

ATHABASCA RIVER
WINTER REAERATION INVESTIGATION
FINAL REPORT

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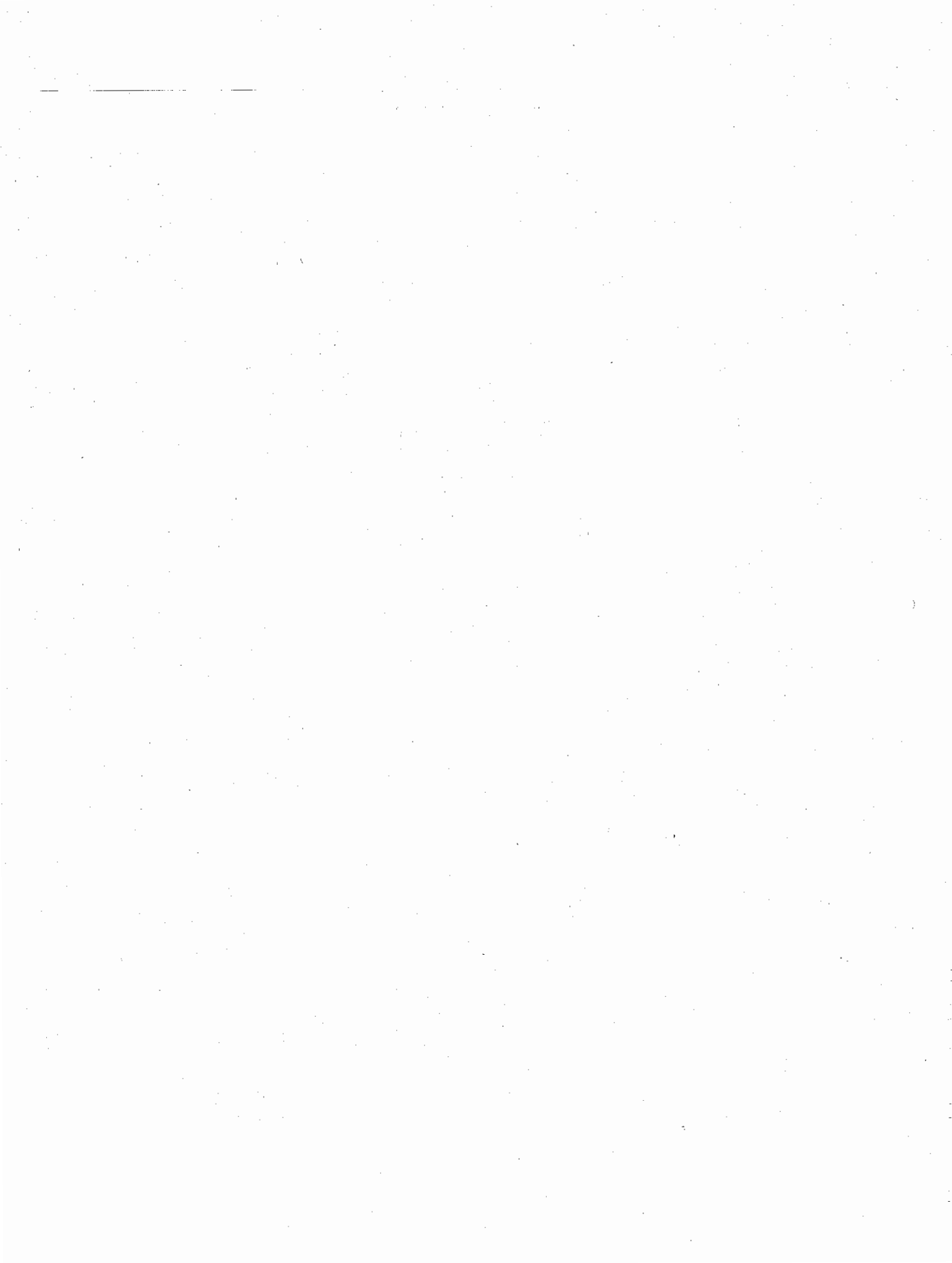
1D	one dimension	
B	channel width	(L)
BOD	biological oxygen demand	(M L ⁻³)
BPS	basic parameter set	
c	constituent	(M L ⁻³)
CBOD	carbonaceous BOD	(M L ⁻³)
C _s	saturation concentration	(M L ⁻³)
DO	dissolved oxygen	(M L ⁻³)
e	transverse diffuse coefficient	(unitless)
F	mass distribution factor	(unitless)
H	average depth	(L)
K	gas transfer rate	(t ⁻¹)
K ₂	reaeration rate	(t ⁻¹)
K ₃	BOD sedimentation	(t ⁻¹)
K ₄	BOD oxidation rate	(t ⁻¹)
K _n	nitrification rate	(t ⁻¹)
K _r	overall BOD removal rate	(t ⁻¹)
K _T	tracer gas transfer coefficient	(t ⁻¹)
L	length	
m	absorption rate	(t ⁻¹)
M	mass	
N	area under tracer gas cloud	(M L ³ t)
N _{1,2}	area under tracer gas cloud at station 1, 2	(M L ³ t)
NOD	nitrogenous oxygen demand	(M L ⁻³)
q	diffuser efficiency	(unitless)
Q	river flow rate	(L ³ t ⁻¹)
R	ratio tracer gas: oxygen transfer rate	(ratio)
R _E	ratio oxygen to ethylene transfer coefficient	(ratio)
R _{Kr}	ratio oxygen to krypton transfer coefficient	(ratio)
R _P	ratio oxygen to propane transfer coefficient	(ratio)
S	natural oxygen source/sink	(M L ³ t ⁻¹)
S'	disturbed oxygen source/sink	(M L ³ t ⁻¹)
t	time	

LIST OF SYMBOLS (continued)

θ	temperature correction parameter	(unitless)
t_B	time of passage	(t)
t_t	travel time for test reach	(t)
U	average flow velocity	(L t ⁻¹)
V	water column volume	(L ³)
X	longitudinal distance from release point	(L)
X'	dimensionless longitudinal distance	(unitless)
y	transverse distance	(L)

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1.0 INTRODUCTION

Proposed and existing pulp mill developments in the Athabasca River Basin impact on winter dissolved oxygen conditions in the rivers that receive their effluent. In 1987, Alberta Environment started using water quality models to simulate dissolved oxygen levels. This information was used to formulate effluent standards and for management of basin water quality. Under winter conditions river oxygen is consumed by the oxidation of organic materials (e.g. pulp mill effluent), and biologically mediated decay of organic sediment (sediment oxygen demand). Oxygen levels are replenished by the addition of oxygenated tributary water and transfer of oxygen from the atmosphere (reaeration). Water quality modelling requires quantification of rates for each oxygen sink and source. The rates used for the initial modelling were based upon published values and professional judgement. Modelling results indicated that reaeration is one of the most sensitive parameters affecting the oxygen balance under winter conditions. For this reason, it is essential that the reaeration rate used for modelling purposes is based on actual field measurements.

Under winter conditions, the river is effectively covered with ice. This would minimize replenishment of river oxygen through reaeration. However, some transfer of oxygen to water may occur within open water leads and from air trapped under the ice. Our objective was to design a procedure and quantify the extent of reaeration under ice cover conditions in the Athabasca River (determination of the reaeration coefficient, K_2). This study is the first documented attempt to successfully measure under ice reaeration. The method was developed and tested with state-of-the-art technology and professional advice and assistance from internationally recognized experts in the area of reaeration.

This report describes the theory of air to liquid gas exchange, methods to measure reaeration, the procedure designed to measure

under ice reaeration, results of the field study, and conclusions from the study.

2.0 REAERATION MEASUREMENT THEORY

The theory of air to liquid gas exchange is presented below. Symbol notation and units are included in the List of Symbols.

2.1 Background

In unstratified rivers, the dissolved oxygen (DO) concentration (c) is generally uniform with depth. The absorption rate (m) per unit of volume (V) in the water column is:

$$m = K_2V(C_s - c) \quad (2.0)$$

C_s is the saturation concentration and K_2 is the rate coefficient for reaeration per unit volume of water. During the 1960's and 1970's many investigators believed that it should be possible to develop a universally applicable predictive equation for K_2 in river systems. Although many different equations were proposed no single approach was universally accepted. Rathbun's (1977) review includes references to this work and most of the published critical reviews. General predictive equations are useful because it is not possible to measure K_2 for every river under different flow conditions. However, there has been renewed interest in field measurements for determining K_2 because of the introduction of tracer gas techniques. These results could be used to develop predictive equations that could be applied on a more local or regional basis.

These sections consider the measurement of K_2 for oxygen directly and indirectly with other gas tracer techniques. Related transport considerations are also discussed.

2.2 Transport of Dissolved Mass in Rivers

2.2.1 Processes Affecting Transport

Advection and diffusion are the primary transport mechanisms for dissolved substances. These physical processes are complex both spatially and temporally. Dissolved substances are maintained in the aqueous matrix by molecular forces and they are not influenced by gravitational forces (settling). Dissolved constituents can, however, undergo transformations, reactions and phase changes (gas to liquid). Depending on the degree to which a dissolved substance is mixed with the river flow, advection and diffusion may be viewed as different parts of the transport processes. For example, advection may refer to the transport due to the average flow velocity for the entire cross section or for a reach of the river. Advection may also refer to the velocity at one point in one cross section. Similarly, diffusion may be the result of all of the mixing processes within a cross section or it may refer to only the effects of turbulence at a point in a cross section. The physical processes represented by these terms depend on the scale of the problem being considered.

Transport processes in rivers are also affected by:

- 1) initial conditions, i.e. the initial spatial and temporal distribution of the substance being transported or of other substances (e.g. BOD) which influence transport,
- 2) condition of the physical boundaries (e.g. storage in "dead water" regions), and
- 3) other physical, chemical, and biological processes, such as gas transfer at the water surface, settling, deposition, entrainment, chemical reactions, biological

degradation, adsorption, etc.

2.2.2 Characteristics of Concentration Distributions

In many rivers without vertical density gradients, neutrally buoyant dissolved substances usually become well-mixed vertically within a distance of no more than about 50 to 100 times the flow depth downstream of an outfall or injection point. However, the transverse mixing processes are such that dissolved mass may occupy only a fraction of the channel width (B) for large flow distances (in medium and large rivers) and the concentration distribution in the transverse direction (y) may be significantly different from what would be indicated by a one-dimensional (1D) analysis. The degree of transverse variation of concentration distributions depends on the dimensionless longitudinal distance x' defined as:

$$x' = \frac{x/U}{B^2/e_y} = \frac{\text{characteristic flow time}}{\text{characteristic transverse mixing time}} \quad (2.1)$$

where x is the longitudinal distance from the release point, U and e_y are the average flow velocity and transverse diffusion coefficient, respectively (Fischer et al., 1979). Although the dimensionless distance required to approach transverse uniformity depends to some degree on the flow hydraulics and on the initial conditions for the release (Fischer et al., 1979). As a first approximation, $x'_{1D} = 0.2$ to 0.3 can be used as a criterion to estimate the flow distance required for obtaining transverse uniformity. For $x' < x'_{1D}$, transverse variations of velocity and mixing are major components of the transport process (two dimensional). If there is a continuous release from a diffuser which covers the full width of a river, the concentration distributions will be uniform in the transverse direction beginning immediately downstream of the diffuser. This would also require no transverse variations of any other sources and sinks that could

affect the concentration distributions (Section 2.2.4).

In general, concentration distributions in rivers can be either constant or variable. The river flow, release rate, and all processes affecting instream concentrations must be constant over time in order to have steady state conditions.

2.2.3 Temporal Distributions of Effluent or Injection Discharges

Loadings from treatment plants are frequently continuous over long periods of time. Even though the loading rate may vary in time, it is often assumed to be constant in analyses. For continuous loadings, longitudinal mixing in rivers is normally negligible so that plug flow analyses can be used. If $x' < x'_{1D}$, then a 2D plug flow representation is needed. Longitudinal mixing is important when there are short-duration accidental spills or releases.

For the disturbed equilibrium and tracer gas techniques, the injections can be either long duration (up to several hours) or short-duration (essentially instantaneous or up to several minutes long). With long-duration injections, the objective is to develop a steady-state condition or plateau at each measurement cross section. For short-duration injections, measurements are made as a transient "cloud" passes the measurement stations.

2.2.4 In-Stream Effects on Transverse Uniformity

Dissolved oxygen may be transversely uniform in a river upstream of an outfall. If the BOD "plume" from the outfall is not, however, uniform in the transverse direction, then DO will be lowered by the BOD in the part of the cross sections containing BOD. This results in transverse variations of DO concentrations (Rood and Holley, 1974). Even when the BOD is uniform across the river width, other processes such as photosynthesis, respiration,

benthic demand can produce nonuniform transverse variations of DO.

Churchill et al. (1962) presented an extensive set of DO measurements in streams without any point pollutant loads. The initial deficit existed because of oxygen-deficient water being released from reservoirs. Essentially all of the data showed definite transverse variations of DO with higher concentrations near the banks. The DO variation within a cross section varied from 0.1 mg/L to 1 mg/L or from 1% to 18% of the average deficit. Reanalysis of their data indicated that the observed variations were probably due to the longer travel time and shallower depths near the banks (Holley and Jirka, 1986). Less water was beneath each unit of surface area near the banks and the water was moving more slowly than in the deeper regions. Hence, oxygen which is transferred through the surface per unit of time will produce higher DO concentrations in shallow, slow moving waters.

2.3 Error Analysis

Sources of errors in experimentally determined gas transfer coefficients can be classified as procedural errors, errors due to uncertainty of the parameters used in the analysis, and random measurement errors (Hovis et al., 1982).

2.3.1 Procedural Errors

The procedures used for a gas transfer experiment may be different from those assumed in analyzing the data. Procedural errors may arise from:

- 1) poor selection or inadequate number of sampling points, e.g. from assuming that 1D conditions exist when they do not,

- 2) failure to collect samples in a manner to assure that the gas concentration in the sample bottle is the same as in the river,
- 3) failure to adequately preserve samples between collection and analysis,
- 4) selection of a test reach that is not representative of the entire reach of interest, and
- 5) failure or inability to account for all sources or sinks of the gas within the test reach.

