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The Measurement of Reaeration in Streams

by

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ABSTRACT

A detailed study of the several methods for the determination of reaeration rates in streams has been made. Particular attention has been given to the floating soluble solids technique which appears to be a simple and reliable method for the measurement of reaeration rates in small streams.

A comprehensive review of both conceptual and empirical mathematical models for the prediction of the reaeration rate coefficient is presented in an attempt to identify the practical outcome and application of these models to natural stream conditions.

A critical review and discussion of the three primary methods usually employed for the reaeration measurement in streams, namely the oxygen balance, disturbed equilibrium and tracer techniques, is presented to allow the understanding of the main principles, related assumptions, degree of applicability and the errors involved in each of these methods. The theoretical basis of a new method, the floating soluble solids technique is introduced, and previous work results presented.

The physico-chemical parameters effect upon the reaeration rate coefficient are discussed in the last part of the literature review.

An extensive laboratory programme has been conducted, during which the individual and interaction effects of three important hydraulic variables (velocity, depth and roughness) upon

atmospheric reaeration, propane gas desorption and solids dissolution processes have been investigated using statistical experimental design and analysis techniques.

The assumption that the ratio between the reaeration and propane desorption rate coefficients is constant and independent of mixing and turbulent conditions has been herein confirmed using a different approach (surface response methodology) from the previously reported tests. A weaker depth dependence of both reaeration and propane desorption rate coefficients has been verified at low velocity levels, and which becomes stronger as average water velocity increases. Natural stram data and energy dissipation response to the same hydraulic factors variation appear to further substantiate the above evidence.

The common parameters and main limitations controlling both reaeration and dissolution processes have been identified and dimensionless correlation equations were developed for the determination of the reaeration coefficient from velocity of solids dissolution measurements.

Field trials, involving the disturbed equilibrium, steady state propane gas tracer, and floating soluble solids methods, appears to confirm the evidence that reaeration coefficients might be successfully estimated from velocity of solids dissolution measurements in small streams.

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LIST OF SYMBOLS

Symbol	Description	Dimension
a	proportionality constant	
a_0	characteristic linear dimension of the solids dissolution model (Shulz,1985)	L
A	surface area between the gas and liquid phases; channel cross-sectional area	L^2
A_m	surface area between the solid and liquid phases	L^2
A_s	surface area of benzoic acid floating solid	L^2
A^γ	collision factor in the kinetic-theory model	
b	proportion of available molecules in the surface layer that escape to the atmosphere (kinetic-theory model)	
b_0	characteristic linear dimension of the solids dissolution model (Shulz,1985)	L
c_0	characteristic linear dimension of the solids dissolution model (Shulz,1985)	L
C	concentration of a diffusing gas or soluble solid	ML^{-3}
C'	depleted DO concentration level (disturbed equilibrium method)	ML^{-3}
C_c	corrected dye tracer concentration	ML^{-3}
C_e	estimated value of the DO concentration	ML^{-3}
C_G	concentration of the tracer gas	ML^{-3}
C_L	concentration of the diffusing gas in the bulk of the liquid	ML^{-3}
C_o	experimentally observed value of the DO conc.	ML^{-3}
C_s	oxygen saturation concentration	ML^{-3}
C_t	diffusing gas concentration at time t	ML^{-3}
C_T	concentration of the conservative tracer	ML^{-3}
C_0	diffusing gas concentration at time t=0	ML^{-3}
C_1	concentration of the diffusing gas at an upstream sampling station	ML^{-3}
C_2	concentration of the diffusing gas at a downstream sampling station	ML^{-3}
C_4	proportionality constant (Dobbins, 1964)	ML^{-3}
C_5	proportionality constant (Dobbins, 1964)	ML^{-3}
d	molecular diameter of a particular gas	L
D	dissolved oxygen deficit	ML^{-3}
D_e	coefficient of eddy diffusion	L^2T^{-1}
D_L	longitudinal dispersion coefficient	L^2T^{-1}
D_m	coefficient of molecular diffusion	L^2T^{-1}
D_0	initial dissolved oxygen deficit	ML^{-3}
D_1	DO deficit at an upstream sampling station	ML^{-3}
D_2	DO deficit at a downstream sampling station	ML^{-3}
E	energy dissipated per unit mass of fluid; random error approximated by a normal distribution $N(0,\sigma^2)$	
E_a	activation energy of a chemical reaction	

