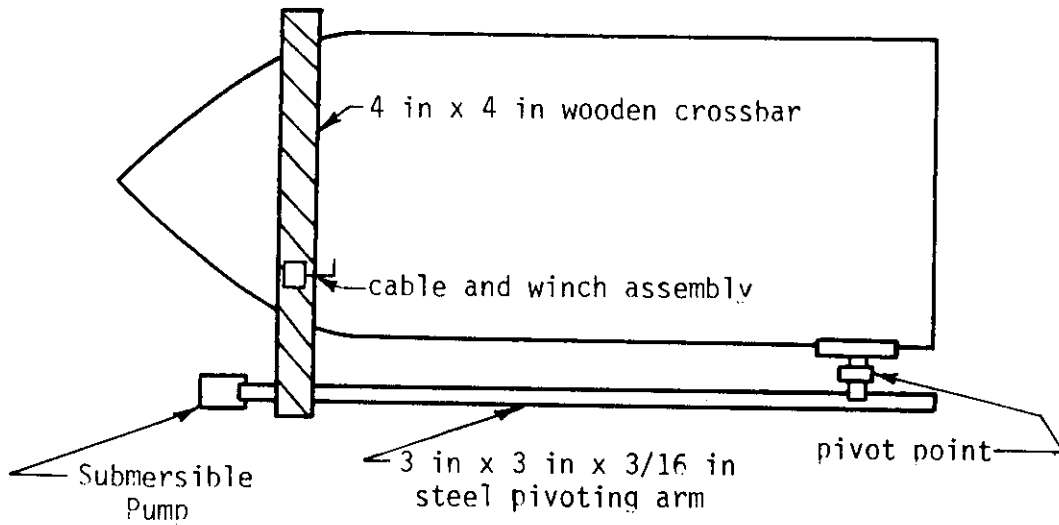
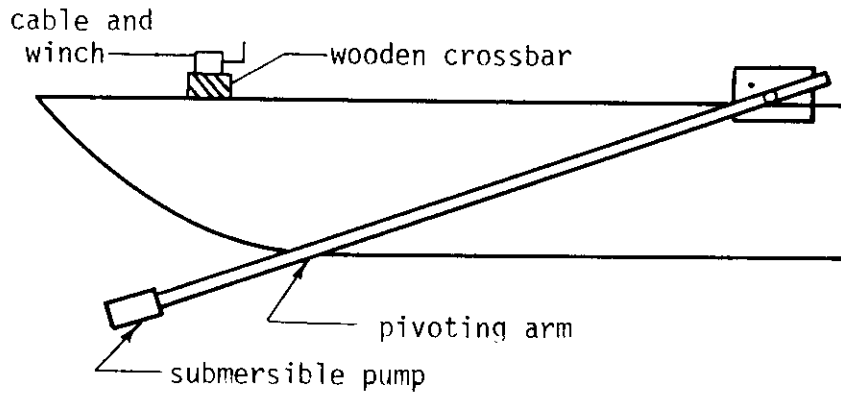


FIGURE 4.4 - EFFECT OF WIND SPEED ON OXYGEN TRANSFER COEFFICIENT FOR TYPICAL LABORATORY DATA (Kim and Holley, 1988)



PLAN



ELEVATION

FIGURE 4.3 - PUMP ARM ASSEMBLY (Bales and Holley, 1987)