2.3.2 Uncertainty of Parameters

In analyzing data on gas transfer rates (depending of the method being used), some of the important parameters may be the saturation concentration (C_s), the temperature correction parameter for K_2 (θ), or the ratio of transfer rate coefficients for a tracer gas and oxygen (R). For studies with measurement of oxygen concentration, C_s and θ enter the analysis, while for tracer gases θ and R enter the analysis since $C_s = 0$ for tracer gases. Uncertainties in any of these parameters can have a direct impact on the accuracy of K_2 values obtained from field testing.

Since C_s changes with water quality (dissolved solids, etc.), it is preferable to determine C_s directly from samples of river water which have been sterilized and mixed to saturation in the laboratory for the same temperature that existed in the field. Values of θ from 1.006 to 1.024 have appeared in the literature, and there is some evidence that θ depends on temperature (Rainwater and Holley, 1983) and turbulence (Metzger, 1968). Thus, at present it is difficult to know the potential errors in a given value of θ even though some specific values are quoted routinely in the literature.

Experiments by Tsivoglou et al. (1965), Rathbun et al. (1978), and Rainwater and Holley (1983) indicate that R does not change with temperature for krypton and propane (the most commonly used tracer gases). These results imply that θ is the same for oxygen and for the tracer gases. Tsivoglou et al. (1965) found R_K to be 1.22 ± 0.06 from 26 tests for temperatures from 13°C to 32°C . Using Rathbun et al.'s (1978) results from 34 tests with propane and their own results from 28 tests for 4°C to 32°C , Rainwater and Holley (1983) obtained $R_p = 1.39 \pm 0.11$ for propane.

2.3.3 Random Errors

There are random errors in all measurements. If these errors can be quantified, it is possible to analyze the propagation of the errors through the calculations and obtain an indication of the possible errors in K_2 resulting from the random measurement errors (e.g. in concentrations, saturation concentrations, travel times, etc.). The analysis is based on standard techniques for propagation of errors (Ang and Tang, 1975). Examples for measurements of surface exchange coefficients are given by Holley and Yotsukura (1984) and by Rainwater and Holley (1983).

At least three important points can be made about the propagation of errors:

- 1) If one of the variables has a large measurement error, this error will dominate in the calculation of K_2 and little may be gained by obtaining extremely precise values for all of the other variables.
- 2) If one (or more) of the variables is expected to contribute a major part of error in K_2 , then the overall error can be reduced by multiple measurements of that variable.

- 3) The relative error in K depends on the value of $K t_r$, where K is either K_2 or K_r for the tracer gas depending on the type of test being done and t_r is the flow time for the test reach. It should be the goal to have $K t_r > 1$ (Yotsukura et al., 1983). For values greater than unity, the errors from the individual variables are attenuated in calculating K . The errors are amplified for values less than unity. So for rivers with a low K_2 , say $0.5 \text{ (day}^{-1}\text{)}$, a test reach with a travel time greater than or equal to two days is desirable. Rivers with higher K_2 rates can be studied with shorter reach travel times. This is an important consideration which has not been recognized in planning some experimental programs.

2.4 Oxygen Balance Method

2.4.1 General Principles

This section is included because of the historical place of the oxygen balance approach in reaeration studies and to illustrate the potentially serious error problems that have led to the preference for other methods, especially the gas tracer methods.

Streeter and Phelps (1925) introduced the concept of using a 1D oxygen balance to obtain reaeration rate coefficients in rivers. Their basic approach has been expanded and generalized in later works. The approach involves measuring the change in dissolved oxygen concentration between the upstream and downstream ends of a reach for steady state conditions. All sources and sinks of DO except reaeration are measured or calculated. The reaeration is the residual of the measured DO change and the evaluated sources and sinks.

2.4.2 Typical 1D Applications

A typical approach (Bennett and Rathbun, 1972; Krenkel and Novotny, 1980) for steady state conditions is to include factors such as:

1. surface reaeration;
2. carbonaceous BOD, CBOD, with $dCBOD/dt = -K_1CBOD$ where K_1 is the overall BOD removal rate coefficient including K_1 for deoxygenation in free-flowing water, K_2 for removal of BOD by sedimentation into an anaerobic benthic layer, and B for absorption;
3. nitrogenous oxygen demand NOD, with $dNOD/dt = -K_2NOD$ where K_2 is the nitrification rate coefficient;
4. benthic oxygen demand;
5. photosynthetic production;
6. plant respiration; and
7. non-point sources.

K_2 can be obtained by some type of best-fit analysis using measurements or empirical estimates of all of the variables and rate coefficients in the mass balance except K_2 .

2.4.3 Error Analysis

2.4.3.1 General Considerations

The indirect oxygen balance approach may lead to relatively large errors in K_2 . Some related results are mentioned in the next subsection. In principle, even though the calculations would be

somewhat tedious, analysis of propagation of errors could be applied to analytical solutions of equations representing oxygen balances to determine the potential error in K_2 . The result would be that the error in K_2 would be some type of combination of the errors in all of the other terms in the equation. In a qualitative sense, the resulting K_2 values should not be expected to be very precise since:

1. some of the biochemical processes (e.g. BOD) and physical processes (e.g. deposition and scour) have a lot of inherent variations and corresponding uncertainty, and
2. many of the processes have strong spatial variations but can be measured at relatively few points so that there is uncertainty concerning whether the measured values are representative of averages for the study reach.

2.4.3.2 Sensitivity Analysis

Bennett and Rathbun (1972) used a sensitivity analysis with assumed errors in various parameters to obtain estimated potential errors in K_2 values calculated from oxygen balances. Their approach was to:

1. assume typical sets of parameters or basic parameter sets (BPS) for use in a DO balance equation to calculate K_2 and select the BPS's which demonstrated the greatest sensitivity;
2. vary one, or occasionally more, of the input parameters to determine the sensitivity of the calculated K_2 to that parameter for each BPS;
3. estimate average and maximum errors for the input parameters which they considered; and

4. multiply the estimated errors by the minimum, average, and maximum slopes of the sensitivity curves to obtain indicated errors in K_2 .

They gave a composite summary with errors in K_2 ranging from essentially zero to 24 day⁻¹. It is difficult to know what significance to place on the numerical values since Bennett and Rathbun (1972) did not identify the errors with specific BPS's or give relative errors and since the range of some of the input parameters used in determining the slopes was greater than normally expected errors. Nevertheless, their results may give an indication of the input parameters which, because of the combination of sensitivity and possible input errors, are likely to cause the greatest errors in K_2 . The parameters with the greatest uncertainty were K_d , photosynthesis, and the measured deficits at the downstream and upstream ends of the reach. The relative errors from these four parameters were 1.0:0.8:0.5:0.4, respectively. All of the other errors (including those due to sedimentation, addition of BOD from bottom deposits, and adsorption) were less than half of the smallest of these four.

2.5 Disturbed Equilibrium Method

2.5.1 General Concept

Gameson et al. (1955) introduced the disturbed equilibrium technique for determining reaeration rate coefficients in small streams. The technique has been applied by Gameson and Truesdale (1959), Owens et al. (1964), and Zogorski and Faust (1973a, 1973b), among others, with various modifications. Gameson et al.'s concept was to introduce catalyzed sodium sulphite into a stream to reduce the DO concentration. Reaeration was determined from the difference between measured concentrations and the concentrations which would have existed under natural conditions without the

sulphite. If all sources and sinks of DO (except surface transfer) are not affected by the depressed DO concentrations, they cancel from the equations representing the transport for the natural and disturbed cases (but this occurs only under restrictive conditions). The original application had a steady-state injection. Later (Gameson and Truesdale, 1959; Zogorski and Faust, 1973b), the method was modified for short-duration releases of sodium sulphite. Gameson et al. (1955) and Zogorski and Faust (1973b) discussed several practical aspects of injecting the sodium sulphite. The large required quantities of sulphite would probably cause this method to be infeasible for medium and large rivers.

The assumption that all of the sources and sinks are the same both under natural conditions (S) and under disturbed conditions (S') is satisfied only for special situations. For example, K_1 may depend on DO concentration. Respiration rates of plants and bottom deposits may also depend on DO (Bennett and Rathbun, 1972). Thus, the assumption that $S = S'$ is questionable for a general case, and much of the potential attractiveness of the method is lost if S is not equal to S' . This discussion of the method is based on the assumption that $S = S'$ and must therefore be viewed as being for a rather idealized situation. Bennett and Rathbun (1972) included variation of respiration rates in their analysis of the disturbed equilibrium method. Even beyond the question of the natural sources and sinks, there are some indications that the catalyzed sulphite does not react as rapidly as first thought so that there may be a residual of sulphite which continues to consume DO during a test (Mattingly, 1977; Bennett and Rathbun, 1972). This results in lower estimates of K_2 .

The depression or oxygen deficit caused by the sulphite can be viewed as a quantity which is being transported by advection and dispersion and which is desorbing through the free surface area. The transport of the concentration defect is similar to that for tracer gases, but the concentration deficit in the disturbed

equilibrium method may be affected by sources and sinks (S , S' , and residual sulphite). This will not occur for an inert tracer gas.

2.5.2 Applications

Gameson et al. (1955) and Gameson and Truesdale (1959) used steady-state distributions in short reaches of small streams. They experienced difficulties in maintaining a steady-state injection of sulphite and found that the region of constant concentration had been eroded by longitudinal mixing at some cross sections. (See comments on required injection duration in Section 2.6.4). They modified the analysis to a method similar to the "area method" that has been used for some tracer gas studies (Section 6.3). However, they limited the analysis to short reaches so that linear variations in the concentration deficit could be assumed. Removing the restriction to short reaches is necessary to reduce the error in the estimate of K_2 ($K_2 t_c > 1$; Section 2.4.3).

2.5.3 Propagation of Errors

Although the error analysis must be done for idealized conditions it provides some indications of factors which can affect the accuracy of K_2 from the disturbed equilibrium techniques:

1. The importance of errors in C (the natural concentration) and C' (the concentration under the disturbed conditions) must be considered in relation to $(C - C')$, not relative to C or C' separately.
2. C' is a measured quantity, but C during the cloud passage must be estimated by interpolation from C values before and after the cloud.

Any errors in estimating C have a direct effect on K_2 . The accuracy of the interpolation is greater for shorter times of passage (t_B) of the concentration defect ($C - C'$) cloud if a stream has a natural temporal variation of C . The desirability of small t_B and large t_r (to have $K_2 t_r > 1$) are conflicting since t_B increases as t_r increases between measurement cross sections.

2.5.4 Alternative Methods

If the disturbed equilibrium methods are applicable in a given situation, then they could also be used by elevating the DO concentration with in-stream aerators rather than depressing the concentration with sulphite. Shieh and Davidson (1971) proposed using an aerator to create a sinusoidal upstream boundary concentration and proposed a method of data analysis which eliminated BOD but retained photosynthesis and respiration. The fact that longitudinal dispersion was neglected in their analysis places a limit on how rapidly the upstream concentration could be varied. This alternate method also suffers from the possibility that S is not equal to S' .

2.6 Tracer Gas Methods

2.6.1 Background

In an effort to obtain a direct measurement of the natural gas transfer in water bodies, Tsivoglou et al. (1965, 1968) proposed the use of gas tracers which are artificially dissolved in the water. Some of the desirable characteristics of a tracer gas are that it should:

1. have no sources or sinks other than surface transfer;
2. not be present in the water naturally;

3. be able to be measured in the microgram per litre range; and
4. have a transfer coefficient (K_T) which is approximately equal to K_2 (say, $\pm 50\%$) and which has a constant ratio (R) to K_2 for all temperatures, hydraulic conditions, and water quality conditions.

The basis for gas tracer methods has been well accepted (Bennett and Rathbun, 1972). However, there have not been extensive investigations of the effects of surface contamination and water quality on R or of possible interferences from processes such as adsorption or from chemical or biological reactions. Most applications have been in rivers, but there have been some in estuaries (Anon., 1972). Research is presently underway on extending the method into bays.

Tsivoglou et al. (1965, 1968) proposed using radioactive krypton as a gas tracer. The krypton method is accepted by the U. S. Environmental Protection Agency and is attractive because it uses a noble gas as the tracer. Because of training and licensing requirements for handling radioactive material, the krypton method has been practised by only a limited group. There is sometimes negative public sensitivity about possible adverse health effects from any amount of radioactivity in natural waters.

The U. S. Geological Survey undertook an effort to find acceptable nonradioactive tracer gases. Rathbun et al. (1975, 1978) proposed using ethylene and propane gases, which are low molecular weight hydrocarbons, and confirmed that the transfer coefficient ratios R_E and R_P are constant and independent of mixing intensity and water temperature in their mixing tank tests. Rainwater and Holley (1983) conducted an independent laboratory assessment of hydrocarbon gas tracers and found R_E and R_P values which agree with those of Rathbun et al. Use of ethylene was later discontinued due

to its apparent nonconservative behaviour in some situations.

For the hydrocarbon gases, Rainwater and Holley (1983) also examined possible adsorption onto sediments. Tests with five different suspended sediments showed no adsorptive losses. Nevertheless, the question of physical, chemical, and biological inertness of dissolved gas tracers has not been completely resolved (Tsivoglou, 1979; Rathbun et al., 1980). Rathbun et al. (1975, 1978) recognized that hydrocarbons may be subject to biodegradation. However, this effect is negligible in a field test with flow times of a few hours.

2.6.2 Some Assumptions in Field Methods

The concentration of tracer gas in solution can change due to surface desorption and due to mixing and dilution in the flow. To account for mixing and dilution, a conservative tracer is released in the same manner as the tracer gas. Since the hydraulic transport is a linear process (Eq. 2.2), the concentration distributions of two simultaneously injected tracers should each be proportional to the mass (M) of tracer released and should evolve in similar fashion due to the hydraulics. The relationship for two conservative tracers a and b with identical initial conditions is:

$$\frac{C_a}{M_a} = \frac{C_b}{M_b} \quad (2.2)$$

for all x, y, and t. It may be assumed that surface transfer is a first-order process if the analysis is limited to the region where the concentrations are uniform over the water depth. The tracer gas concentration decays exponentially with time and is reduced with mixing so that:

$$\frac{C(x,y,t)}{M} = \frac{C_c(x,y,t)}{M_c} \exp(-K_T t) \quad (2.3)$$

where C and M are for the tracer gas, C_c and M_c are for the conservative tracer. K_T is the tracer desorption coefficient and t is the time after tracer injection. After determining K_T , K_2 is obtained using the appropriate value of R (Section 2.3.3).