E_v	energy dissipated per unit volume of fluid	
E_z	transverse mixing coefficient	L^2T^{-1}
f	exchange coefficient	LT^{-1}
F	Froude number; volumetric flow rate in the oxygen balance equation (Owens & Edwards, 1963)	
F_c	chemical enhancement factor	
g	acceleration due to gravity	LT^{-2}
h	depth of flow	L
h	change in stream bed elevation	L
H	Henry's law coefficient; average depth of flow	L
Ha	Hatta number	
k_r,	chemical reaction rate coefficient	
k_r'	macroscopic reaction rate coefficient	
k_2	reaeration rate coefficient (base 10)	T^{-1}
K_a	chemical dissociation rate	
K_D	dye loss rate coefficient	T^{-1}
K_e	ethylene gas desorption rate coefficient	T^{-1}
K_{Kr}	krypton-85 loss rate coefficient	T^{-1}
K_L	overall liquid film coefficient	LT^{-1}
K_n	nitrification rate coefficient	T^{-1}
K_{oL}	overall mass transfer coefficient	LT^{-1}
K_p	propane gas desorption rate coefficient	T^{-1}
K_{Rn}	radon-222 loss rate coefficient	T^{-1}
K_s	solids dissolution rate coefficient	T^{-1}
K_1	deoxygenation rate coefficient	T^{-1}
K_2	reaeration rate coefficient (base e)	T^{-1}
K_2obs	experimentally measured reaeration rate coefficient	T^{-1}
K_2pred*	reaeration coefficient computed from an empirical predictive model	T^{-1}
K_2pred**	reaeration coefficient computed from velocity of acid benzoic dissolution measurements	T^{-1}
K_{2w}	reaeration rate coefficient under wind conds.	T^{-1}
K_3	rate coefficient for the removal of BOD by sedimentation into an anaerobic benthal layer	T^{-1}
l	diameter of a mixing tank	L
L	linear dimension [L]; biochemical oxygen demand (BOD)	ML^{-3}
L_f	film thickness in the kinetic-theory model	L
L_m	mixing length required for traveltime test	L
L_s	segregation scale in Shulz's (1985) model	L
L_t	BOD at time t	ML^{-3}
L_y	film thickness	L
L_0	ultimate carbonaceous BOD	ML^{-3}
L_0^n	ultimate nitrogenous BOD	ML^{-3}
m	flux of the dissolved gas at injection site	MT^{-1}
M	molecular weight of a particular gas	M
M_G	mass of tracer gas injected into a stream	M
M_s	modulus of compression	MT^{-2}
M_T	mass of conservative tracer injected into a stream	M
n	general exponent, Manning's coefficient	
n_s	number of new surface layers exposed per unit of time (kinetic-theory model)	T^{-1}
N	area under the (C - C') versus time curve at a	

	particular sampling station	L^2
P	photosynthetic production	$ML^{-2}T^{-1}$
P/V	specific power dissipation	$ML^{-1}T^{-3}$
Pe	Peclet number	
q	rate of change of oxygen per unit area	$ML^{-2}T^{-1}$
Q	channel discharge $[L^3T^{-1}]$; rate of gain or loss of oxygen per unit area (Odum,1956)	$ML^{-2}T^{-1}$
r	rate of surface renewal	T^{-1}
R	ideal gas constant; hydraulic radius [L]; rate of plant respiration per unit area	$ML^{-2}T^{-1}$
R'	reaction rate term as defined in equation 128	
R_e	ratio of reaeration to ethylene desorption rate coefficients	
R_p	ratio of reaeration to propane desorption rate coefficients; plant respiration parameter in the oxygen balance equation	$ML^{-2}T^{-1}$
Re	Reynolds number	
Re_t	turbulent Reynolds number	
S	slope of the energy gradient; source and sink term in the general oxygen balance equation	
S_b	benthal oxygen demand	ML^{-3}
S_c	pressure adjusted channel slope	
Sc	Schmidt number	
t	time of travel of the centroids of tracer masses passing sampling stations	T
t	travel time between two sampling stations	T
t_e	exposure period	T
t_p	traveltime of the peak concentration	T
T	absolute temperature in ^oK	
T_p	elapsed time to the peak concentration	T
u	velocity of fluid flow	LT^{-1}
u'	instantaneous eddy fluctuation velocity	LT^{-1}
u'	root mean square velocity fluctuation	LT^{-1}
u_ϵ	dissipation velocity	LT^{-1}
u_*	shear velocity	LT^{-1}
u_x, u_y, u_z	fluid velocity in the x-y-z directions	LT^{-1}
u_0'	velocity fluctuation in the bulk of flow	LT^{-1}
U	average velocity of flow	LT^{-1}
U_*	water shear velocity	LT^{-1}
V	volume of body of liquid	L^3
V_c	critical volume of a particular gas	L^3
V_j	velocity of jet enering the annular channel	LT^{-1}
V_s	velocity of solids dissolution	LT^{-1}
V_w	wind speed	LT^{-1}
W	channel width [L]; weight of a soluble solid after being exposed to the water surface for a certain time t	M
W_0	initial weight of a soluble solid (t=0)	M
x	linear dimension	L
x'	undetermined constant in Shulz and Giorgetti (1986) model	
X	undetermined constant which depends on energy distribution and kinematic viscosity (Shulz and Giorgetti, 1986)	
X_1, X_2	covariates in the response surface models	

y	vertical distance below the water surface	L
z	linear dimension	L
Z_e	equilibrium roughness (O'Connor, 1983)	
α	proportionality constant; velocity factor in the multi-variate analysis of variance model	
β	general parameter in a regression model; depth factor in the multi-variate analysis of variance model	
Γ	roughness factor in the multi-variate analysis of variance model	
δ	thickness of the region near the interface over which velocity fluctuations are damped	L
∂	partial differential operator	
Δ	change in or increment of	
Λ	velocity scale	LT^{-1}
θ	temperature correction coefficient	
K	Von Karman's constant	
λ	turbulent length scale	L
μ	absolute viscosity of the fluid	$ML^{-1}T^{-1}$
ν	kinematic viscosity of the fluid	L^2T^{-1}
ρ	fluid and solid density	ML^{-3}
σ	standard error; surface tension	MT^{-2}
τ	shear stress	
τ_0	dimensionless parameter related to the thickness of the viscous sub-layer (O'Connor,1983)	
ϕ	non-dimensional distribution factor (Yotsukura et al.,1984)	
ϕ_a''	rate of conversion (mass flux) of a substance A	
Φ	empirical function	

INTRODUCTION

The achievement of water quality targets often involves substantial capital investment. Increased public involvement in water resources planning has changed engineering approaches to resource management. The main objectives of water resource development and management schemes often involve aspects ranging across the whole spectrum of social decision making. They include regional development, increases in social well-being, international trade, increase in national economic development, and improvement of the natural environment.