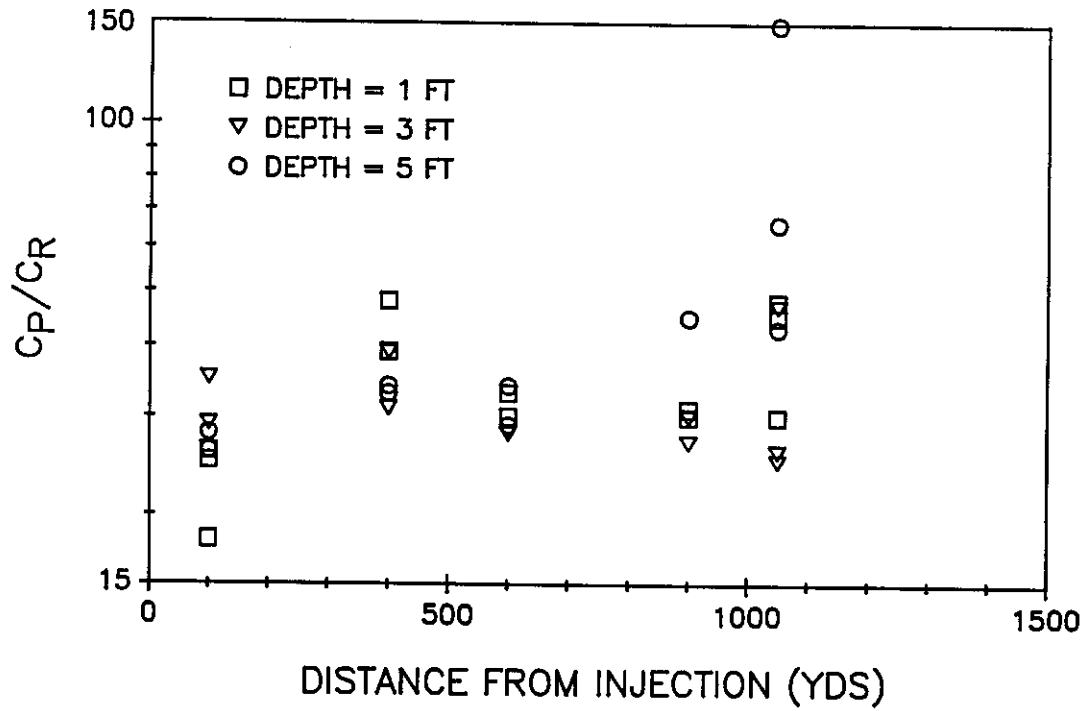


FIGURE 4.5 - FIELD TRACER GAS TEST RESULTS

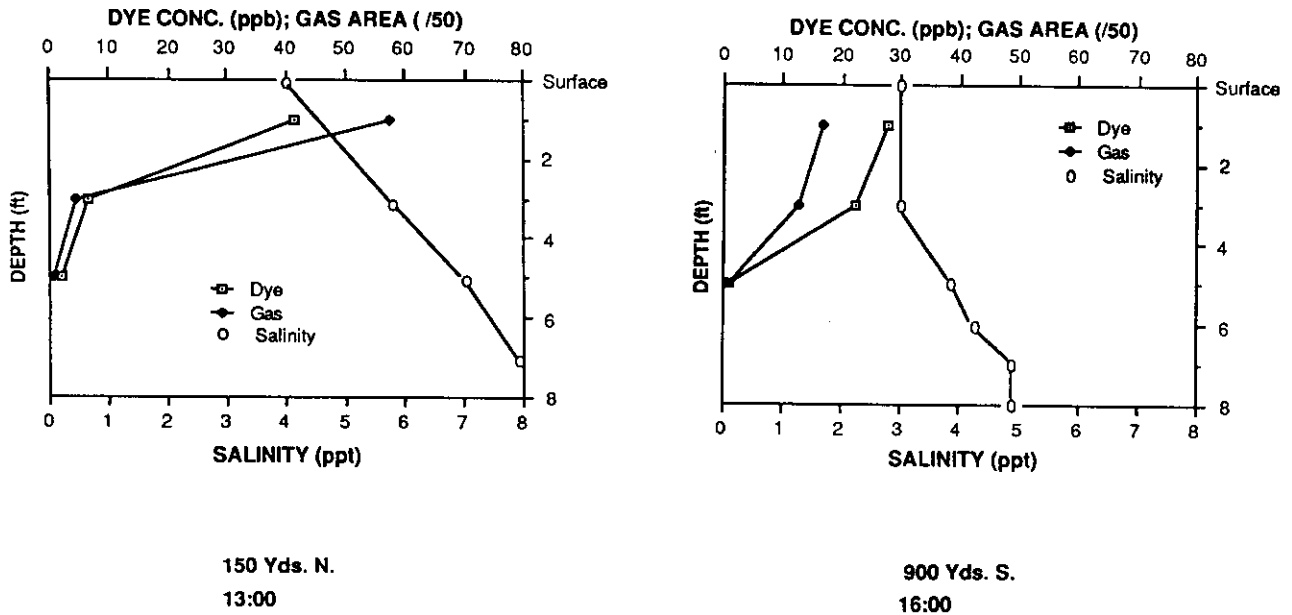


FIGURE 4.6 - SALINITY, PROPANE, AND RHODAMINE-WT PROFILES FROM JUNE 20, 1986