2.6.3 Short-Duration Injection Method

When a short-duration injection is used, a cloud of the tracer gas and the conservative tracer move downstream. Samples are taken as the cloud passes. If the cloud is well mixed in the transverse direction, then one sampling point at each cross section is representative of the entire cross section. If the cloud is not transversely mixed, then multiple sampling points may be needed at each cross section to determine the overall reaeration characteristics of the river. Because of the difficulty of taking multiple samples from a moving cloud, long-duration injection methods (Section 2.6.4) are frequently used when transversely uniform conditions do not exist. Thus, the remainder of this section will address 1D conditions.

2.6.3.1 Krypton

In the krypton method, dissolved krypton gas along with tritium as a conservative tracer and Rhodamine WT as a field monitoring tracer are in a bottle which is broken under water to provide an instantaneous release (Tsivoglou et al., 1968). By using a field fluorometer to monitor the Rhodamine concentration, water samples are collected in the vicinity of tracer peaks and analyzed for concentrations of krypton and tritium. For samples collected at any two times, Eq. 2.4 gives

$$\frac{(C_c)_2}{C_c} = \frac{(C_c)_1}{C_c} \exp[-K_T(t_2 - t_1)] \quad (2.4)$$

This equation can be rearranged and solved for K_T . In order to obtain a value of K_T which is representative of flow through the reach, it is common to take t_1 and t_2 at the centroids of the conservative tracer distributions at the upstream and downstream locations, respectively. The difference $(t_2 - t_1)$ is approximately the flow time (t_f). It is important to note that the flow time should be determined from the centroids of the conservative tracer cloud, not the tracer gas cloud (for either krypton or propane).

2.6.3.2 Hydrocarbons

Injection - In the hydrocarbon gas method (Rathbun et al., 1975, 1978), bottled propane is bubbled from diffusers placed on the stream bed. Because propane is not highly soluble in water, it must be injected over a period great enough to produce detectable concentrations at the downstream end of the study reach. Injection periods for rivers have varied from a few minutes to a couple of hours. Typically, 5% to 20% of the gas goes into solution with the remainder bubbling through the water surface. The "conservative tracer" and also the field monitoring tracer is Rhodamine WT which is released in a manner to simulate the source configuration and duration of the gas tracer. Rhodamine is subject to photochemical decay (plus other possible reactions, depending on the water quality). Corrections for dye loss must be made in the "peak method", but not in the "area method".

Peak Method - In the "peak method", the dye concentrations are used quantitatively so compensation must be made for the dye loss. The entire rhodamine concentration (C_d) curve is obtained to determine the amount of dye recovery. This calculation requires knowledge of the river flow rate (Q). The recovery data is used to correct

C_d to an equivalent conservative concentration ($C_c = C_d/\text{recovery ratio}$). Tracer gas measurements at the peak (or centroid) of the C_d curve at two or more cross sections are used to obtain C/C_c and Equation 2.4 is used to obtain K_T .

Area Method - This method requires measurement of the entire gas concentration vs. time curve. Rhodamine WT is used only as the field monitoring tracer in this method so that no correction for dye loss is needed. If the amount of reaeration while the cloud is passing the measurement station is negligible, then K_T can be obtained from

$$K_T = \frac{1}{t_f} \ln \frac{N_1 Q_1}{N_2 Q_2} \quad (2.5)$$

where N = area under the tracer gas cloud, Q = river flow rate, and t_f is the flow time between the two measurement cross sections (Holley and Yotsukura, 1984).

2.6.4 Long-Duration Injection Method

The long-duration injection method has been tested mostly with transversely well-mixed tracer plumes in a steady flow (Yotsukura et al., 1983). This situation will be considered first, then the extension to nonuniformly mixed plumes will be briefly described. No examples of long-duration injections with the radioactive krypton tracer gas are known.

Transversely Uniform (1D) Conditions - If the hydraulics and gas transfer are expected to be steady state during the test, the field procedure uses an instantaneous injection of Rhodamine WT at the beginning of a long-duration injection of hydrocarbon gas. The gas injection lasts long enough to allow collection of steady-state data for gas concentration at all measurement cross sections. Only dye concentrations are determined (using a field fluorometer) while

the dye cloud is passing. When the dye concentration declines to approximately 2% of the peak concentration, the gas concentration will be essentially steady state. The dye measurements are then stopped and gas sampling is initiated and continued as long as desired during the steady-state period. Discharge measurements are also required at each section. The reach-averaged desorption coefficient (K_T) is calculated from

$$(C Q)_2 = (C Q)_1 \exp(-K_T t_i) \quad (2.6)$$

where C is the steady state gas concentration. If the leading edge of the dye cloud arrives at the measurement section at t_A and the trailing edge (say the 2% level) arrives at t_D and if the duration of the gas injection is t_i , then the steady-state period for gas concentration is from t_D to $t_i + t_A$ (Yotsukura et al., 1983). Before the actual tracer gas test is done, it is desirable to do only a Rhodamine WT injection with determination of t_i , t_A , and t_D as an aid to planning the tracer gas test.

The long-duration injection method has demonstrated excellent reproducibility of tracer data. The method is limited to essentially steady flow.

Nonuniform (2D) Plumes - For wide rivers, the distance required for achieving transverse uniformity may be longer than the study reach for gas transfer measurements. For such cases a nonuniform plume method can be used. For steady hydraulics and gas transfer, the field procedure uses an instantaneous injection of Rhodamine WT at the beginning of a continuous injection of gas tracer at a fixed location in a cross section. At several transverse locations in the measurement cross sections, measurements are made for only dye concentration while the dye cloud is passing and then are switched to gas concentration, as for uniformly mixed plumes. Until more analytical work can be done on the interpretation of 2D data, the current practice is for transverse sampling locations to

be chosen on the same depth-averaged streamline (e.g., the streamline with 20% or 50% of the discharge between that point and the left bank). Also, enough dye data must be collected to provide the transverse distribution of mass passing each cross section (Eq. 2.8).

The reach-averaged desorption coefficient (K_{Tj}) for the j -th streamline is calculated from

$$\frac{(C_j Q)_2}{F_j} = \frac{(C_j Q)_1}{F_j} \exp(-K_{Tj} t_{ij}) \quad (2.7)$$

where all quantities are measured on the same (j) streamline. The nondimensional mass distribution factor (F_j) is determined from stream gauging and from the measured rhodamine concentrations:

$$F_j = \frac{QN_j}{\int_0^B N_j U H dy} \quad (2.8)$$

where U = local depth-averaged velocity, H = local depth, B = channel width, and y = transverse distance. N_j is the area under the dye cloud on each streamline, i.e.

$$N_j = \int_0^{\infty} C_{d,j} dt \quad (2.9)$$

The method appears to provide an operationally feasible measurement method for wide rivers (Yotsukura et al., 1984). Like the long-duration method for a 1D plume, the theory and procedure are restricted to essentially steady flows. There have not been enough field applications of the methods to determine whether the same K_{Tj} would be obtained with injections at different transverse locations.

2.7 Summary

In conducting and analyzing field studies for determination of surface transfer rate coefficients in rivers, it is important to consider whether the processes to be measured are one dimensional or two dimensional with significant transverse variations. The characteristics of 1D and 2D hydraulic transport processes can be used as guidelines. Natural 2D variations of DO exist for a variety of reasons.

Errors enter the determination of surface transfer rate coefficients due to procedural errors, uncertainty of parameters used in data analysis, and propagation of random measurement errors. It is possible to obtain numerical estimates of errors in K from an analysis of the propagation of random errors. The error analysis indicates the desirability of having $Kt_r > 1$.

There are three primary field techniques which have been used for the evaluation of reaeration. The original oxygen balance method has been generalized, but still suffers from potentially large errors resulting from the many oxygen sources and sinks which may be non-uniformly distributed and unpredictable. Application of the disturbed equilibrium method may be limited to streams with no temporal variation of the natural DO concentrations and no sources and sinks which depend on DO concentration. Verifications of no residual sulphite transported downstream is also required.

Tracer gas techniques are now being used widely and hold the greatest promise for a variety of applications especially as answers are obtained for the remaining questions. More information on chemical and biological interactions with the tracer gases and development of proper techniques and data analysis for 2D tracer gas distributions will increase acceptance of the method for

evaluating gas exchange in aquatic systems.

3.0 METHODOLOGY FOR ATHABASCA RIVER FIELD TRIAL

The procedure we selected as being the best for the field trial was the short-duration injection using propane as a tracer-gas. The long-duration was more desirable because it provides a steady state condition enabling easier dye and propane measurement. However, this method was not feasible because it would require a 30 h continuous injection due to the large travel times and longitudinal dispersion in the upper Athabasca River.

This section describes the field study design.

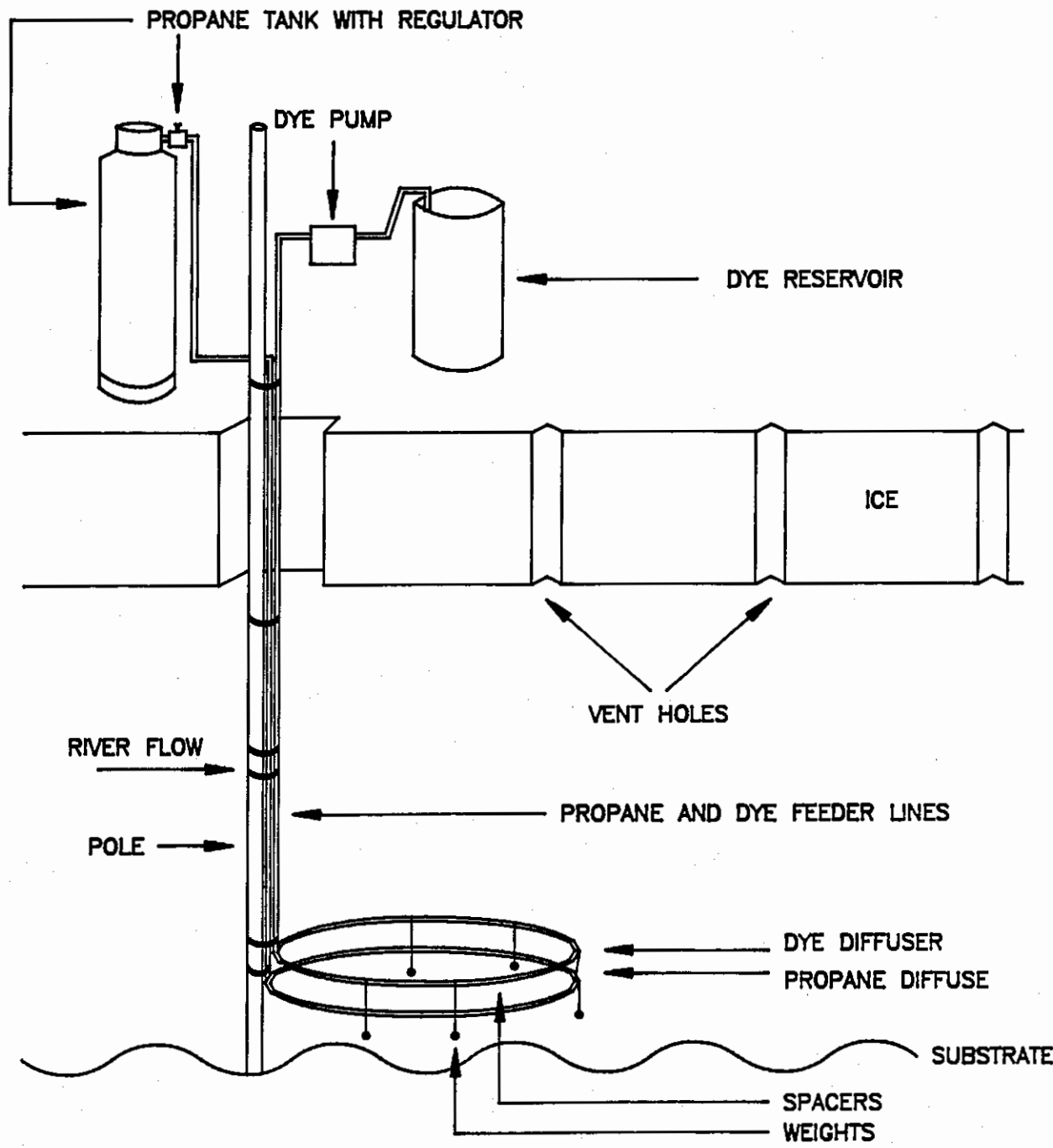
3.1 Injection Technique

The criteria for designing the injection apparatus were:

1. To provide even, numerous small propane bubbles over as large a surface area as possible for maximum efficiency in dissolving gas into water
2. Enable an even release of dye immediately above the propane to ensure equal mixing of dye and propane
3. Design must be easily installed on and removed from the bottom of the river through a greater than one meter ice-cover.

The final design is shown in Figure 1. It has two nine-foot loops of a porous rubber hose, the top loop is connected to an adjustable displacement pump and a dye container, and the other to a 100 lb propane tank with an adjustable regulator. The porous hose was designed by Leaky Pipe® for slow irrigation and is constructed from old automobile tires. It was tested against ceramic diffusers (the conventional apparatus for injecting propane) in laboratory studies and found to be more effective for oxygenating water.

FIGURE 1. PROPANE/DYE INJECTOR APPARATUS



The two loops were attached to a 15 foot pole which was used to hold the loops in place on the bottom of the river. Weights were fixed to the bottom of the propane loop to prevent the loops from floating. In order to ensure the loops remained vertically aligned, they were wired together with a six inch gap between them.

Rubber was an ideal compound for the diffusers because it was sufficiently rigid to maintain a loop in a strong current and was malleable enough to pass through an eight inch diameter hole in the ice, even when air temperatures were near -30°C .

The Rhodamine WT dye was mixed one-to-one with methanol to create a liquid with a specific density similar to water. The dye solution was held in a 10 litre plastic carboy and was fed to the diffuser loop through half inch tygon tubing. A Cole Parmer 0.25 to 2.5 L/min positive displacement pump was used to inject the dye solution. The pump was powered by a portable generator and calibrated in the lab to the required flow rate. The dye solution was kept at room temperature until just prior to injection. An insulated box was used to keep the dye from freezing during the injection.