Those responsible for the formulation and development of water quality plans and management policies must have a means of estimating and evaluating temporal and spatial economic and environmental impacts that might result from each alternative. This need has stimulated the development and application of a wide range of mathematical modelling techniques for predicting the various physical and economical impacts of alternative pollution control planning.

For any specific situation, the appropriate mathematical model and the required data depend on the purpose of the study. The evaluation of a proposed industrial waste outfall or discharge site requires the collection of much more detailed data than regional long range water quality planning does.

There is no best single water quality model for all river systems and for all planning situations. An important decision which must be made early in the planning process is the selection of the most appropriate modelling method. This should be flexible enough for development, calibration, validation and execution to be possible within the limits of available time and money.

Most of the water quality models are extensions of Streeter and Phelps' (1925) early work on the quantification of the waste assimilative capacity of rivers. Often used with these so called BOD-DO models are other fairly simple first order exponential decay, dilution and sedimentation models for non-conservative and conservative substances. Relatively more complex multi parameter water quality models have been proposed and applied to more accurately predict the physical, chemical and biological interactions of many constituents and organisms found in natural water bodies. These multi-constituent water quality simulation models generally require more data and computer time, but they can also provide much more detailed and comprehensive information on the quantity and quality of water resulting from various water and land management policies.

Many streams and rivers suffer from depletion of dissolved oxygen due to the discharge of organic material (e.g. domestic and industrial wastewater) which undergoes natural degradation in the river system. The maintenance of reasonable oxygen levels in a stream is essential for the aerobic breakdown of organic matter into simpler compounds. Micro-organisms which feed on organic material require oxygen to respire and so reduce the available oxygen demand. If the requirements of the pollutant are too large, the rate of oxygen removal is greater than the rate of reaeration. Oxygen disappears from the river causing distress to both flora and fauna in the area. If anaerobic conditions prevail, microbial activity may result in the production of toxic compounds such as CH_4, NH_3 and H_2S.

In order to determine the oxygen deficit in a stream for different temperatures, flow conditions and so forth, several methods were developed for the measurement of the pertinent parameters. In the oxygen balance model design, these parameters are generally separated into five categories: (1) hydrologic parameters, (2) hydraulic parameters, (3) oxygen sinks, (4) oxygen sources and (5) temperature effects. Of the oxygen sources, the atmospheric reaeration rate is recognised as one of the most important parameters to be determined since the ability of a water body to assimilate organic waste depends on the oxygen absorption characteristics of the water.

The specific reaeration capacity is therefore a critical design parameter in determining waste treatment requirements, limiting the size of existing industrial facilities and waste treatment plants, selecting the most effective sites for new plants, and planning for pollution control and waste management in river basins.

In most streams atmospheric reaeration makes an important contribution to the oxygen budget and it is important that despite recent developments in the use of hydrocarbon gas tracers, there is no simple satisfactory technique for the reaeration measurement.

Both conceptual and empirical models developed for the indirect estimation of the reaeration coefficient in streams can give widely different estimates when applied outside the range for which they were developed.

In the oxygen balance approach, K_2 values are usually estimated by making appropriate assumptions for other parameters, such as photosynthetic activity and community respiration rates. It is therefore subjected to relatively large errors, and any deviation from those conditions assumed in the model will be reflected in an altered, and incorrect K_2 value.

The disturbed equilibrium method developed in the mid 50's requires the measurement of upstream and downstream DO concentrations at two different values of the upstream deficits. These values may be produced by diurnal variations in photosynthesis and respiration or in BOD inflow, or by the addition of a reducing chemical, such as sodium sulphite. It is also subjected to large errors with its application being limited to those streams with no temporal variation of the natural DO concentration, with no oxygen sources and sinks (except that of atmospheric reaeration). It is essential that there is no residual sulphite within the study reach, otherwise inaccurate measurements will result.

The use of tracers for the determination of the reaeration rate coefficient is the most widely accepted and accurate method. The radioactive tracer method however, has its application limited due to the potential hazardous effects of radiation to which both technical personnel and the populations along the river may be exposed. The sophisticated equipment needed for sample analysis and the need for special authorisation from the local Water Authority for the employment of radioactive substances in public waterways are the other related limitations of the method.

The modified gas tracer technique which employs a low molecular weight hydrocarbon gas (e.g. propane) as a gas tracer and a dye tracer to account for dispersion came as an apparently satisfactory alternative to the radioactive tracer technique. It is a method which is still under investigation and problems concerning the accuracy of the actual measured K_2 values have been reported in the literature. It also requires sophisticated equipment and specialised personnel, so that relatively high costs can often be involved in its employment.

It was not until recently that a new method based on the dissolution of solids floating on the water surface was proposed as a simple and apparently reliable alternative. The method had been originally developed under the assumption that the dissolution of a solid is increased by turbulent eddies which are randomly renewed at the water surface, in a similar way to the oxygen absorption process.

Although strong correlations have been obtained between reaeration and solids dissolution, no one has yet attempted to quantify this relationship mainly because of data scarcity.

The studies now reported are aimed at identifying the commom parameters and limitations controlling both reaeration and solids dissolution processes so that a relationship between the two can be identified. A different approach to the propane gas tracer method for reaeration measurement is also reported. Comparative tests are therefore employed including reaeration rate, velocity of solids dissolution and propane gas desorption rate measurements in an attempt to evaluate the individual and combined effects of three different hydraulic factors, at two experimental levels, upon the characteristic rate coefficients. Field trials, where the relationship developed from laboratory data is more thoroughly evaluated followed.