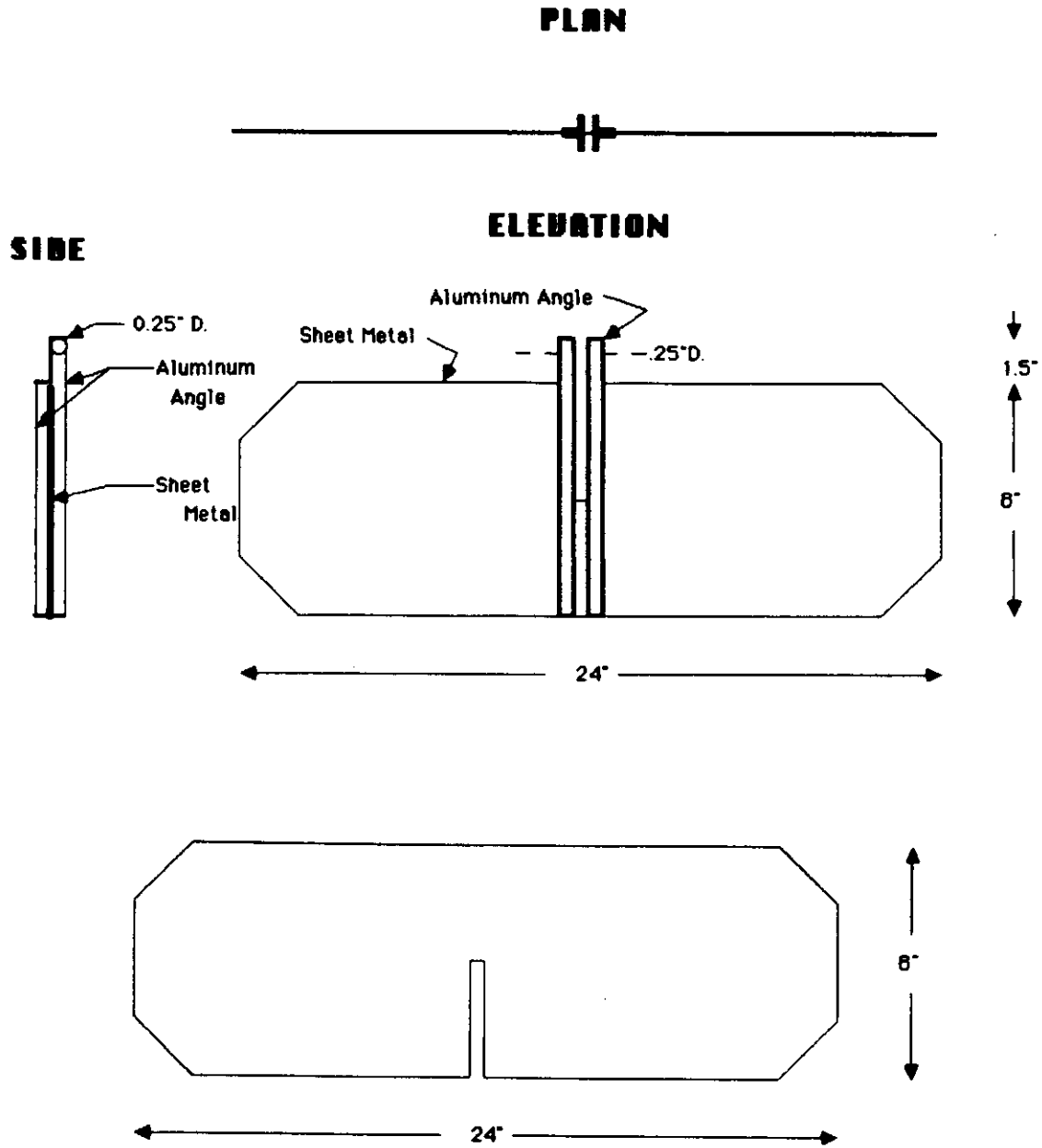


FIGURE 4.7 - DIAGRAM OF DROGUE FINS

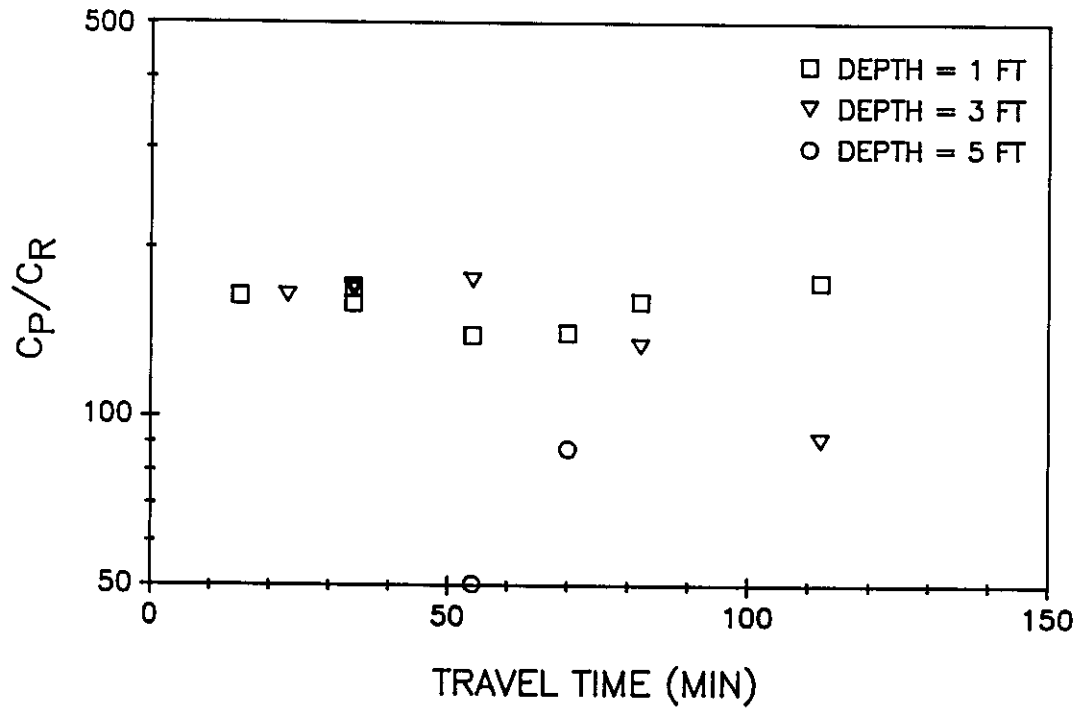


FIGURE 4.8 - FIELD TRACER GAS TEST RESULTS
JULY 29, 1986

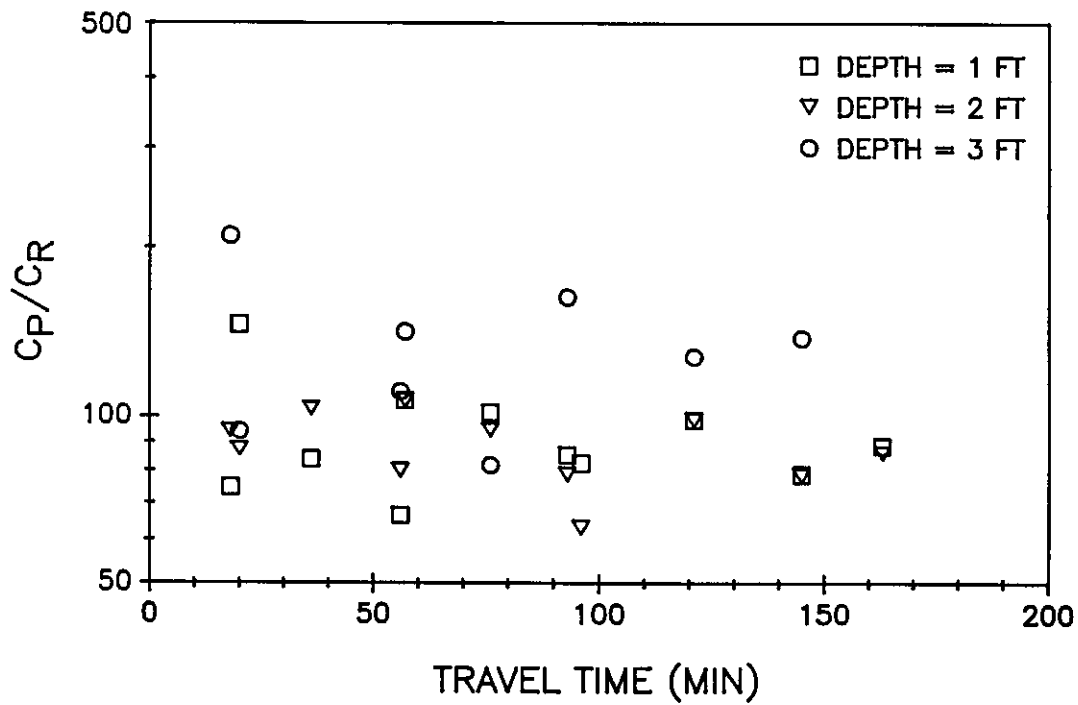