A one hundred pound propane cylinder was filled with commercial grade propane and weighed before each injection. Although we were not attempting to inject one hundred pounds of propane, the large tank was required to maintain a relatively high, constant flow rate for 30 minutes at low atmospheric temperatures. It was recommended that a flow-meter be installed on the tank so that a constant flow could be maintained at a known rate (Kilpatrick et al., 1987). However, due to the volume of flow in the river, and the large longitudinal dispersion, high flow rates (greater than 100 L/minute) were required. High flow and low pressure metering devices were either not available or impractical. Instead, a two-stage adjustable pressure regulator was used to maintain the

pressure and achieve flow.

The mass of propane and rhodamine dye which must be injected can be calculated based upon the design dye/propane concentration at the sampling site furthest downstream (C_{max}), the river discharge (Q), the expected time at which the dye/propane cloud would arrive (t_a) and depart (t_d) the downstream sampling site, the estimated remaining fraction of propane not lost from surface transfer (C_r) and the efficiency of the diffuser to dissolve propane gas into water (q). The relationship is:

$$\text{mass} = \frac{QC_{max} (t_d - t_a)}{2C_r q} \quad (3.1)$$

This is based on the general assumption that a graph of tracer (dye/propane) concentration versus time at the downstream location would approximate a triangle and thus the mass equal to the area under the triangle.

3.2 Sample Collection

Using the short-term injection technique, it is necessary to sample the entire dye-cloud from before it arrives until concentrations in the tail are well below fifty percent of the peak concentration. Samples were collected at sufficiently regular intervals to have 10 to 15 measurements for the curve analysis.

Eight inch diameter holes were augered through the ice and water samples were collected in 0.25 L Qorpak bottles with a 2 litre displacement sampler clamped to the end of a 15 foot pole. The sampler was lowered to a point six inches below the underside of the ice. Once the sampler was full (approximately two minutes) it was removed from the water. Roughly one half of the sample volume was decanted into two 50 ml glass bottles. The Qorpak was then capped with a teflon-lined septa and stored for later propane

analysis. The other two bottles were for determination of the Rhodamine dye concentration in the field and later in the lab.

3.3 Rhodamine Dye Analysis

The concentration of Rhodamine WT in the samples was measured using a Turner Designs model 10 fluorometer. In the field the samples were analyzed primarily to identify when the dye/propane cloud was at the monitoring site and when it had mostly passed to ensure that the propane samples were collected at the correct times.

Although the dye was analyzed in the field, a sample was also kept for analysis in the lab. This was done to ensure the quality of the measurements. The fluorometer, while being portable, is sensitive to warm-up time and requires frequent calibration checks. Hence only crude measurements are possible under adverse field conditions. The laboratory values were used for determination of the reaeration coefficient.

3.4 Propane Analysis

The bottles for propane analysis were incubated at room temperature with occasional shaking for a minimum of two hours. During this period, the propane in solution equilibrated with the gas phase. A 0.25 ml sample of the headspace gas was then removed for analysis of propane in a Photovac Model 10A10 portable gas chromatograph equipped with a photoionization detector. Propane was separated on an 18 cm column packed with diatomaceous earth with air as the carrier gas (16 ml/min). The detection limit for propane in a one ml gas sample was 0.01 ml or 0.02 μg . A propane standard was prepared by dilution of the gas taken from a 20 lb tank of commercial propane in a specially designed glass gas mixing container.

The sample and headspace volumes were determined gravimetrically. The bottles with caps were weighed empty and full before collection of the sample. These weights were used to calculate the sample and headspace volumes from the weight of the bottle with sample. The amount of propane in solution was calculated from those volumes and Henry's Law constant corrected for temperature (0.0625 g/L or 0.034 μ l/l at 20°C and 1 atm.).

4.0 LABORATORY TESTS WITH PULP MILL EFFLUENT

The potential effects of pulp mill effluent on dissolved propane were evaluated using laboratory tests with the Weldwood mill effluent. The testing began on the day that the effluent was received and was continued for four days. Two containers of effluent were each diluted 10:1 with distilled water to represent the approximate average dilution between the effluent flow and the river flow after complete mixing (and to provide adequate volume for the samples to be analyzed). Propane was added to both batches of diluted effluent. The initial propane concentrations were approximately 7 $\mu\text{g/L}$ for one batch and approximately 115 $\mu\text{g/L}$ for the other. A control batch was also prepared with approximately 7 $\mu\text{g/L}$ in distilled water. The absolute values of all concentrations are approximate since only relative concentrations are needed in the tracer gas method. Replicate sample bottles were filled from each of the three batches using standard sampling procedures for determination of dissolved gas concentrations. All of the sample bottles were stored in ice water to maintain the temperature at 0°C. Samples were then analyzed for propane concentrations at regular time intervals. As shown in Table 1, there was no trend for the propane concentrations to change with time. All of the variations in concentrations for various samples from the same batch were within the normal range of variation for replicate samples. The maximum coefficient of variation (relative standard deviation) for any of the three batches was 1.9%.

Pulp mill effluent contains compounds which have surfactant properties which, in theory, could affect gas transfer rates. This was not evaluated in the laboratory study. Propane and oxygen have similar physical properties, thus any effect of surfactants on propane exchange (K_p) would likely be similar for oxygen (K_2).

Table 1. EFFECTS OF PULP MILL EFFLUENT ON DISSOLVED PROPANE

CONTROL IN DISTILLED WATER		EFFLUENT DILUTED 10:1 WITH DISTILLED WATER			
time hr	conc ug/L	time hr	conc ug/L	time hr	conc ug/L
0.5	7.12	0.8	7.40	1.0	115
1.6	6.99	1.8	7.34	2.0	113
2.6	7.08	2.7	7.37	3.0	115
4.1	7.04	3.8	7.27	4.3	113
5.0	6.97	5.1	7.21	5.3	114
6.0	6.99	6.1	7.36	6.3	112
7.2	7.11	7.3	7.30	7.5	114
12.8	6.79	12.9	7.23	13.3	112
23.6	7.03	23.7	7.25	23.9	113
38.0	6.87	38.1	7.21	38.3	112
53.5	6.95	53.9	7.08	54.1	114
66.1	7.12	66.3	7.34	66.3	114
74.7	6.97	74.8	6.89	75.0	112
88.9	6.98	89.0	7.33	89.2	114
96.8	7.26	96.9	7.50	99.3	115
number	15		15		15
max	7.26		7.50		115
avg	7.02		7.27		113
min	6.79		6.89		112
deviation of max from avg (%)	3.4		3.1		1.4
deviation of min from avg (%)	3.2		5.3		1.3
coef. of variation (%)	1.6		1.9		1.0

5.0 FIELD TRIAL

During the week of March 13 to March 17, 1989 the technique described in Section 3.0 was used to measure reaeration on the Athabasca River between the Town of Hinton and the confluence of the Athabasca River and the Berland River. A letter of Permission to discharge dye and propane to the Athabasca River was received from Alberta Environment, Standards and Approvals Division prior to the study (Letter of Permission No. 89-LP-007). The Letter of Permission specified maximum allowable river concentrations and required HydroQual to notify all licensed water-withdrawal users in the test reach and the appropriate authorities in Pollution Control Division. Permission was also required from the Weldwood pulp mill in Hinton to use their property for access to one of the injection sites.

5.1 Description




Two study reaches were selected, one which was completely ice-covered and one which had an open-water zone created by the discharge of the thermal pulp mill effluent. Map 1 shows the study reaches (A, B) and the injection (I) and monitoring locations which were used during the study (A1, A2; B1, B2). The two studies (open-water and ice-cover) will be described in the following sections.

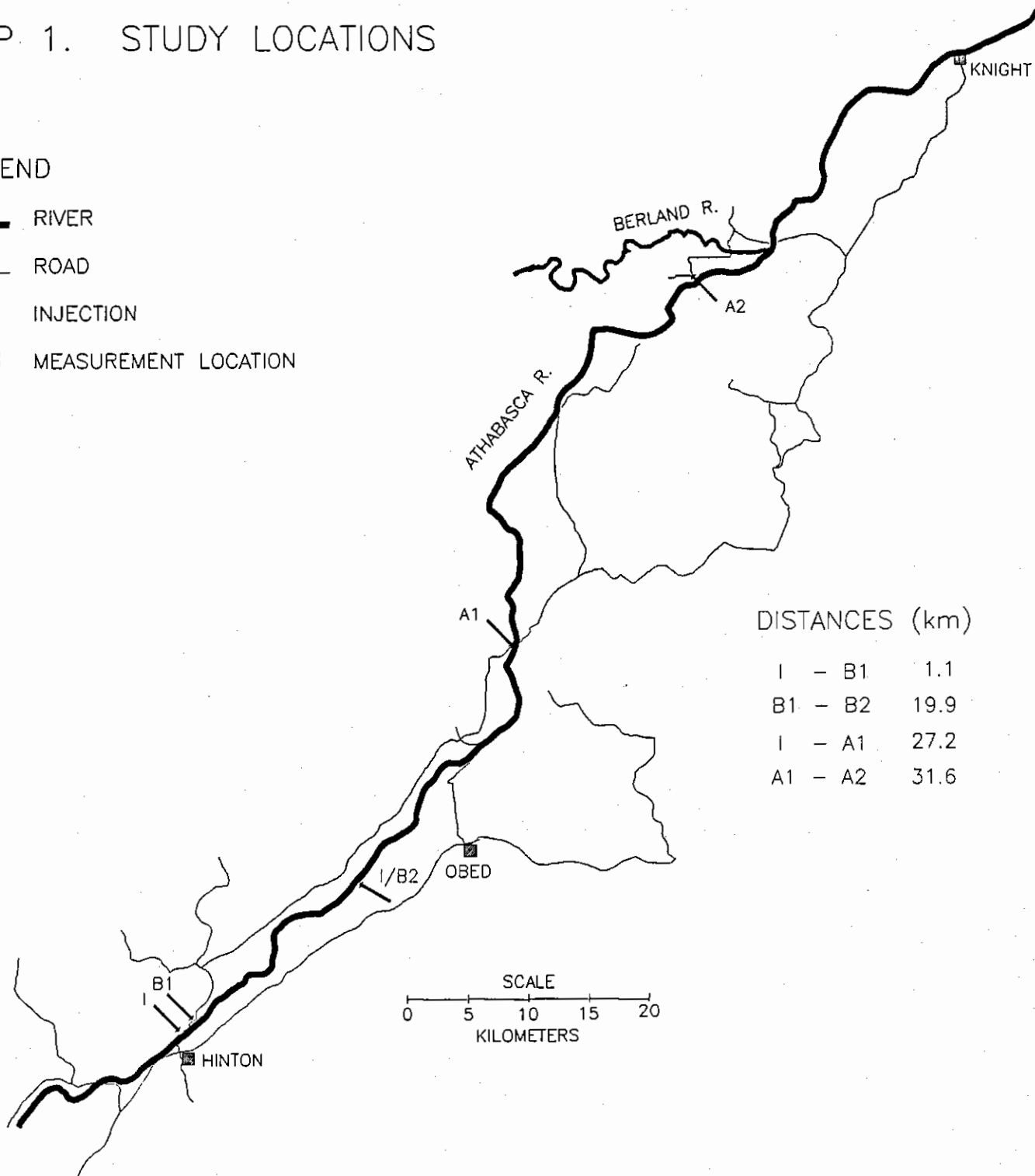
5.1.1 Ice-Covered Reach (A)

The reach from the Dalehurst Bridge (Site I/B2) to upstream of the confluence between the Athabasca River and the Berland River was selected to measure reaeration under complete ice-cover. This reach was selected because there is very little inflow between the upstream and downstream points (only Oldman Creek), and with the exception of a few cracks, there was complete ice-cover. The

MAP 1. STUDY LOCATIONS

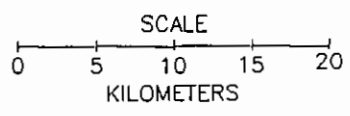
LEGEND

-  RIVER
-  ROAD
-  INJECTION
- A/B MEASUREMENT LOCATION



DISTANCES (km)

I	- B1	1.1
B1	- B2	19.9
I	- A1	27.2
A1	- A2	31.6



travel-time within the reach was long enough such that significant propane exchange could occur between the two monitoring sites at the estimated rate $K_p = .08 \text{ day}^{-1}$ (Section 2.3.3).

Monitoring sites were selected primarily on the basis of access. However the first monitor site (A1 - Emerson Lakes Bridge) had to be far enough downstream to ensure that the dye and propane were completely mixed laterally within the river. The point of complete mixing was roughly estimated from channel morphometry.

The injection and monitoring sites were visited prior to the injection. At each of the three sites access was confirmed (not all roads are plowed), holes were augred across the river width to ensure adequate depth, velocity and that the ice and hydraulic conditions were not highly irregular.

At the injection site (I), a hole located 20 meters upstream from the bridge and 20 meters off the left downstream bank, was selected for the injection. At this site there was approximately 1.5 meters of water with a good flow under 1.2 meters of ice.

The dye solution consisted of ten litres of Rhodamine WT mixed with ten litres of methanol. The dye pump was calibrated to deliver 20 litres of liquid to the diffuser in 60 minutes. For the first injection, two 100 pound propane tanks with independent adjustable regulators were positioned adjacent to the injection hole, and connected to the diffuser.

At 19:54 h on March 14, 1989, with the diffusers in place on the bottom of the river, the dye pump was started and the propane valves opened. Pressure readings on the second stage of the pressure valves were set to 15 p.s.i. The valves were then opened slowly in an attempt to maintain a second stage pressure of 15 p.s.i. Within 20 minutes, the pressure in one tank dropped to 11 p.s.i. The second tank remained at 15 p.s.i. At this point, the

top half of the first tank, regulator and feed hose were heavily frosted while the second tank and lines remained clear. The injection was stopped at 20:46 (total injection time of 52 min). Pressure on the first tank had dropped to 7.5 p.s.i. while the second tank had not changed and remained frost-free.

Immediately downstream (<10 m) of the injection a dozen vent holes were drilled to prevent a build-up of propane bubbles under the ice surface. The vent holes were percolating violently throughout the injection period.

After the first injection, it was determined that only 6.0 kg of propane and 9 litres of Rhodamine dye were discharged to the river. Most of the propane came from one tank probably because of a faulty or frozen regulator. Based on our mass balance calculations, 90 percent of the dye and 40 percent of the propane were injected (Section 3.1).