An extensive literature review is presented to permit an understanding of the principles of gas transfer and subsequent attempts to apply these to practical situations such as natural streams. The limitations of these attempts have been identified and a suitable programme of laboratory and field work devised.

CHAPTER 1

The Mathematical Models Used to Predict the Reaeration Rate Coefficient

1.1 GENERAL ASPECTS:

The absorption of oxygen from the atmosphere into the water is recognised to be a very complicated process. Theoretical and experimental studies developed so far have been only partially successful in explaining the process. An over-simplified view of the physical reaeration process, given by Holley (1977), is as follows:

> "In turbulent water there is a random motion of the water. This random motion carries different parcels of water to the free surface at different times. If a parcel of water is below saturation concentration, then oxygen from the atmosphere is absorbed at the surface and moves into this parcel by molecular diffusion while the parcel is still at the surface. This parcel, with its newly acquired dissolved oxygen then moves back into the bulk of the liquid and is thoroughly mixed with the surrounding water."

Although general agreement about a gas-liquid mass transfer theory has not yet been obtained, considerable information concerning this phenomenon is available both in the chemical and in the sanitary engineering literature. Fairly reliable theories were developed for flows in straight circular pipes, stirred cells, smooth and rough inclined plates, and so on, but were intended for application to totally different conditions (e.g. in industrial process equipment) from the ones observed in natural streams (Dobbins, 1964).

Due to the complexity of the mechanism of flow in open channels, many simplifications have had to be assumed and the theories developed to explain the gas transfer process in natural situations are less rigorous and, thus, less reliable than those used to describe it in pipe flow.

These theories generally fall into two main groups, namely the conceptual and the empirical theories, which will be reviewed in the next sections.

1.2 CONCEPTUAL MODELS:

A critical and comparative description of the available models of gas exchange into liquid surfaces is presented in an attempt to identify the practical outcome of these theories and their application in natural bodies of water.

Most of these models were developed from two classical theories of gas transfer into liquids: the film and renewal theories. The concept of turbulent diffusion, which was later introduced, is largely based on statistical theories of turbulence (well reviewed by Shulz, 1985) and on Taylor's theory of diffusion. The models were then divided into two major classes: the eddy-diffusivity and the eddy-structure models, as described by Theofanous (1984) . The former being concerned with damping effects due to the presence of an interface, and the latter neglecting any damping phenomena.

The kinetic theory is usually considered as a separate group and it is based on the difference between the rate of entry of gas molecules and the rate of loss of these molecules from a surface layer of a liquid.

1.2.1 The Two Film Model:

The film theory developed by Lewis and Whitman (1924) was the earliest attempt to mathematically explain the process of gas transfer at liquid surfaces. It postulates that two laminar fluids exist at the gas-liquid interface and that the resistance to mass transfer is concentrated in these two films. In the case of low solubility gases, such as oxygen in water, the gas film resistance is considered insignificant compared to the liquid film resistance. The gas diffuses so slowly through the liquid film that only a small concentration difference is required across the gas film. It then follows that the concentration of the gas at the interface is equal to the saturation concentration, and that the entire resistance to the diffusion process is in the liquid film. The theory is also based on time-averaged concentration distribution which corresponds to a linear concentration distribution throughout the film, decreasing from the saturation concentration at the free surface to the concentration in the body of the liquid at the bottom of the film.

The rate of change of the concentration in the bulk of the liquid is expressed by:

$$\frac{dC_L}{dt} = K_L \frac{A}{V} (C_s - C_L) = \frac{D_m}{L} \frac{A}{V} (C_s - C_L) \qquad (1)$$

where C_L is the concentration in the bulk of liquid, C_s is the saturation concentration, A is the surface area of the liquid, V is the volume of the liquid, D_m is the molecular diffusivity of the gas in the liquid and K_L is the overall liquid film coefficient.

The assumption of a stagnant film at the free interface of a turbulent liquid has raised many objections to the film theory and is considered physically unacceptable. But according to Holley (1973), the authors do not make it clear that they considered the film to be physically stagnant. In his opinion, "the essence of their model was a region in which molecular diffusion is the controlling factor in the transport process".

The other common objection to the film model is concerned with the assumption of a linear concentration distribution in the film which corresponds to steady-state distributions. This assumption is considered to be highly suspect when considering absorption in natural bodies of water, since in a turbulent liquid mass, the surface film is being continually replaced by liquid from below.

Although the two-film concept has provided a convenient method of analysis and an important means of reporting data on gas absorption, it is generally agreed that it cannot explain satisfactorily the process of oxygen transfer into turbulent liquids (e.g. Bennett and Rathbun, 1972 and Lau, 1972).

The concept of diffusion into laminar layers with an infinitesimal area had to be extended to take into consideration the replacement of fluid elements at the interface from the bulk flow.

1.2.2 Renewal Models:

The mass transfer coefficient predicted by this class of models is generally a function of the molecular diffusivity, average rate of surface renewal and the thickness of the surface layer. The diffusion into the surface layer is assumed to be purely molecular and the diffusivity below this layer is assumed to be infinite.

1.2.2.1 Penetration Models:

The penetration model was first described by Higbie in 1935. He argued that the first stage in the absorption process should be the penetration of the liquid film by the dissolving gas and that the liquid film resistance depended on what was occurring during the penetration period. He considered the laminar film to be present at all times but moving rapidly as a whole, i.e. he assumed that the entire body of water remains stagnant for short periods of time when gases are absorbed and transported downwards by molecular diffusion.