FIGURE 4.9 - FIELD TRACER GAS TEST RESULTS
JULY 30, 1986

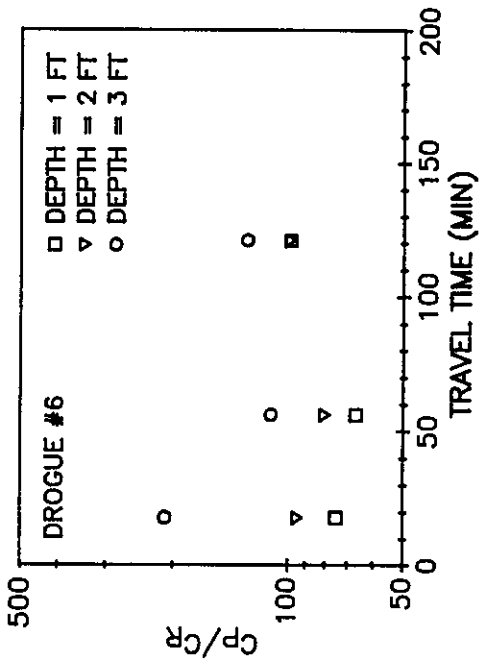
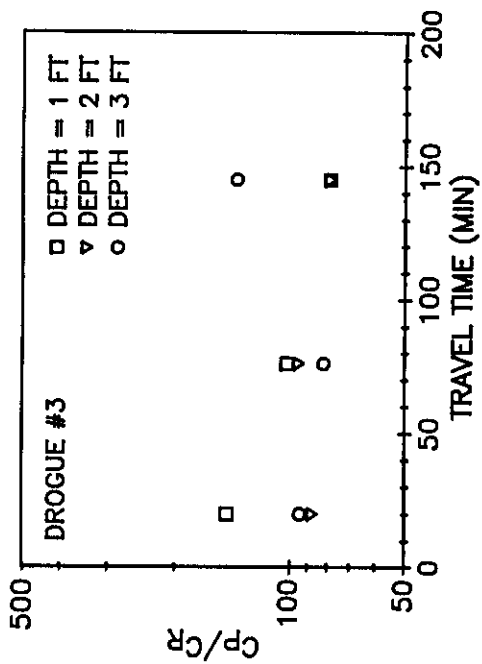
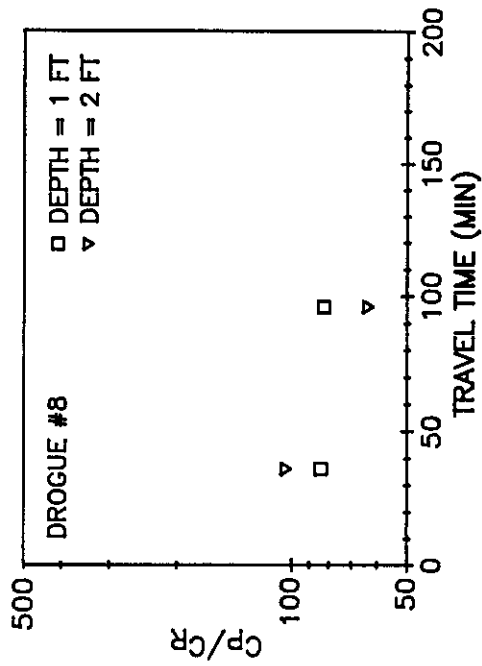
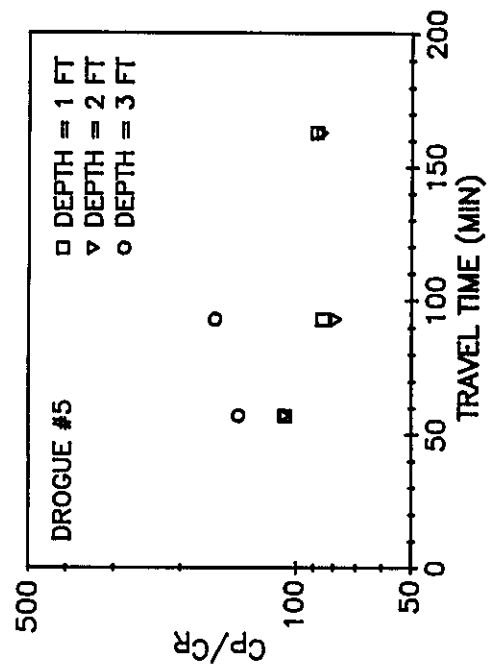