Monitoring at the first site (A1 - Emerson Lakes Bridge) began at 6:35 h on March 15 and continued to 17:35 h on March 15. The best hole for sampling was in the center of the channel immediately upstream of the bridge. There was approximately 0.75 m of water flowing over a fine particulate substrate. Samples were collected every half hour until the dye/propane cloud arrived following which they were collected every hour. The maximum dye concentration was measured at noon.

The second monitoring site, upstream of the confluence with the Berland River was more difficult to access. Although the road came near the river it was still a ten minute cross-country ski from the vehicle to the sampling hole. The river at this point flows through a canyon with occasional rock outcrops. River flow was forced to the right downstream bank and the ice surface was irregular upstream and downstream of the sampling hole. The initial test holes indicated that the flowing channel was only

about thirty meters wide. We subsequently discovered that there were two ice layers in the sampling hole. The two layers were 0.5 m thick. There were 0.3 m of stagnant water between the layers and rapidly flowing water beneath the lower layer. The flowing water was greater than 1.5 meters deep.

Sampling began at 19:50 hr on March 16 and continued every hour until 14:50 h on March 17. Despite ambient air temperatures near -30°C the only equipment or sampling problems were with ice formation on the screw threads of the displacement sampler. This was resolved by keeping the sampler in the water when it was not being used.

While samples were being collected in the field, other samples were being analyzed in a rented laboratory at the Alberta Forest Technology School in Hinton. It was imperative to know that the propane levels in the river were detectable, so that crews were not out monitoring needlessly and so that any required modifications could be made to the technique before the second injection.

Despite only injecting 40 percent of what was calculated to be required, the propane levels at the furthest downstream site were well above our detection limit for propane. The likely reason for the difference between the observed and calculated concentrations is the diffuser efficiency factor (q ; Section 3.1). We believe that with an ice-cover and cold water, a greater proportion of the injected propane was dissolved in the water. This indicates a higher diffuser efficiency factor than used in the initial calculation.

5.1.2 Open-Water Reach (B)

The open-water study reach extended from the Weldwood pulp mill water intake site (I) to the Dalehurst Bridge (Site B2), although

the ice-free zone is only from the point of discharge to a point 7.9 km upstream of the Dalehurst Bridge. The open-water zone appeared to represent roughly 75 percent of the surface water area.

For this injection only one propane tank and five litres of dye were required because the study reach was significantly shorter than the ice-cover reach. As a result, longitudinal dispersion would play a smaller factor in reducing the river propane/dye concentrations. In the first study, we also achieved higher propane injection efficiency than previously expected.

At 09:43 h on March 17, 1989 the propane and dye injection began with a propane pressure reading of 12 p.s.i. By 09:48 h the propane pressure had dropped to 10 p.s.i. and we began shaking the propane tank. Shaking the tank made it easier to maintain the pressure (reduced surface cooling of the liquid propane in the tank). The injection ended at 10:03 h when the dye injection was complete. The total injection time was 20 min and achieved an input of 5 litres of dye and 2.7 kg of propane.

Access ability and the fact that we could not inject dye above the mill water intake, dictated the injection and measurement points. Our first measurement point was at the Weldwood Bridge (Site B1). Ideally this first site should have been far enough from the injection site that the dye/propane would be completely mixed laterally. However, complete transverse mixing was not possible.

The river at the Weldwood Bridge is open so sampling was done by suspending the displacement sampler on a rope and lowering it from the bridge. Being so close to the injection site, the sampling frequency was as rapid as possible to enable full description of the dye/propane cloud as it passed. The cross-channel sampling location was estimated by visually judging where the maximum flow was and where the maximum dye concentration was. It was not possible to sample at more than one cross-channel location.

Sampling began at 10:15 h, well before the dye arrived and continued until 12:51 h. The peak dye concentration was measured at 11:27 h.

Site B2, Dalehurst Bridge, although ice-covered was used as the downstream site, because the alternative of sampling at the exact end of the open-water zone proved infeasible. A hole was drilled at Site B2 immediately upstream of the Site A injection hole. Sampling commenced at 16:14 h on March 17 and continued until 4:17 h on March 18 sampling every hour.

The analyses of the propane and dye samples were completed in Hinton prior to leaving the field.

5.2 Results

The propane and dye concentrations for each of the four sampling sites were plotted against the time since the injection. Sampling at each of the monitoring sites stopped after dye/propane concentrations came down below half of the peak concentrations. The natural logarithm of concentration for the last three points were regressed against time and the resulting equations used to extrapolate the remaining concentrations (see Appendix 1). This extrapolation technique adequately describes the dye and propane traces for all but the traces at Site B1. This is the site which was very close to the injection. The plot of natural log concentration versus time shows a change of slope in the last three measurements. Concentration versus time curves were integrated to calculate the areas and the centroid under the concentration versus time curve. These results will be presented in the following sections.

5.2.1 Ice-Covered Reach

Figures 2 and 3 are the dye and propane concentration versus time plots for monitoring Sites A1 and A2. At Site A1 maximum dye and propane concentrations are 3.0 $\mu\text{g/L}$ and 4.5 $\mu\text{g/L}$ respectively. These are reduced to 1.3 $\mu\text{g/L}$ and 2.6 $\mu\text{g/L}$ by Site A2. The areas and centroids under these curves are listed in Table 2. At both monitoring Sites A1 and A2 the centroid time of travel is greater for propane than for dye. This may be due to propane bubbles trapped under the ice which may slowly dissolve into the water column.

Table 2. Ice-cover Study Reach Results

	Area ($\mu\text{g/L}\cdot\text{min}$)	Mass (kg)	Centroid (min)
Site A1			
Propane	1641.2	3.15	1167.8
Dye	881.2	1.69	1102.5
Site A2			
Propane	1600.9	3.19	2009.9
Dye	735.5	1.47	1990.1

The best information available on Athabasca River flows during this week were provided by Alberta Environment, Hydrology Branch. They suggested a flow of 32.0 m^3/s at Hinton with approximately a 4 percent (1.3 m^3/s) inflow (Oldman Creek) between Hinton and the confluence with the Berland (Dave Graham, personal communication). Assuming these flows, the mass of dye at Site A1 was 1.69 kg and 1.47 kg at Site A2. These values are lower than the initial calculated mass of 2.03 kg.

FIGURE 2

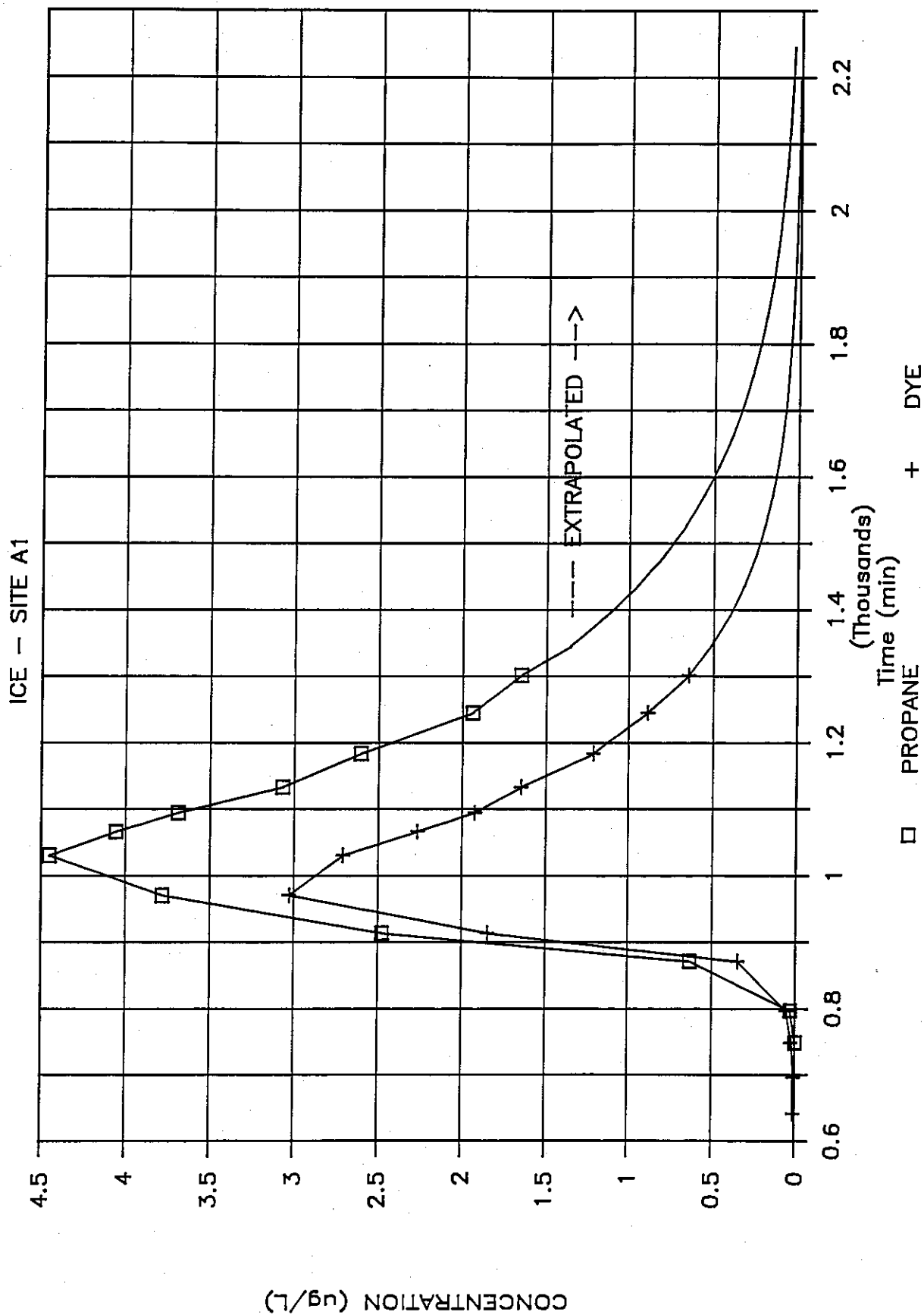
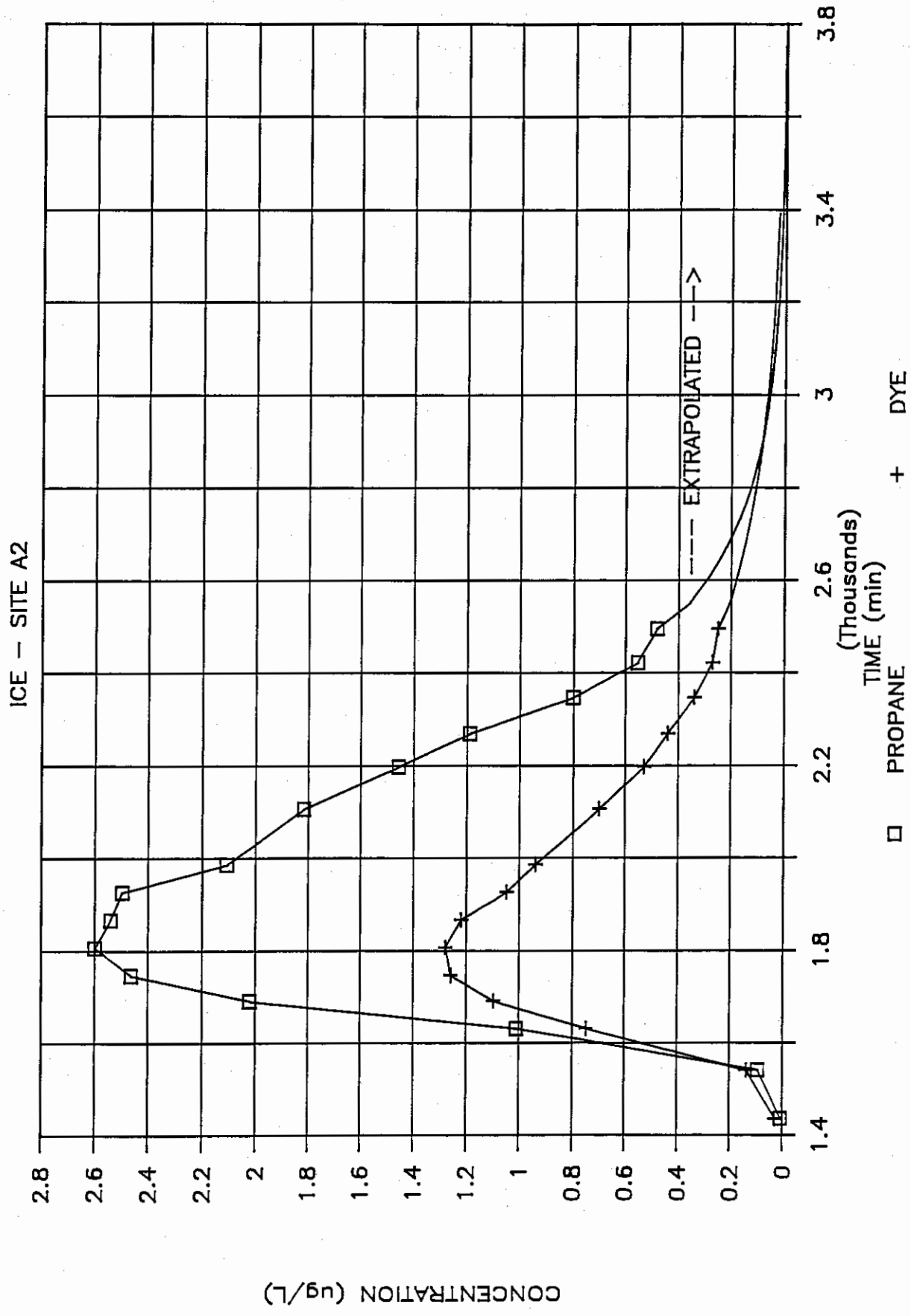


FIGURE 3



The dye loss is unfortunate. We believe that the loss is too great to explain by dilution and have assumed that the loss must be a function of decay or adsorption onto suspended material in the pulp mill effluent, onto the ice surface and/or the river bed. In other words, the dye is lost due to processes that would not likely affect propane.