He then solved the diffusion equation,

$$\frac{\partial c}{\partial t} = D_m \frac{\partial^2 c}{\partial y^2} \qquad (2)$$

where y is the vertical distance below the water surface, over the entire depth of the fluid for each exposure period t_e followed by an instantaneous complete mixing after each stagnant period, leading to a new expression for K_L:

$$K_L = 2.\left(\frac{D_m}{\pi . t_e}\right)^{1/2} \qquad (3)$$

The assumption that the surface elements are all exposed for an average time t_e and all replaced at the same time is not quite acceptable when the randomness of turbulent flows are taken into account (Lau, 1972).

In 1951, it was visualised by Danckwerts that the ages of the differential elements of the laminar surface film could be distributed according to a function of the type:

$$f(t) = r.\exp(-rt) \tag{4}$$

where r is the average rate of surface renewal. He also considered the fluid at the surface to consist of elements which had been exposed for varying periods of time and that the probability of any surface element being replaced independent of its time of exposure. By solving equation (2) up to the moment the surface elements were replaced, and by using equation (4) to account for mixing, he derived an expression for the transfer coefficient given by:

$$K_L = (D_m.r)^{1/2} \tag{5}$$

Although much controversy still exists related to the process of gas absorption into the water, it is well recognised that both the film and penetration theories, formed the basis for the development of the models which will now follow:

1.2.2.2 Film-Penetration Models:

The film-penetration model initially developed by Dobbins (1956) and later by Toor and Marchello (1958), consists of assuming the bulk concentration to be constant and applying the diffusion equation (2) to the surface layer only. The existence of a thin film of thickness L_y whose elements are continually being replaced and which absorbs gas by molecular diffusion before being replaced is also assumed. The ages of the surface elements are distributed according to Danckwerts' (1951) distribution function as given by equation (4), leading to the following expression:

$$K_L = (D_m r)^{1/2}\coth[(r\ L_y{}^2/D_m)^{1/2}] \qquad (6)$$

At large renewal rates, the coth term approximates the unity and equation (6) reduces to the surface renewal model. At small renewal rates, because coth(x) ⟶ 1/x for small x, equation (6) reduces to the two-film model.

Certain modifications of the film-penetration model were presented later by Harriott (1962) and Marchello and Toor (1963). In Harriott's model, eddies arriving at random times come to within random distances from the surface, sweeping away the accumulated solute. His model predicts a gradual increase in the effect of diffusivity on the transfer coefficient as diffusivity is decreased. Marchello and Toor (1963) attempted to generalise the film-penetration model by including fluid elements which are not necessarily adjacent to the interface. They assumed that the low level of turbulence near a boundary causes localised mixing rather than gross displacement of fluids. Their model differs from the film-penetration model in that instead of one-element which is randomly replaced by fresh fluid from outside the element, a number of elements in series are considered, each of which is randomly mixed rather than replaced.

In the earliest attempt to relate theoretical development to the parameters of an open channel flow, O'Connor and Dobbins (1956) reasoned that the coth term in equation (6) was close to unity for most practical cases and therefore the liquid film coefficient was proportional to the square root of the renewal rate. Various arguments and relationships were presented (well discussed by Bennett and Rathbun, 1972) for relating r and L_y to flow and fluid characteristics in order to arrive at an expression which could be used for predicting the value of K_2 for natural streams:

$$k_2 = \frac{(D_m\ U)^{1/2}}{2.31\ H^{3/2}} \qquad (7)$$

where U is the mean stream velocity and H is the mean stream depth.

Many doubts concerning both the approach and the validity of the above expression for computing K_2 in natural streams were soon raised (e.g. Diachishin, 1956) and it is agreed that the assumptions made by O'Connor and Dobbins (1956) are not as straight forward as it was initially thought (Lau, 1972).

In 1962, Dobbins conducted a theoretical and experimental study of the mechanism of absorption of gases of low solubility (hydrogen, helium, oxygen, nitrogen and propane) by a turbulent mass of water to verify the applicability of equation (6). He showed that the absorption coefficient K_L is not independent of the properties of the gas and that it decreases with decreasing value of molecular diffusivity D_m. He also compared the absorption coefficients of two different gases (helium and nitrogen) for the same mixing conditions and computed the value of the exponent n, in the expression,

$$\frac{K_1}{K_2} = \left[\frac{(D_m)_1}{(D_m)_2}\right]^n \qquad (8)$$

to be $1/2 \leq n \leq 1$, with n decreasing for increasing mixing conditions. He claimed that his results provided a good verification for the validity of the random distribution function suggested by Danckwerts (1951).

Again, some doubts were raised about Dobbins' method of calculation of the renewal rate (Holley,1973) and also about his methods of data analysis (Rainwater and Holley,1984). The former is concerned with the assumption that for a given mixing condition the two gases were absorbed through the same film thickness, and the latter about his curve fitting procedure, where slight variations of the curves lead to significantly different conclusions. Davies et al. (1964), in their gas absorption studies, verified that none of the values of the exponent n was significantly different from 0.5 and that there was also no significant variation of n with type of agitation. They further stated that the D_m values used by Dobbins (1962) for helium and nitrogen ($D_m(He)=4.45\times10^{-5}cm^2/s$ and $D_m(N_2)=1.88\times10^{-5}\ cm^2/s$ at 20^oC) were "almost certainly too low" (as also verified by Baird and Davidson,1962 and Wise and Houghton,1966). Davies et al. results ($D_m(He)=7.15\times10^{-5}cm^2/s$ and $D_m(N_2)=2.1\times10^{-5}cm^2/s$) led to a variation of n from 0.695 to 0.46 in Dobbins' work.