FIGURE 4.10 - FIELD TRACER GAS TEST RESULTS FOR FOUR DROGUES

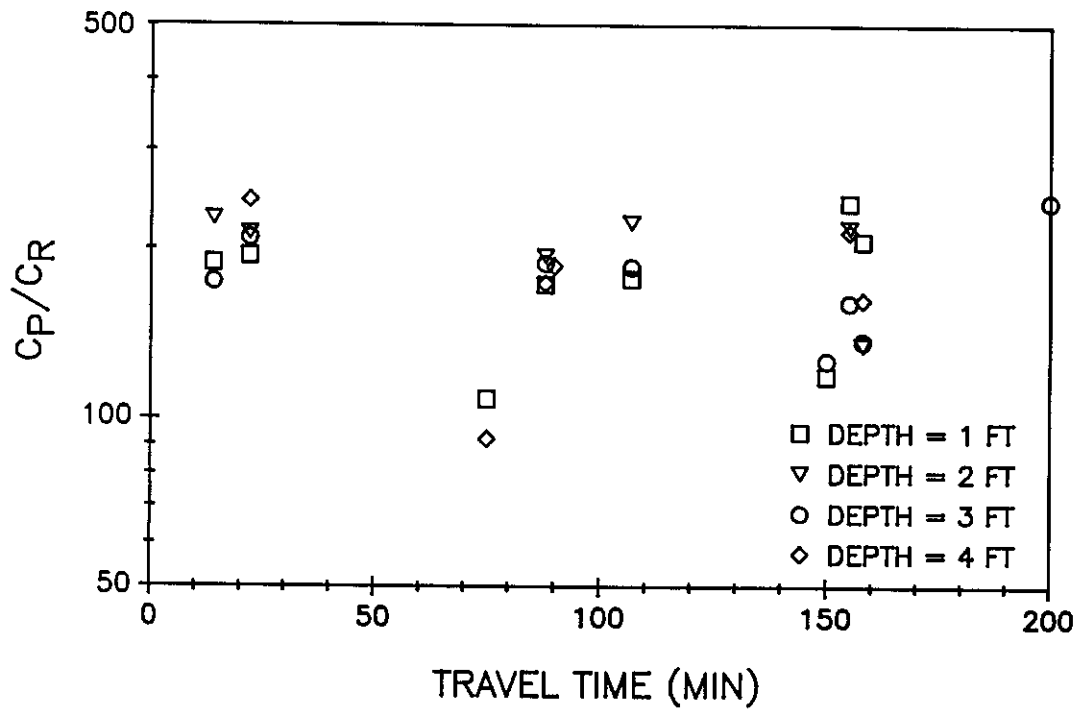


FIGURE 4.11 - FIELD TRACER GAS TEST RESULTS
JULY 31, 1986

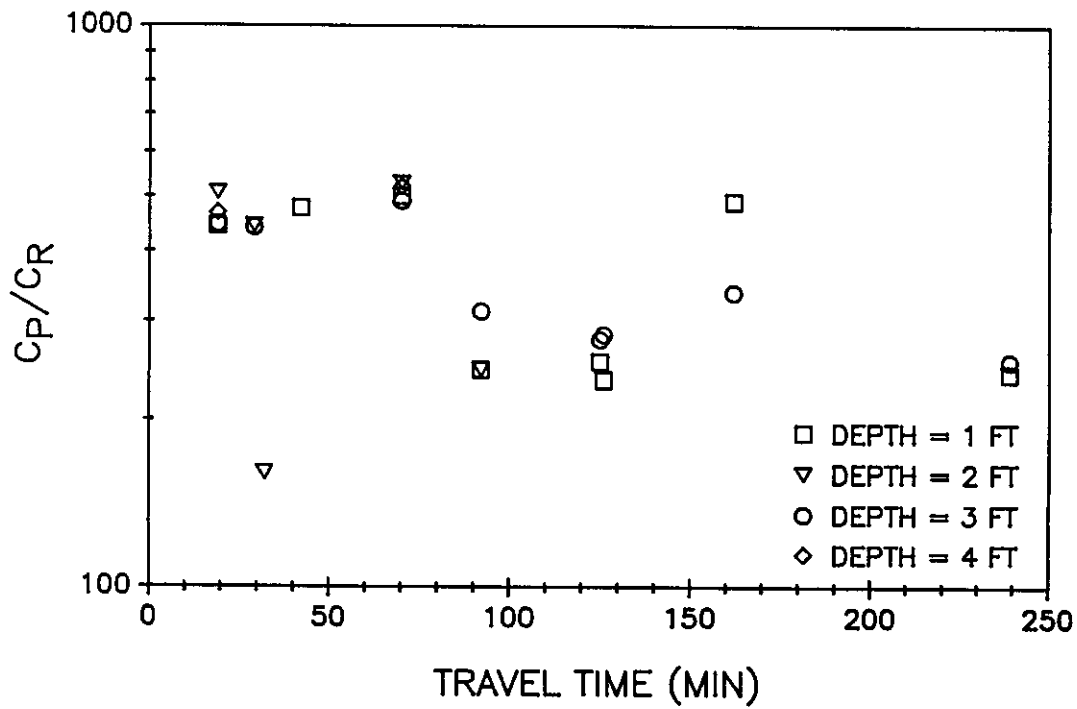


FIGURE 4.12 - FIELD TRACER GAS TEST RESULTS
AUGUST 1, 1986

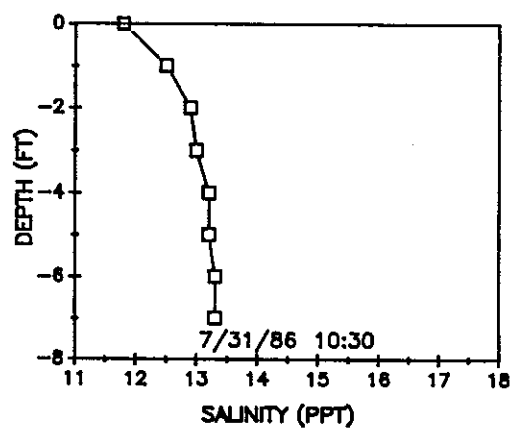
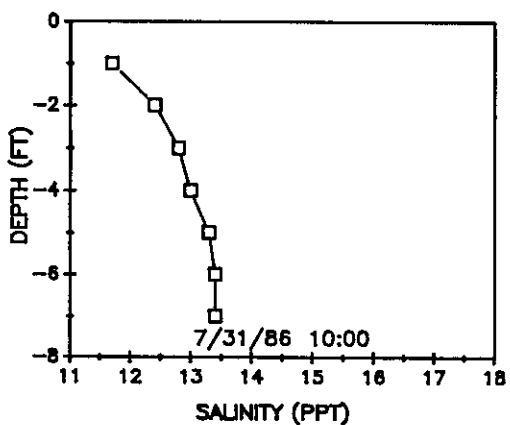
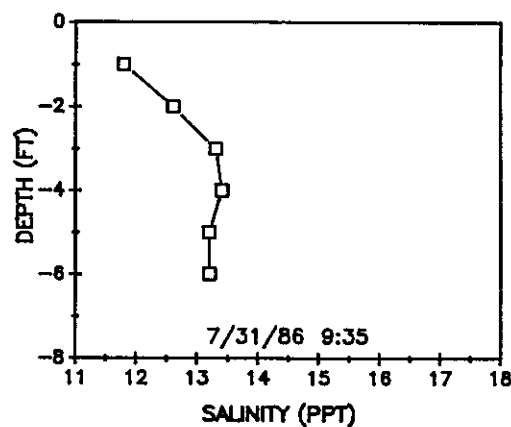
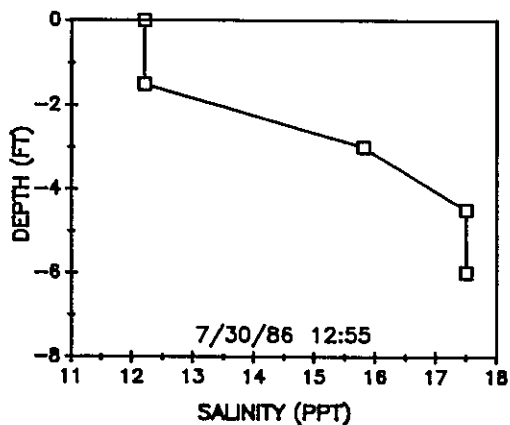
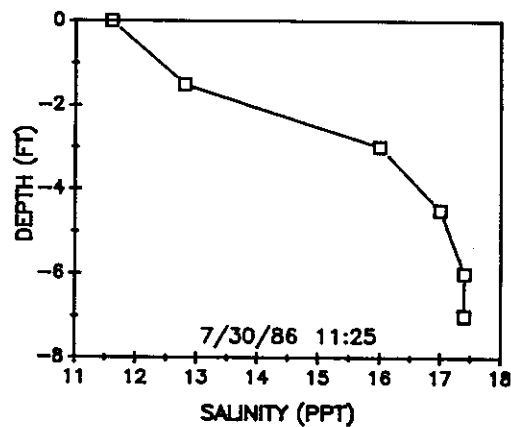
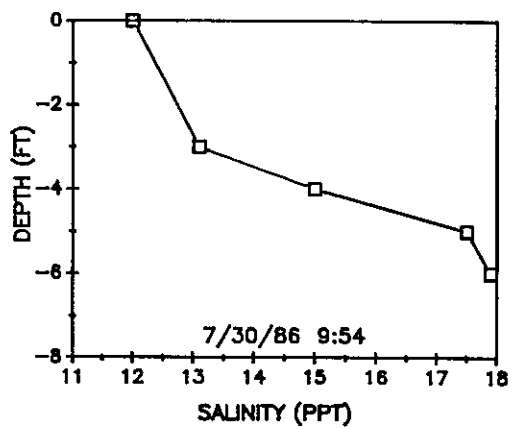