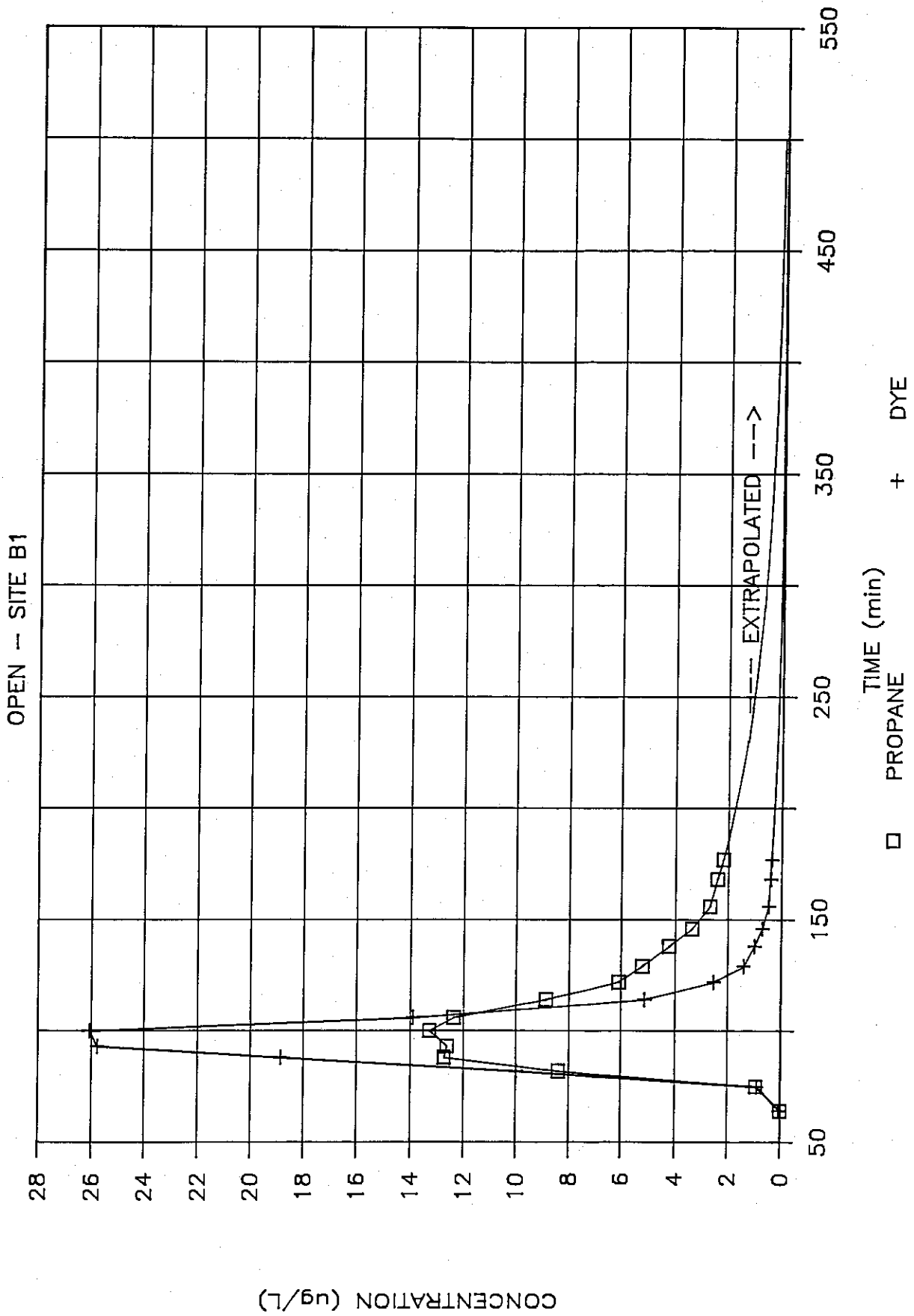
The total mass of propane, measured simultaneously with the dye, was 3.15 kg at Site A1 to 3.19 kg at Site A2 indicating no measurable change. The injection mass was approximately 6.0 kg. Although only a fraction of this would be dissolved while the remainder released to the atmosphere through the vent holes or remained trapped under the ice near the injection site.

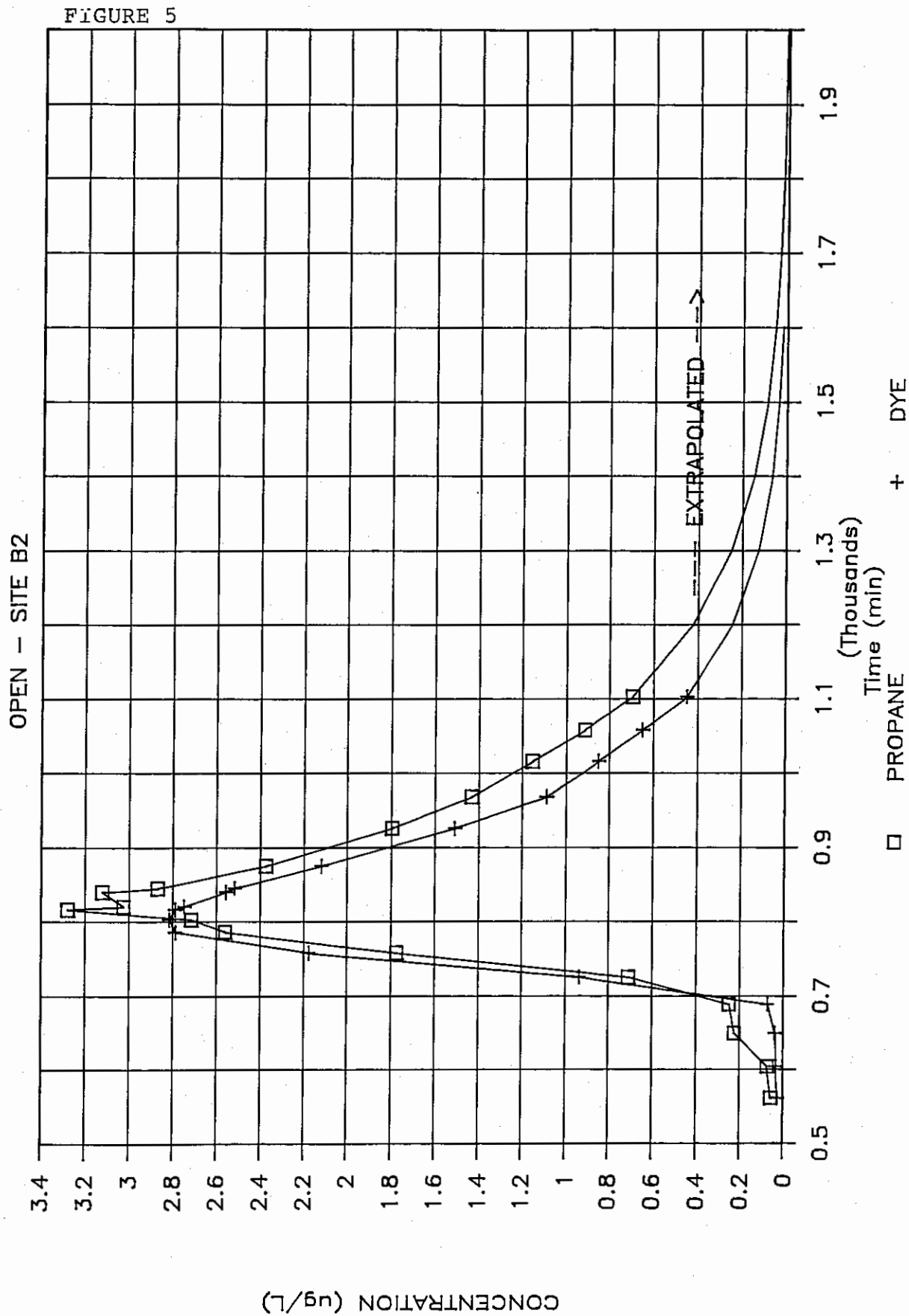
5.2.2 Open-Water Reach

Concentration versus time plots for the two open-water monitoring Sites B1 and B2 are presented in Figures 4 and 5, respectively. At the upstream monitor Site B1, which was only a few kilometers below the injection site, the maximum propane and dye concentrations measured were 13.0 $\mu\text{g/L}$ and 26.0 $\mu\text{g/L}$ respectively. Maximum concentrations at Site B2 were reduced to 3.3 $\mu\text{g/L}$ and 2.8 $\mu\text{g/L}$ for propane and dye respectively. It is important to note that at both Sites B1 and B2, prior to peak concentrations, measured propane concentrations were less than corresponding dye concentrations. However, this was reversed following the peak indicating that the shape of the propane cloud differs from the shape of the dye cloud.

This difference is possibly caused by propane bubbles trapped under the ice near the injection site. Propane in the bubbles could have dissolved into the water following the regulated injection period. Water in the tail of the propane/dye curve would have a longer contact time with more gas bubbles than water in the leading edge of the cloud.

FIGURE 4





Areas and centroids under each of the concentration versus time curves are listed in Table 3.

Table 3. Open-Water Study Reach Results.

	Area ($\mu\text{g/L}\cdot\text{min}$)	Mass (kg)	Centroid (min)
Site B1			
Propane	853.6	1.64	143.9
Dye	710.5	1.36	102.3
Site B2			
Propane	803.2	1.54	927.2
Dye	664.4	1.27	893.1

A dye loss was also measured through the reach. The calculated mass at Site B1 was 1.36 kg compared to 1.27 kg at Site B2. The corresponding values for propane were 1.64 kg and 1.54 kg for sites B1 and B2 respectively.

5.3 Calculation of the Reaeration Coefficient

Methods for calculating the reaeration coefficient (K_2) for studies using the short-injection technique are described in Section 2.6.3.2. At the beginning of this study, the intent was to use the "peak method" for calculation as this provided numerous measurements which could provide a higher degree of reliability in the calculated K_2 value. This technique was rejected and replaced with the "area method" when the results showed that there was a loss of dye in the two study reaches and that the propane and dye distributions had different shapes in the open-water reach. Gas transfer rates are specific to hydraulic and temperature conditions. All rates reported here are for 0°C and 32.0 m³/s.

To calculate K_2 for the ice-covered reach, the area under the propane clouds and the dye centroid to centroid travel time (in days) between monitoring locations (Table 2, Section 5.2.1) were used in Equation 2.5 to calculate the transfer coefficient for propane (K_p).

$$K_p = \frac{1}{0.62} \ln \frac{(1600.9 * 33.3)}{(1641.2 * 32.0)}$$

$$K_p = -0.02 \text{ day}^{-1}$$

The transfer coefficient for propane (K_p) can be converted to that for oxygen (K_2) using a factor of 1.39 (Section 2.3.2). K_2 for the ice-covered study reach is then equal to -0.03 day^{-1} (0°C), however, this indicates that the amount of dissolved gas increases instead of the expected reduction. Clearly the river is not gaining propane from the atmosphere, and the difference between the upstream and downstream propane curve areas, and consequently the calculated rate, is a function of measurement imprecision. Therefore, the conclusion from the ice-covered reach study is that the reaeration rate is not significantly different from zero.

Calculations for the open-water study reach were not straightforward because the dye/propane clouds were not completely mixed laterally at the first monitoring Site B1. To correct for this, the area under the downstream (Site B2) dye curve and the dye loss rate (calculated between the two ice-covered monitoring locations) were used to back calculate the probable dye curve area under completely mixed conditions at B1. This assumes that the dye-loss measured between Site A1 and A2 would be the same as that between B1 and B2. This assumption would not be valid if dye is reacting with mill effluent. In this case the dye-loss rate would be greater between B1 and B2.

The A1 to A2 dye loss rate was calculated to be $1.6 \times 10^{-4} \text{ min}^{-1}$, so with a measured dye area at Site B2 of $664.4 \text{ } \mu\text{g/L}\cdot\text{min}$ the corrected area at B1 would be:

$$\text{Corrected B1} = \text{Measured B2} * \exp [\text{dye loss} * (t_2 - t_1)]$$

The corrected area under the dye curve at B1 is $754.0 \text{ } \mu\text{g/L}\cdot\text{min}$ compared with the uncorrected area of $710.5 \text{ } \mu\text{g/L}\cdot\text{min}$.

Using the corrected dye area and the measured dye a mass distribution factor (F) can be calculated. The measured propane area at B1 can then be corrected so that it equals the area at B1 under completely mixed conditions.

For well-mixed conditions (such as Site B2) this factor is equal to 1.0, whereas it was calculated to be 0.94 at B1.

Knowing the mass distribution factor for Sites B1 and B2, the propane transfer rate for the open-water study reach can then be calculated by dividing the area under each propane curve by the site specific mass distribution factor before using the areas in Equation 2.5. The calculated K_p for the reach is 0.24 day^{-1} . However, this transfer could only take place in the open-water section of the reach assuming that the ice-covered transfer rate is zero. Aerial surveillance of the river identified that 45 percent of the study reach was open water. Assuming that the travel time is constant within the reach, then the effective propane transfer rate would have to be 0.53 day^{-1} , which when converted becomes an oxygen transfer rate (K_2) of 0.74 day^{-1} (at 0°C).

Our measured value for under-ice reaeration of 0 day^{-1} (20°C) is lower than other values previously reported (the literature on cold water, under ice reaeration is limited. TenEch (1978) recommends a factor of 0.05 to convert open-water rates to ice-cover rates).

For the Athabasca River between Hinton and the confluence with the Berland River an open-water rate of 1.1 day^{-1} (0°C , $32 \text{ m}^3/\text{s}$) would be predicted using the O'Connor and Dobbins (1958) equation. This compares reasonably well with our measured rate of 0.74 day^{-1} .

As previously discussed, the "peak method" for calculating K_2 was intended in the study design to provide a higher degree of reliability. Having to accept the "area method" as the best calculation technique means that there is no measurement replication and consequently no method of quantifying the measurement precision. Generally, the ice-cover measurement is more precise than the open-water measurement due to the incomplete mixing in the latter.

6.0 SUMMARY

In conducting reaeration experiments, it is important to consider transport and mixing to determine whether one- or two-dimensional distributions are likely to exist. The three primary methods that have been used for reaeration measurements are based on oxygen balances, disturbed equilibrium and tracer gases. The oxygen balance approach is not widely used now because of the potentially large errors associated with the many sources and sinks of dissolved oxygen. If temporal variations of natural dissolved oxygen concentrations exist, the disturbed equilibrium method suffers from the conflicting requirements of a short travel time for estimation of natural dissolved oxygen concentrations and long travel time for error considerations. Although all questions concerning tracer gas techniques have not been addressed, these techniques seem to hold the greatest promise for reliable gas transfer measurements under field conditions. For each of the methods, it is possible to analyze the propagation of random measurement errors to estimate the error bounds on gas transfer coefficients.