In 1964, Dobbins proposed another theory relating the parameters of the film-penetration model to the mean flow parameters. Based on the Kolmogoroff's limit for the size of the energy dissipating eddies he obtained:

$$L_y = C_4 \left(\frac{\nu^3}{E}\right)^{1/4} \qquad (9)$$

where C_4 is a constant, ν is the kinematic viscosity of the liquid and E is the energy dissipated per unit mass of the liquid by the entire flow. He reasoned that the rate of expenditure of energy required to overcome the effect of surface tension is proportional to the renewal rate, the surface tension and the square of a scale factor related to the eddy size, allowing him to derive the expression below:

$$r\, L_y^3 = C_5 \frac{\rho \nu^3}{\sigma} \qquad (10)$$

where ρ is the mass density of the liquid and σ its surface tension. The value of the constant was reported to be 14.3 for an oxygen-water system at 20°C, but in order to apply the proposed theoretical formulation, he had to establish a relationship between the various flow parameters and obtain the constant C_4 from a plot of a series of experimental results, given by

$$C_4 = 0.65 + 15000 \left[\frac{(\nu^3/E)^{1/4}}{H}\right]^2 \qquad (11)$$

allowing the derivation of a new prediction equation for K_2, which is given by

$$K_2 = 2.60 \frac{1.0+F^2}{(0.9+F)^{1.5}} \frac{(US)^{0.375}}{H} \coth \left[\frac{4.75(US)^{0.125}}{(0.9+F)^{0.5}}\right] \qquad (12)$$

where K_2 is the reaeration rate coefficient (base e) in hours^{-1} at 25°C, F is the Froude number, S is the slope of the energy gradient, U is the average velocity and H is the average depth of flow.

Thackston and Krenkel(1965) raised some doubts about Dobbins' assumption that the overall rate of the gas absorption is controlled by molecular diffusion and about the lack of a rational basis for C_4 which also casts doubt on the validity of the related constants.

In 1967, Metzger and Dobbins tried to extend the applicability of the film penetration model in predicting gas absorption rates at the gas-liquid interface. From their point of view, the model was limited by the lack of a verified theory for the determination of r and L_y. Based on surface tension and on elasticity theories, they suggested that the resistance to a dynamic pressure, which is developed when an eddy approaches the surface, comes from the elastic character of the surface region. They considered that a compressional modulus could reflect this character, and also based on Kolmogoroff's velocity factor, $(\nu E)^{1/4}$, they obtained the following expression:

$$r L_y^3 = C_5 \frac{\rho \nu^3}{M_s} \qquad (13)$$

where M_s is the modulus of compression. The difference existent between the above equation and a previously proposed equation (11), is that M_s increases in the presence of surface active agents, while the surface tension σ, in equation (11), decreases, thus in agreement with observations that surface active agents retard surface renewals.

From their experimental tests, the group C_5/M_s was found to be constant and equal to 1.3 s^2/g over the range 15° to 30°C. They also argued that M_s was not strongly dependent on the system dynamics, and claimed that the validity of the above equation was therefore established. Metzger (1968) later verified that the presence of 0.5 mg/l of ABS did not affect the value of C_5/M_s, suggesting that the previously determined value of 1.3 s^2/g could be applied to natural waters.

It is generally agreed that the film-penetration model has wider applicability than the two-film or the penetration models alone. The main weakness of this model is that the diffusion process is visualised as taking place in two steps, first molecular diffusion, and second, turbulent diffusion, rather than as being governed by the classical diffusion equation embodying both molecular and turbulent diffusion (Bennett and Rathbun, 1972), leading to difficulties in relating model parameters to flow parameters.

1.2.2.3 Eddy-Diffusivity Models:

The eddy-diffusivity approach emphasises the damping due to the presence of an interface. The governing differential equation (2) is replaced by:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial y}\left[(D_m + D_e)\frac{\partial c}{\partial y}\right] \qquad (14)$$

where D_e is the characteristic eddy-diffusivity defined in terms of the Prandtl mixing length and fluctuation velocity (see Hinze,1959, Orlob,1959 and Krenkel,1960 for a complete discussion of the concept of eddy diffusion and its application in gas transfer problems).

In all eddy-diffusivity models, D_e is assumed to be proportional to some power n (generally n=2) of the distance from the interface, as below:

$$D_e = a\,y^n \qquad (15)$$

where a is a proportionality constant. Equation (15) is consistent with continuity and with the experimentally confirmed trend that the liquid phase mass transfer coefficient K_L is proportional to the square root of the molecular diffusivity D_m. The proportionality constant "a" in the above equation is obtained from the length and velocity scales implied by the particular damping system (Theofanous,1984).

Unique among the eddy-diffusivity models is the Kishinevsky and Serebryansky (1956) one. They have presented experimental results indicating the same values of K_L for gases with different D_m values under vigorous and extremely intense turbulence levels. For these tests, they concluded that K_L was independent of D_m (i.e. n=0).

In one of the earliest attempts to develop a generalised eddy-diffusivity model for the gas transfer process, King (1966) postulated that the mass transfer near the surface is not only due to D_m, but also due to turbulent diffusion caused by small scale eddies. The reasoning behind his model is that there is a zone of primary resistance to mass transfer near the surface, and eddies larger than this zone contribute to the surface renewal, while smaller eddies add to the gradient diffusion within this zone in the form of eddy diffusivity. By solving equation (14) for large surface ages, he obtained:

$$K_L = D_m^{1-1/n} \frac{a^{1-1/n}}{\pi} \sin\left(\frac{\pi}{n}\right) \qquad (16)$$

which gives asymptotic values of K_L at large t for various values of n. He also showed that if n=4 (thus $K_L \alpha D_m^{0.75}$, see

Kozinski and King,1966) and a is given by

$$a = 0.006 \frac{E_v \rho}{\mu^2} \qquad (17)$$

where E_v is the energy dissipation rate per unit of liquid volume and μ is the absolute viscosity of the liquid, the rate of surface renewal r for open channel flows can be described by:

$$r \,\alpha\, \frac{\rho}{\mu} [\frac{E_v H}{\rho}]^{2/3} \qquad (18)$$

It is agreed (Bennett and Rathbun,1972 and Lau,1972) that although his model is physically more realistic than previous models by assuming a continuous eddy-diffusivity profile, thus eliminating the artifice of a surface layer, it has not achieved any improvement for use in the prediction of K_2 since there are now three parameters (a,n and t) to be evaluated.