FIGURE 4.13 - SALINITY PROFILES

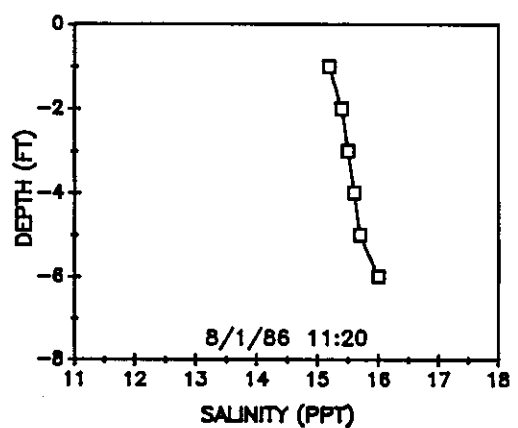
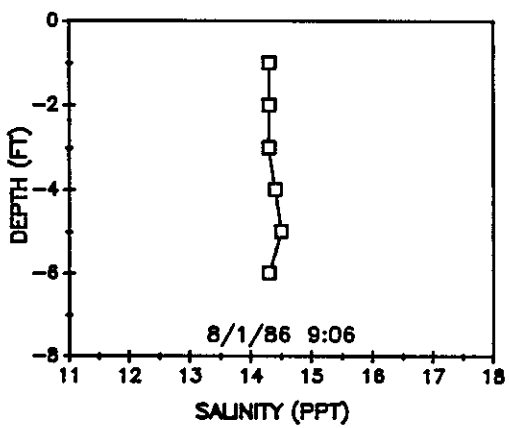
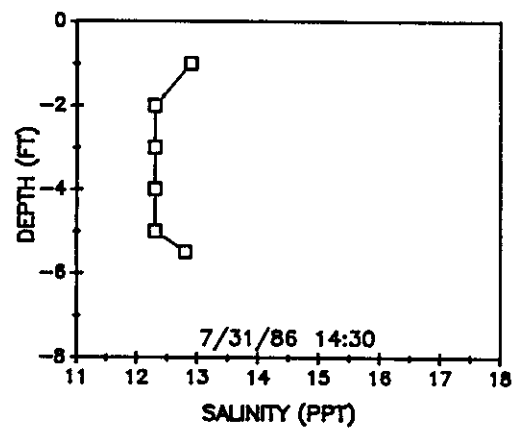
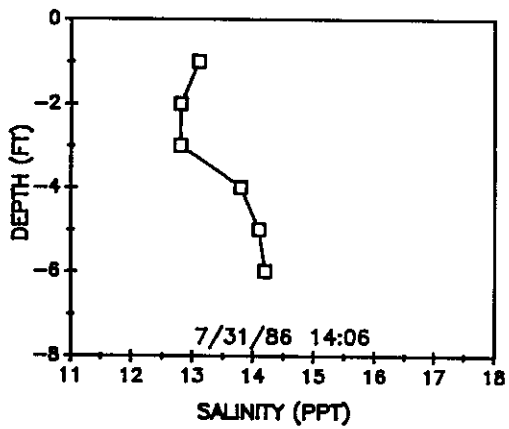
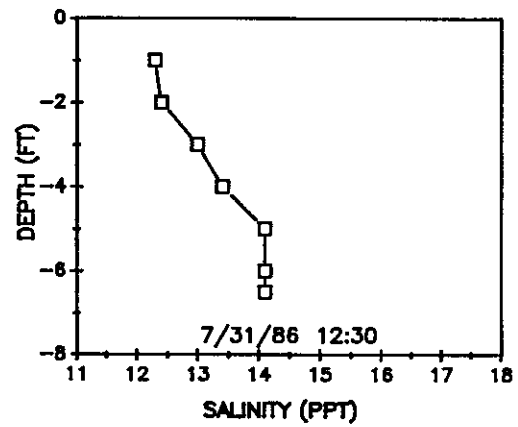
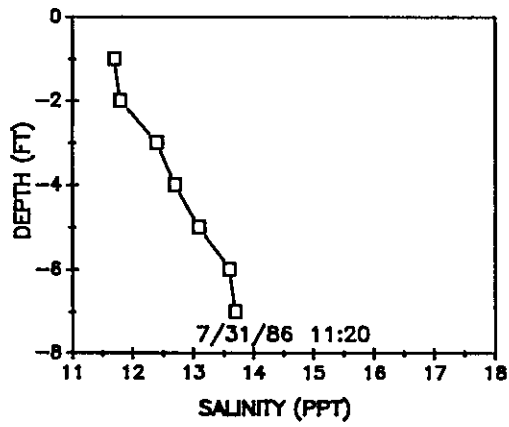


FIGURE 4.14 - SALINITY PROFILES

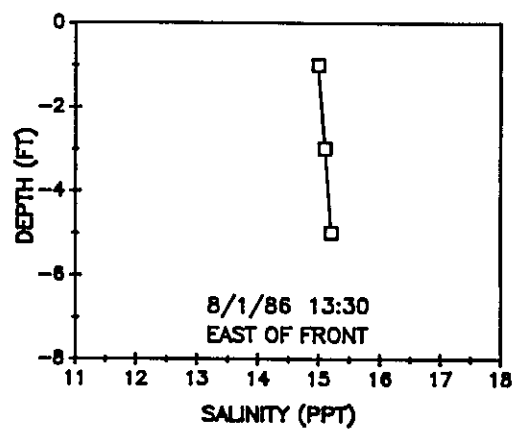
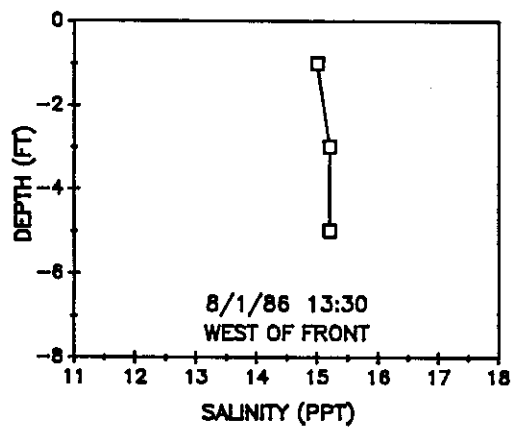