A technique was developed and an apparatus created which simultaneously injected propane and a tracer dye into the Athabasca River through a hole in the ice. This injection could be maintained at a relatively constant rate for 20-30 minutes. At downstream locations, both propane and the tracer-dye could be accurately quantified at levels well above the analytical detection limit after travelling for more than 50 kilometers or two days time-of-travel.

Laboratory experiments were conducted to test the effect of pulp mill effluent on dissolved propane to ensure that measured losses would be due to gas transfer and not a reaction with effluent in the river; no effects were measured. Unfortunately, similar studies were not done with Rhodamine dye, and it showed measurable

losses in the field studies. This dye loss, coupled with problems associated with gas bubbles under the ice at the injection point, meant that the desired 'peak method' calculation could not be used and was replaced by the 'area method'.

For the ice-covered study reach a small negative reaeration coefficient was measured, meaning there was a small increase in the amount of propane in the river between upstream and downstream monitoring locations which was attributed to measurement imprecision. Consequently, the measured atmospheric reaeration rate for the ice-covered study reach was not significantly different from zero at 0°C.

Limited access in the open-water study reach required us to take upstream dye/propane measurements at a river location which was too close to the injection location where lateral mixing was not yet complete. Consequently, measured values had to be corrected using a mass distribution factor before calculating the reaeration coefficient. Based on these considerations, we derived an open-water reaeration rate of 0.74 day⁻¹ at 0°C.

In conclusion, the technique we developed is a viable method for measuring reaeration in ice-covered and open-water conditions. Most confidence can be placed on the under-ice reaeration coefficient since fewer assumptions were required to derive it compared to the open-water value. However, more reaeration studies are required to verify our rates for open-water and ice-cover conditions.

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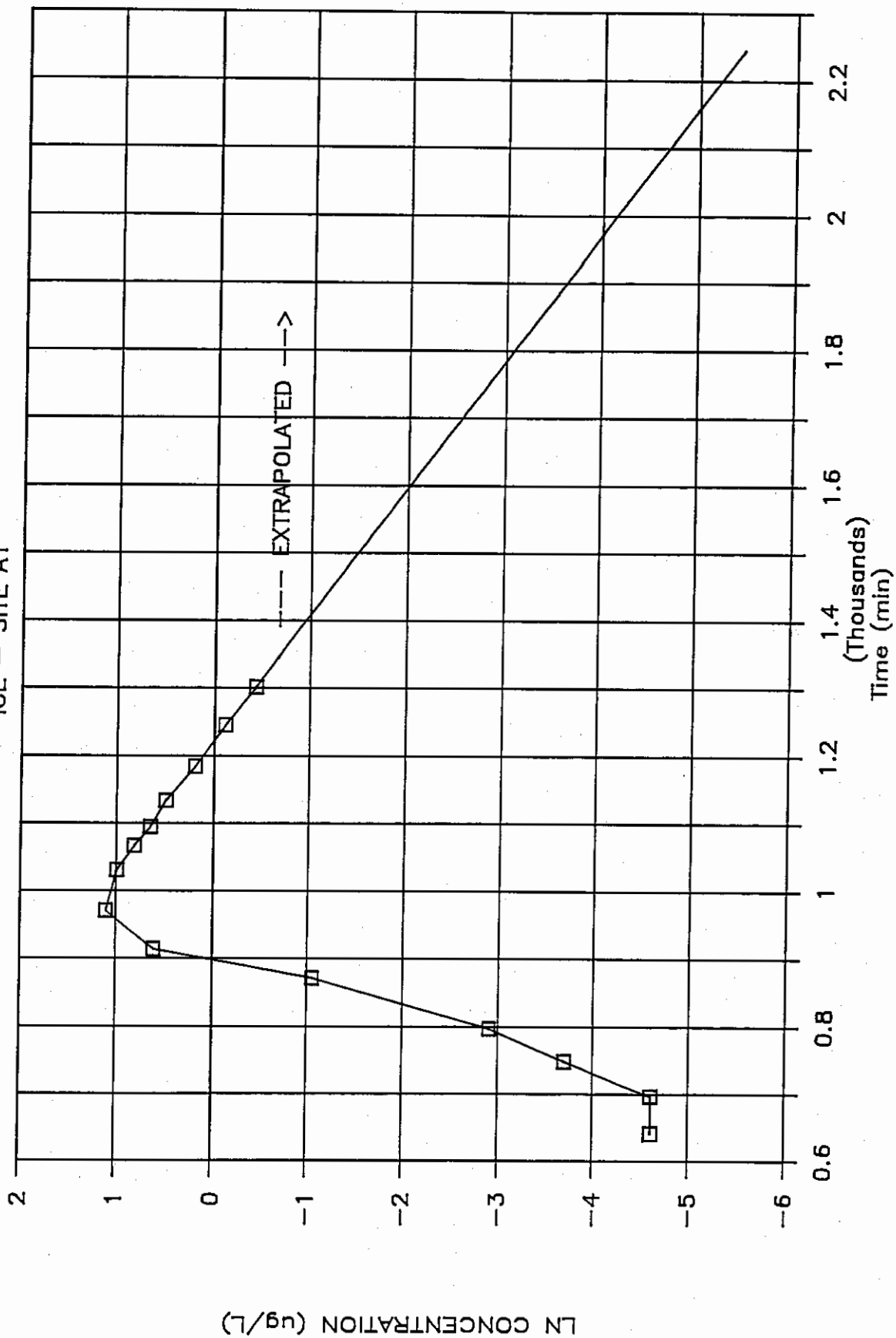
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APPENDIX 1