The eddy-diffusivity models were later classified by the particular damping system, as already mentioned. In the surface tension damping models, the turbulent length scale λ , as given by Davies (1972) from the consideration of the forces damping an eddy at surface, is given by:

$$\frac{1}{\lambda} = \rho \frac{(u')^2}{\sigma} \qquad (19)$$

where u' is the instantaneous eddy fluctuation velocity, ρ is the density of the fluid and σ is the surface tension.

The surface tension damping model is based on Levich's (1962) approach and is well discussed by Davies (1972). Experiments on free turbulent jets of liquids in gas revealed that the mass transfer coefficient varied with Reynolds number

(Re) to a relatively high power (1.3 to 1.5), thus considered to be in agreement with theory. For falling films, the theoretical equation obtained by Davies (1972) was as follows:

$$K_L = 0.32\ D_m^{1/2}\ m^{3/4}\ g^{3/4}\ (\sin\theta)^{3/4}\ \ {}^{1/2}\ \sigma^{-1/2} \qquad (20)$$

where m is the film thickness (which increases with Re), g is the gravitational acceleration, θ is the angle of plate inclination. According to Theofanous (1984), the above model predicts a weak Re dependence (K_L is proportional to $Re^{0.39}$) and reveals the absence of viscosity effects.

Henstock and Hanratty (1979) presented a method for predicting gas absorption rates for liquid layers flowing along a wall based on previous studies on the rate of oxygen absorption from a flowing air stream into water layers on the bottom of a horizontal enclosed channel and on the inside of a vertical pipe. They assumed that the absorption process is controlled by eddies whose length (l_o) and velocity (u_o') are characterised by bulk turbulence properties and that in a region of thickness δ close to the interface the turbulence is dampened by viscosity, so that

$$\frac{\delta u_o'}{\nu} = \text{constant.} \qquad (21)$$

The so called viscous damping model obtained by them for the fully turbulent range (Re > 2000) is given by

$$\frac{K_L}{\nu^{1/3}\ g^{1/3}}\ Sc^{1/2} = 37\times10^{-5}\ Re^{3/4} \qquad (22)$$

where Sc is the Schmidt number ($Sc = \nu/D_m$). According to them, no theory exists to estimate δ, mainly because the kinematics of the convective motions close to the interface are not known. It is expected that $\delta = f(u_o', l_o, \nu$, interfacial properties), but in this case the influence of surface properties have been ignored in estimating δ.

Empirical eddy-diffusivity models were developed in an attempt to satisfactorily predict the dependence of the mass transfer coefficient on Reynolds number and on liquid properties. They were generally developed for turbulent films, and typical examples of this kind of study are given by Chung and Hills (1976) and Lamourelle and Sandall (1972). Both of these models assume that the film thickness is given by:

$$\delta = 0.0672 \left(\frac{\nu^2}{g}\right)^{1/3} Re^{2/3} \qquad (23)$$

Lamourelle and Sandall (1972), studying the absorption of helium, hydrogen, oxygen and carbon dioxide into distilled water over a Re range of 1300 to 8300, obtained the following relationship for K_L:

$$K_L \propto Re^{0.84} D_m^{0.54} \qquad (24)$$

From a combination of the above equation with Danckwerts' model (equation 5), empirical relationships for the rate of surface renewal and the eddy diffusivity were also obtained:

$$r \propto Re^{1.678} \qquad (25)$$

and

$$D_e \propto Re^{1.678} y^2 \qquad (26)$$

Chung and Hills (1976) correlated their data by means of a similar model given by:

$$K_L \propto Re^{0.67} \qquad (27)$$

According to Theofanous (1984), Chung and Hills data indicate that the Re exponent is a rather strong function of viscosity, and as an example, he gives the value of n for 20% glycol solution (n=1.14) which is three times the viscosity of the water. The value of n was correlated by Chung and Mills (1976) as

$$n = 2.08\ Sc^{0.095}\ [\nu\,(g\rho^{3}/\sigma^{3})^{1/4}]^{0.277} \qquad (28)$$

Despite the fact that the above empirical models were developed for falling films, the effects of viscosity need to be explicitly recognised in conceptual model applications and it is also suggested by Theofanous (1984) that Chung and Mills data on viscosity trends should be verified.

1.2.2.4 Eddy-Structure Models:

The eddy-structure models are based on the idealised configuration of turbulence "eddy-structure" neglecting any damping phenomena (Theofanous,1984), have the form suggested by Danckwerts (1951), and approximate the average rate of surface renewal by the ratio of the length-to-velocity scales of the turbulent field.