FIGURE 4.15 - SALINITY PROFILES

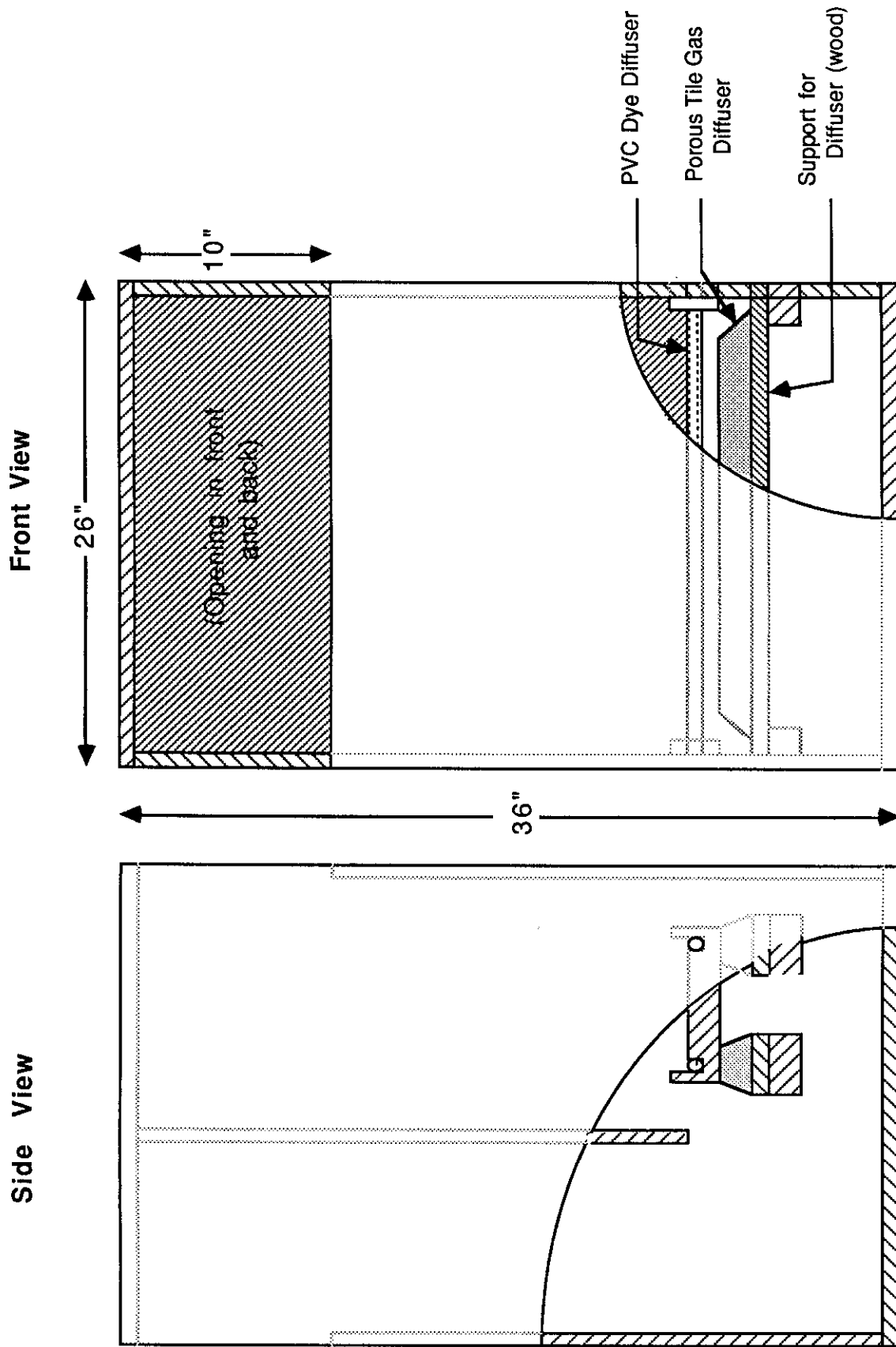


FIGURE 4.16 - INJECTION BOX

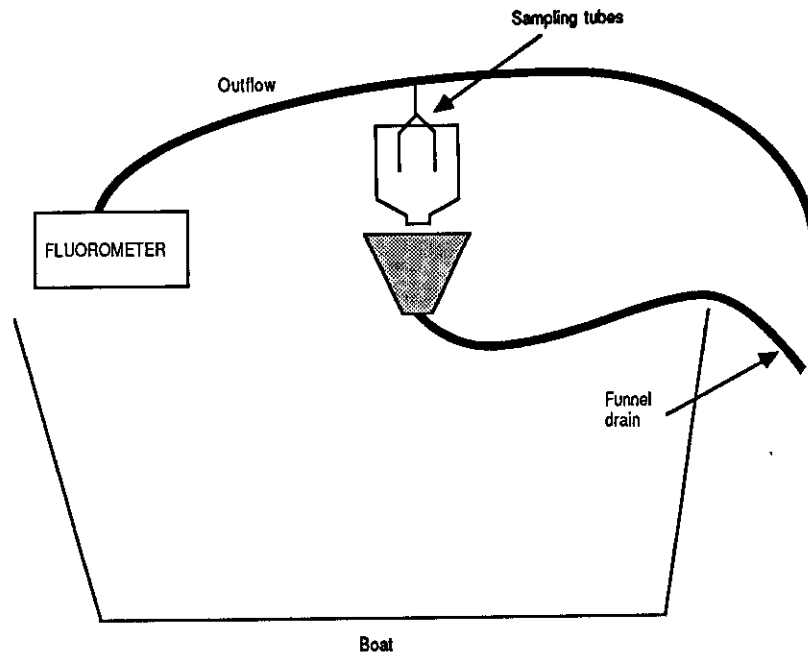


FIGURE 4.17 - SAMPLING EQUIPMENT MODIFICATION

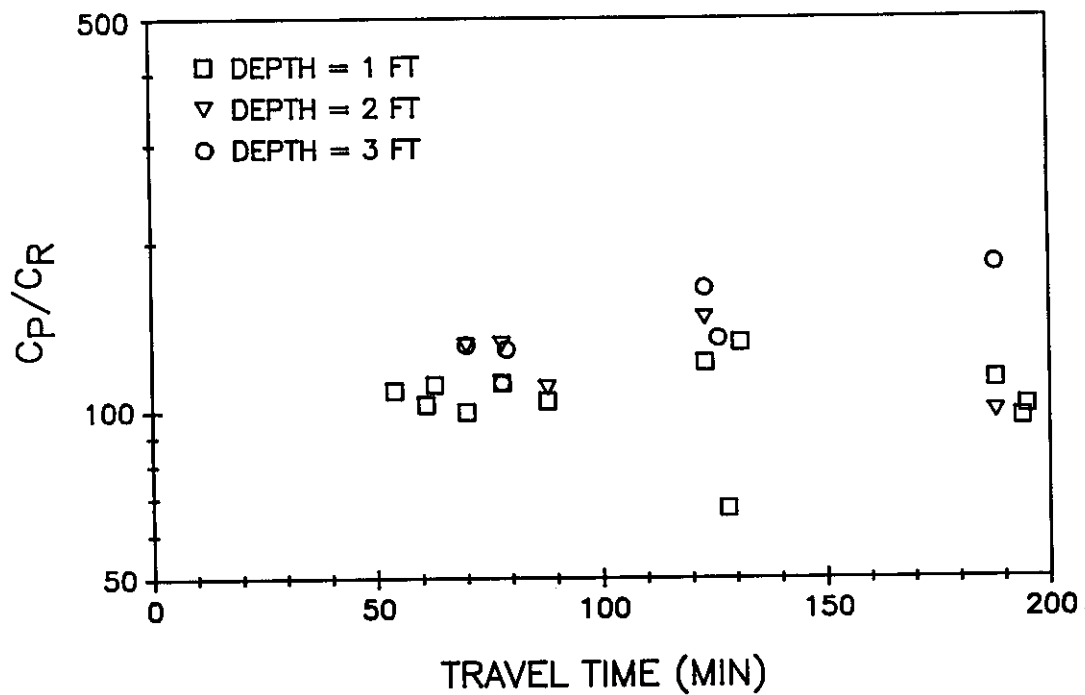