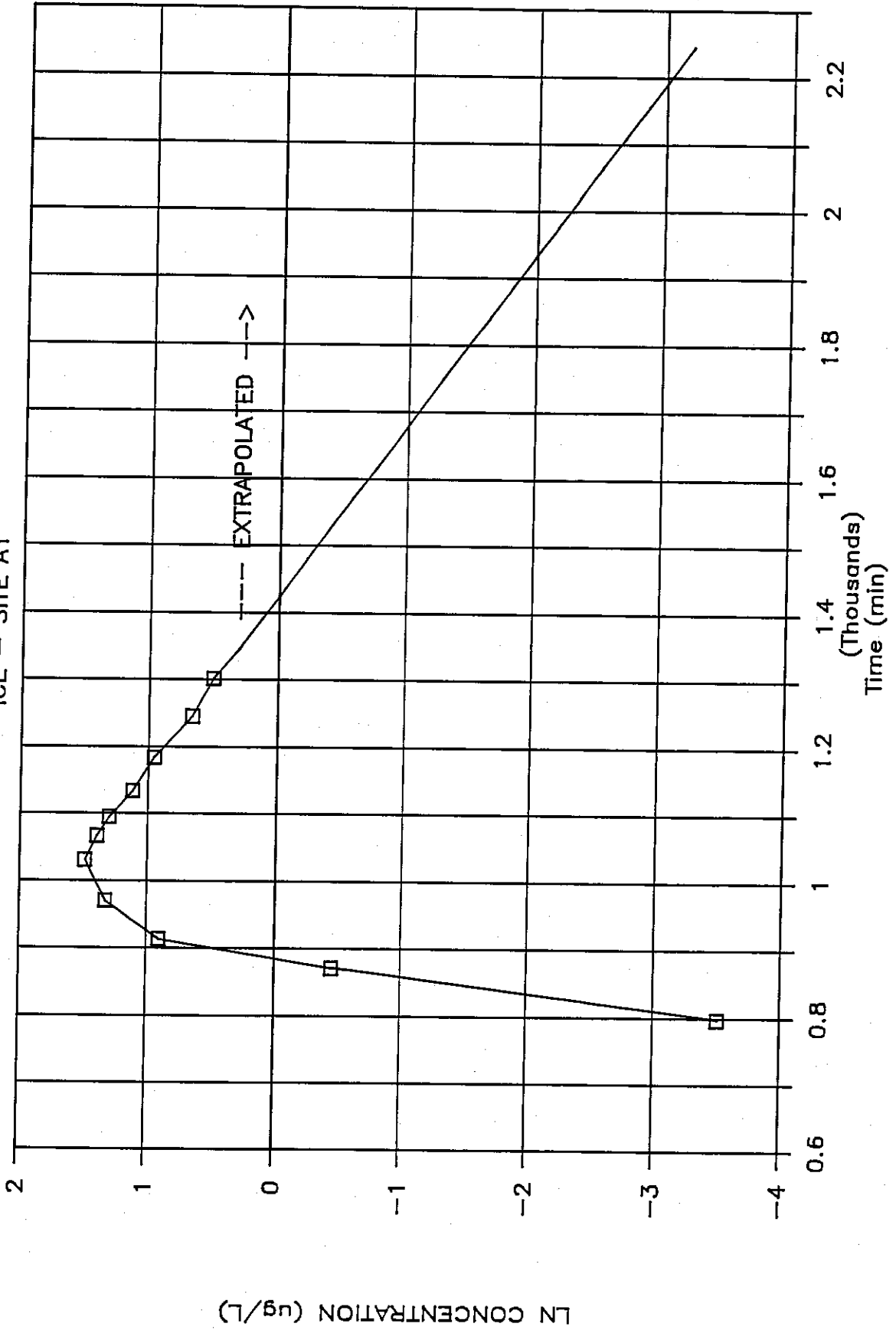
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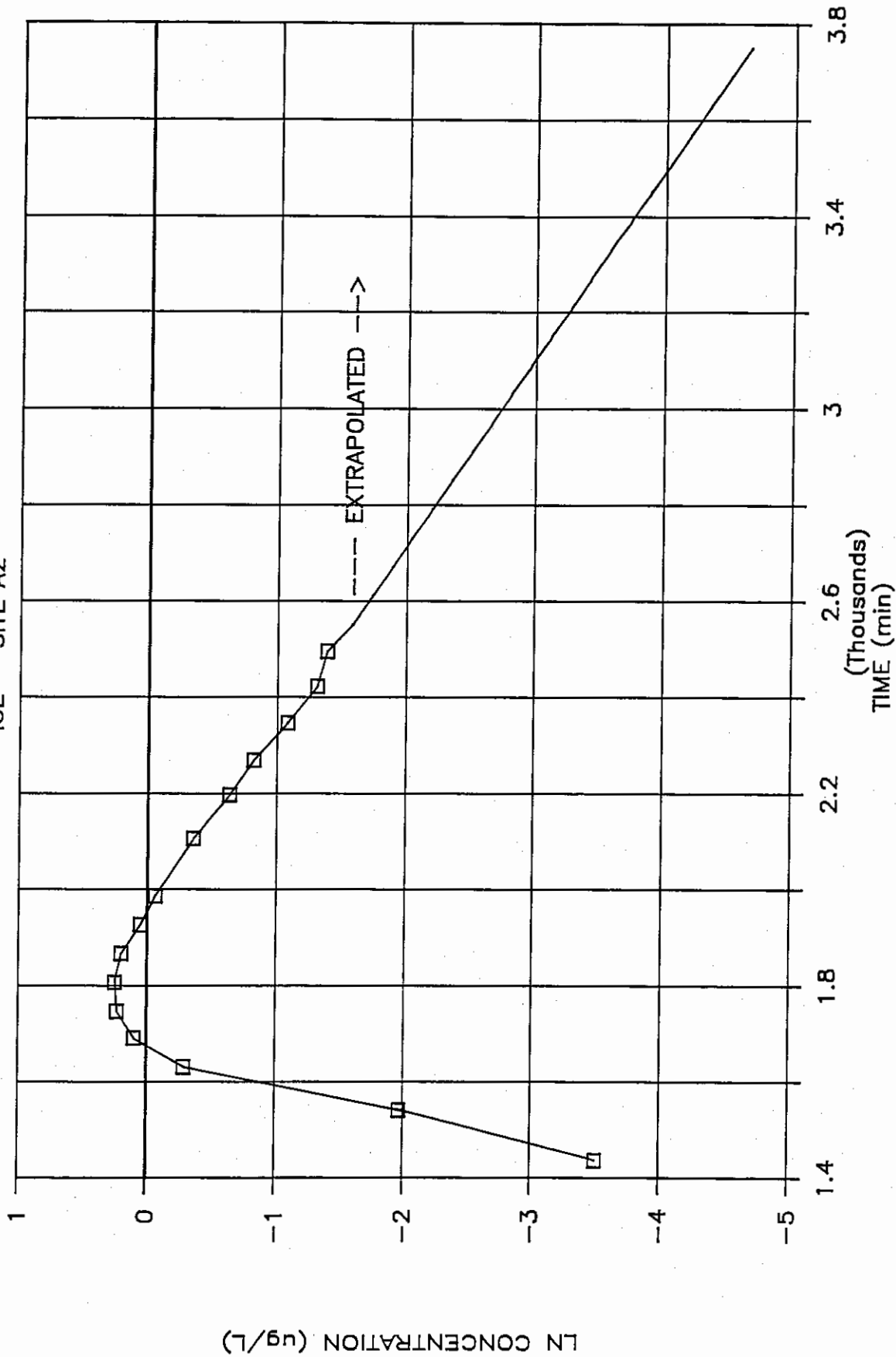
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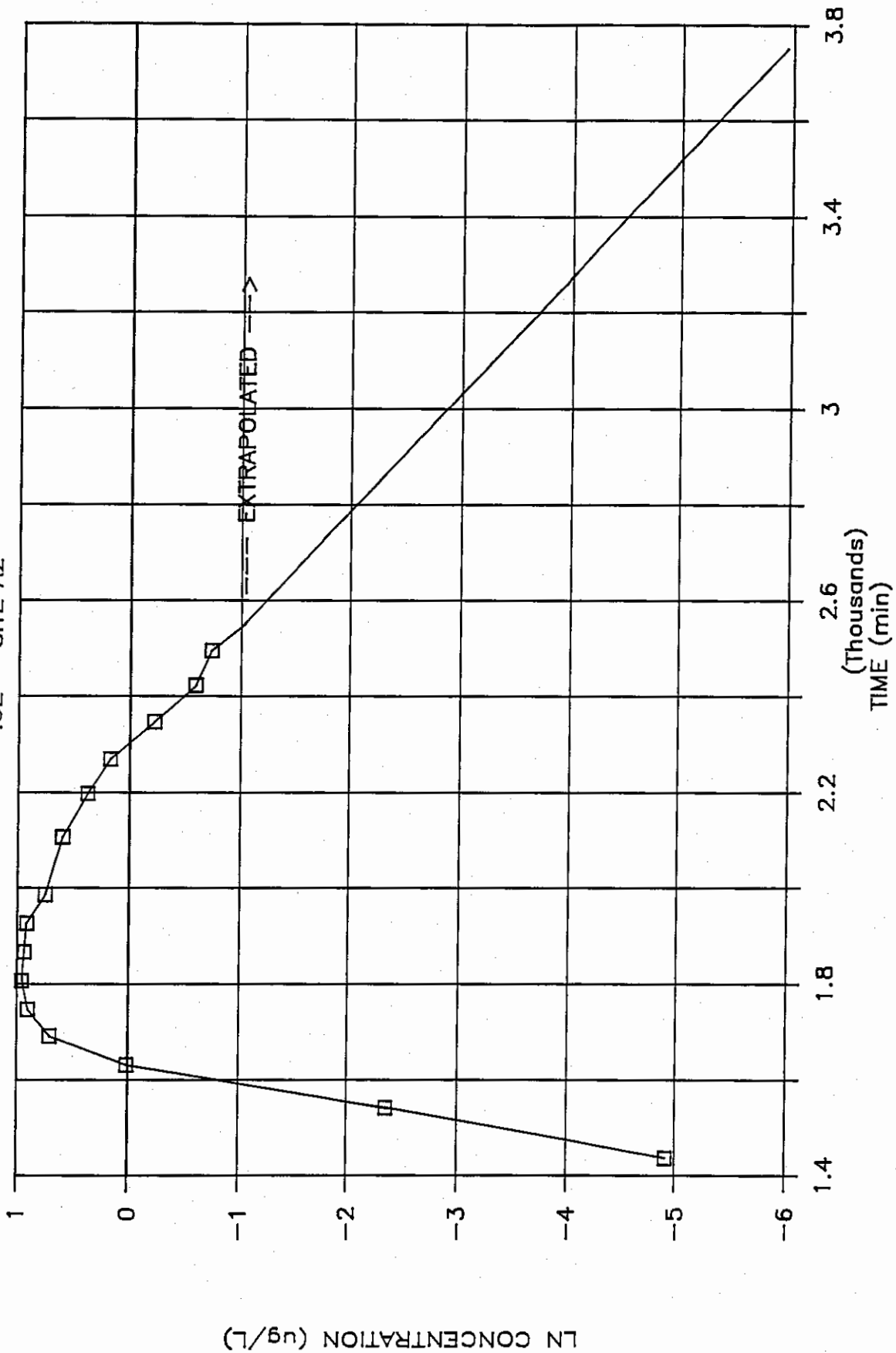
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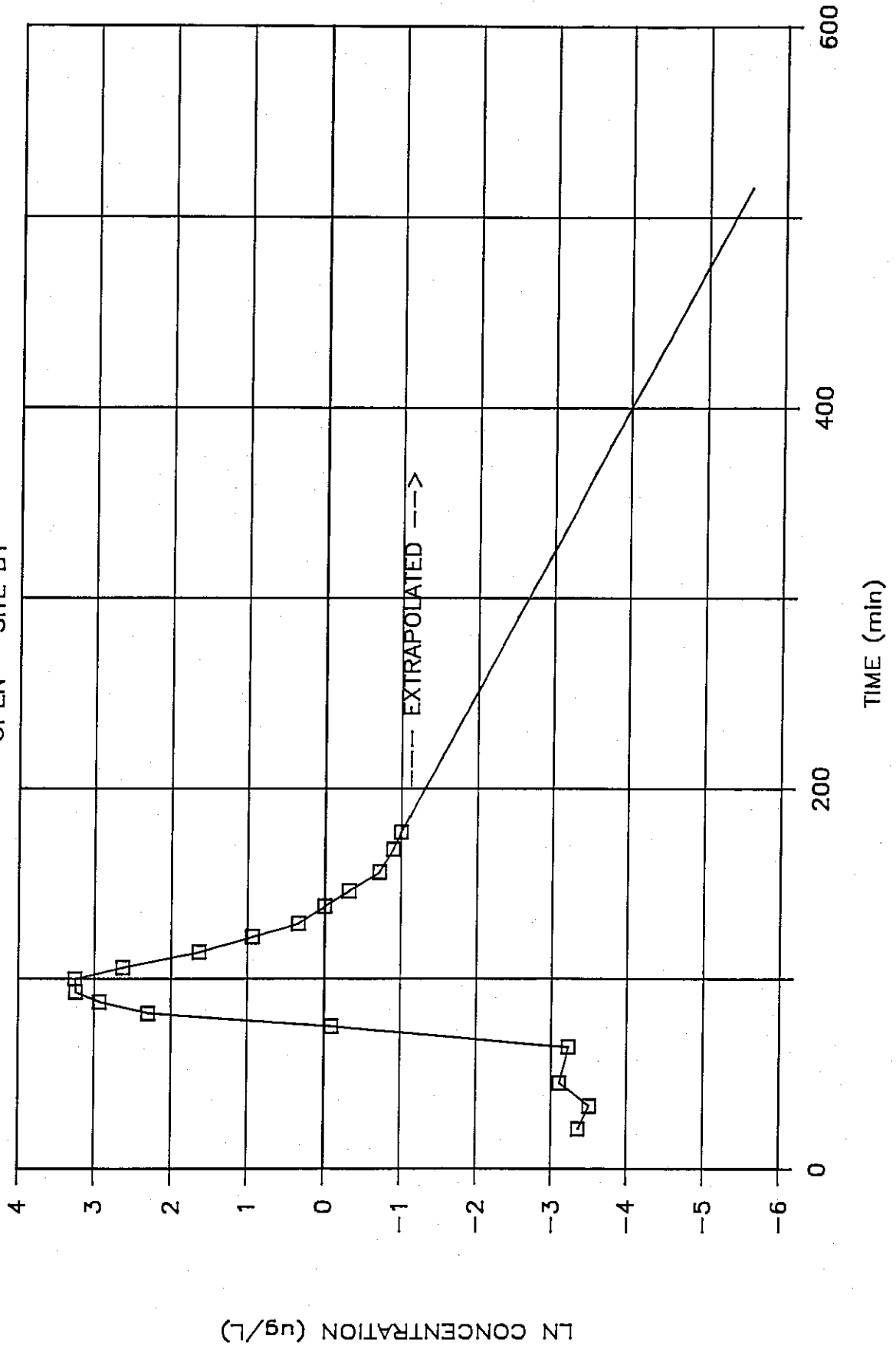
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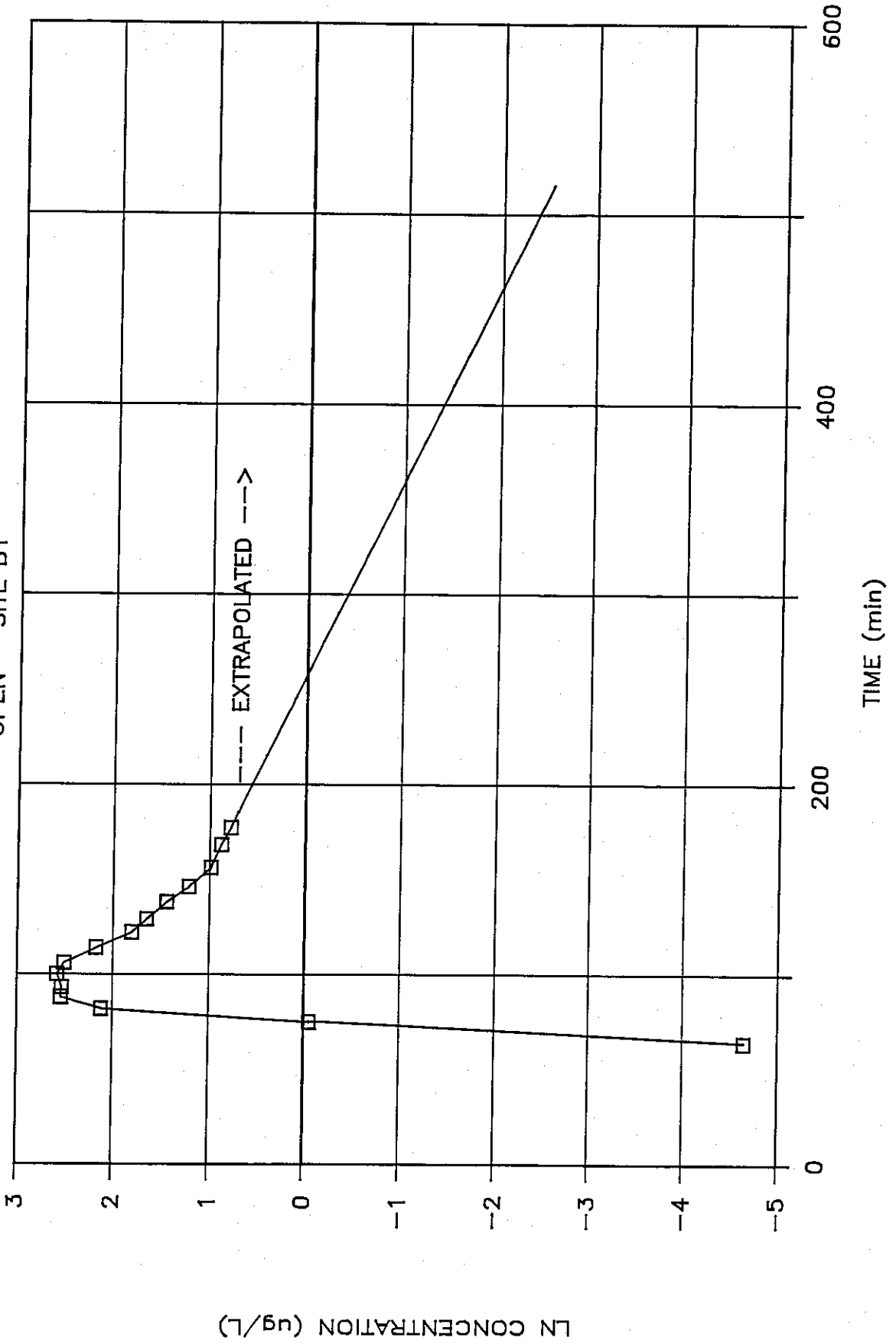
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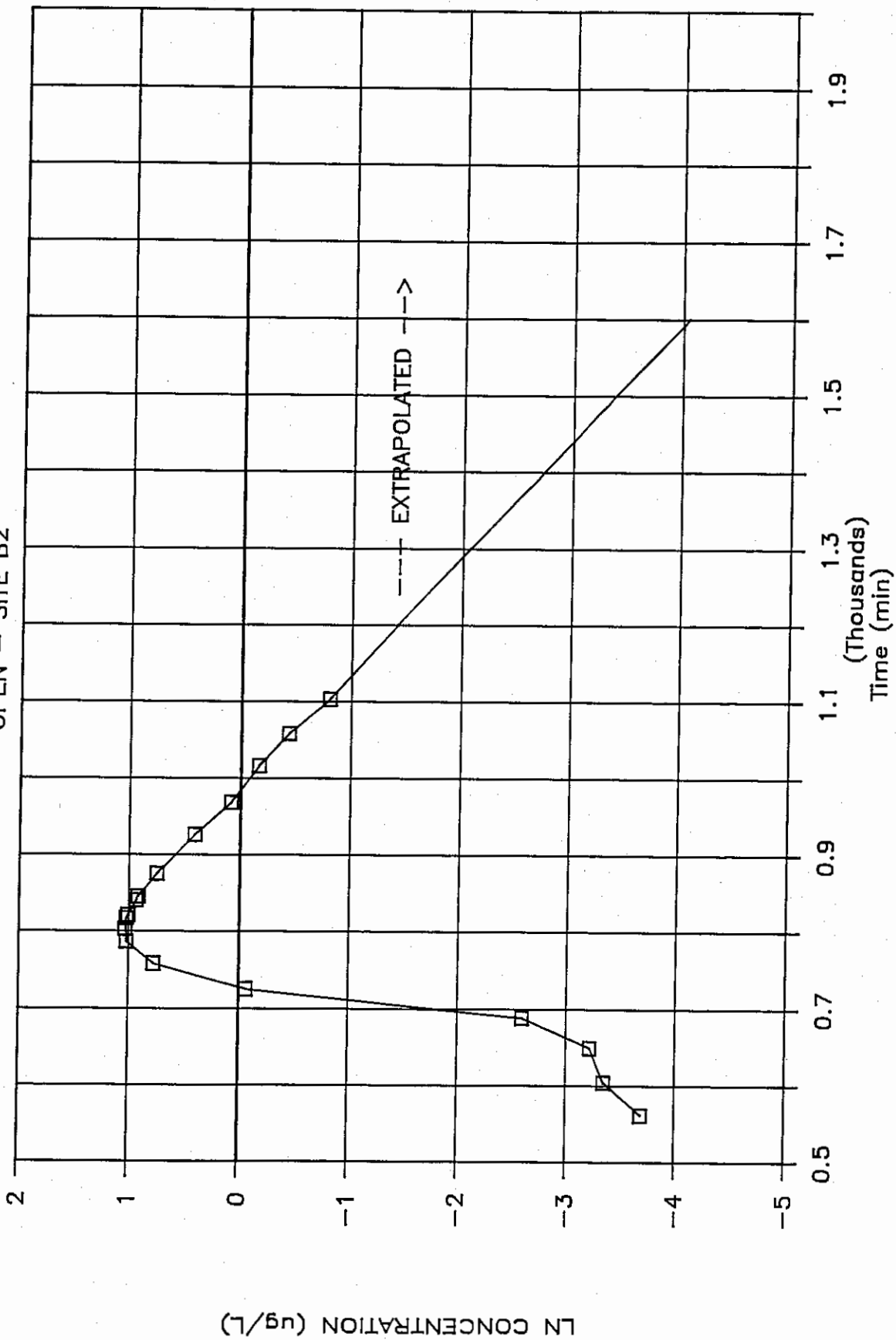
PROPANE

OPEN - SITE B1



DYE

OPEN - SITE B2



PROPANE

OPEN - SITE B2