FIGURE 4.18 - FIELD TRACER GAS TEST RESULTS
APRIL 2, 1987

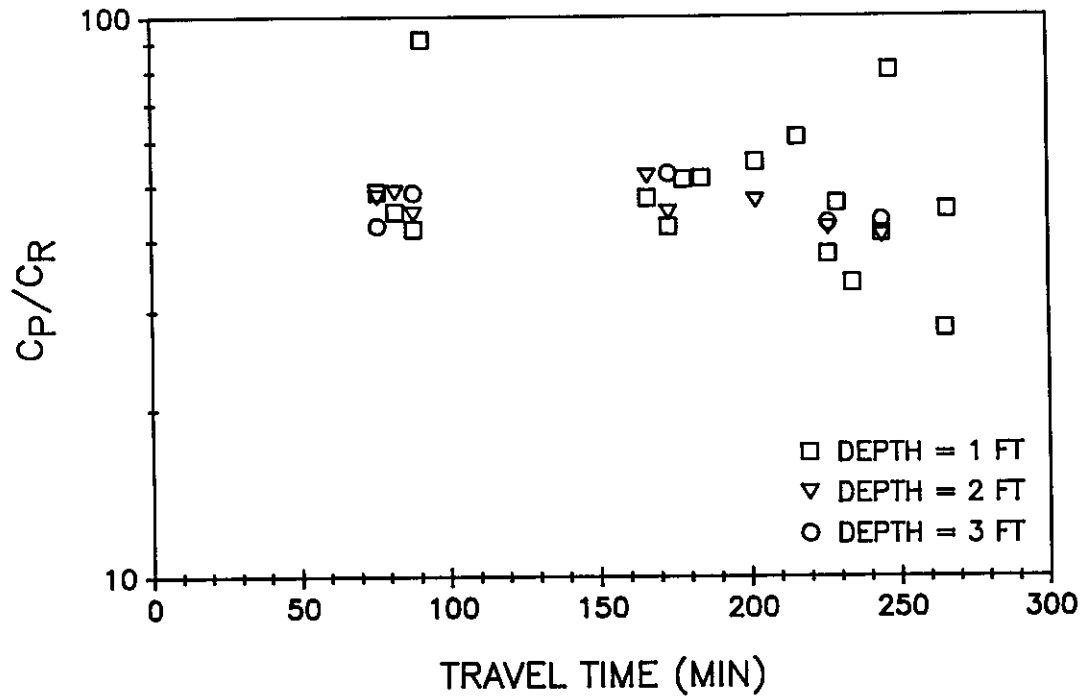


FIGURE 4.19 - FIELD TRACER GAS TEST RESULTS
APRIL 3, 1987

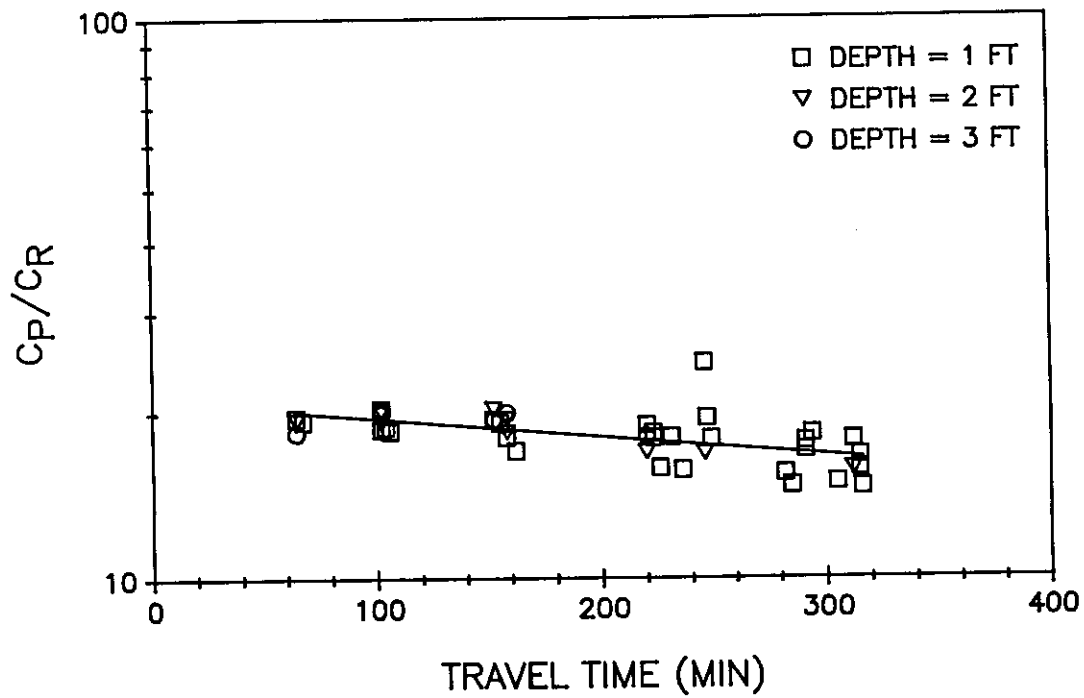


FIGURE 4.20 - FIELD TRACER GAS TEST RESULTS
APRIL 4, 1987