Fortescue and Pearson (1967) presented a model assuming that mass transfer across the surface of turbulent flowing liquid is determined by relatively large eddy scales. They postulated that the mass transfer properties of a turbulent surface can be modelled by a series of steady square roll cells touching the surface and convecting downstream as a whole with the local mean surface velocity. The large eddies are characterised by the integral length of the turbulent scale, and the velocity pattern within a cell is given by:

$$u_x = \Lambda \sin(\pi.x/L) \cos(\pi.y/L) \quad (29)$$

$$u_y = -\Lambda \cos(\pi.x/L) \sin(\pi.y/L) \quad (30)$$

$$u_z = 0.0 \quad (31)$$

where u_x, u_y, u_z are surface velocities in the x-y-z directions, Λ is a velocity scale approximated by twice the root mean square (RMS) turbulent intensity. The characteristic parameter describing the large eddy model is the Peclet number ($Pe=L.A/D_m$), and they reported that for Pe values "over the range that was relevant", i.e. solution is limited to high values of Pe, the numerical solution of equation (14) yields:

$$K_L = 1.46 \left(\frac{D_m \bar{u}'}{L}\right)^{1/2} \quad (32)$$

where $\bar{u}'$ is the RMS velocity fluctuation. They claimed that the above model gives rather better predictions than either Higbie's (1935) or O'Connor and Dobbins'(1956) models.

It was stated by Brown (1970) that the mass transfer coefficient predicted by the Fortescue and Pearson roll cell model for his experimental system was not as sensitive to changes in the observed coefficients as would be desired, due to the fact that the values of $\bar{u}'$ and L computed from the data tended to be positively correlated. He further stated that there was some indication that the turbulence disturbances in the order of 1/3 the integral length scale could provide more sensitive estimates of K_L than those obtained from the integral length scale itself.

In the small scale model (Lamont and Scott, 1970), scales of the Kolmogoroff eddies are considered to be controlling the gas absorption process. The view in their model is that the small scale motions may be more efficient for interface transfer in spite of their lower energy because they cause mixing within the very surface of a large eddy. The overall mass transfer coefficient obtained by them is given by:

$$K_L = 0.4 \, (\nu / D_m)^{-1/2} (E \, \nu)^{1/4} \qquad (33)$$

where E is the rate of energy dissipated per unit mass of liquid.

In an attempt to approximate the necessary input parameters for the large and small eddy models, Brtko and Kabel (1978) indicated that the large eddy model should give better predictions of the liquid phase mass transfer coefficient when Re_t is less than 70, and that the eddy cell model should give better predictions when Re_t is greater than 750 (where Re_t is the turbulence Reynolds number given by Lu'/ν). At intermediate values , either model is satisfactory. It should be noted that the method of approximation for the input parameters used by Brtko and Kabel yielded predictions of K_L about 3 and 6 times greater than those observed in the laboratory and field, respectively.

Theofanous et al. (1976) in reconsidering the differences between the eddy cell models stated that the essential difficulty in these models is with the arbitrary and conflicting assumptions regarding the group of motions controlling the transfer process. Fortescue and Pearson's large eddy model assumes that the energy containing motions control the process (with u' and L as the relevant properties), while Lamont and

Scott's small eddy model assumes that the dissipating motions are controlling (E is needed instead).

From a comparison of mass transfer models and based on the fact that the magnitude of the turbulent Reynolds number provides a measure of the degree of independence between the large scale energy containing motions and the small scale dissipating ones, Theofanous et al. (1976) developed the so called augmented large eddy models expressed by:

$$K_L = 0.75\ F(\alpha)\ D_m^{1/2}\ (u'/L)^{1/2} \quad \text{for } Re_t < 500 \qquad (34)$$

and

$$K_L = 0.25\ D_m^{1/2}\ (E/\nu)^{1/4} \quad \text{for } Re_t > 500 \qquad (35)$$

where

$$\alpha = 2^{1/2}.t_e/(L/u') \qquad (36)$$

and $F(\alpha)$ is a specified function of α.

According to Theofanous (1984), at high values of turbulence the small eddies may be relevant to the mass transfer phenomena and the relatively small experimental coefficient (about 0.25) is an indication of some damping at the interface. At low turbulent levels, on the other hand, the relatively high experimental coefficient (about 0.75) indicates that the control is shifting to motions of different scales. Indeed, Theofanous et al. (1976) have indicated that these coefficients are only a weak function of surface tension, yet it would be desirable to incorporate corrections for such effects in the models above.

In summarising mass transfer results in terms of the augmented large eddy model, Theofanous (1984) claimed that the above model provides the most consistent fundamental description of the available data.

In 1979, Davies and Lozano, measured turbulence intensity and velocity spectra in water, very close to an air interface in a stirrer, in a submerged jet and in a falling film using a hot wire anemometer. They concluded that 60 to 80% of the total eddy energy lies in the larger eddies, with only 1% (or less) in the Kolmogoroff range, thus controlling the mass transfer process at a free surface. Their results are also in agreement with Danckwerts (1951) model.

As an extension of a statement made by Lau (1972), it can be said that the problems of defining circulation patterns (e.g.within an eddy cell), measuring velocity and length scales, and the necessity of numerical solution even for a simplified model, limits the eddy-structure models to an explanatory role only.

1.2.3 Kinetic Theory Models:

The kinetic theory originally developed by Miyamoto (1930) was presented by Krenkel (1960) and Krenkel and Orlob (1962). The only assumption required here is that those molecules with a velocity component normal to the interface with a certain value, could enter or leave the liquid, and the resulting equation is given by:

$$K_L = \frac{1}{1000} \left(\frac{R.T}{2\pi M}\right)^{1/2} \exp[-(M.u_o'^2/2RT)] \qquad (37)$$

where R is the ideal gas constant, T is the absolute temperature, M is the molecular weight of the gas and u_o' is the velocity which a solute molecule must attain, normal to the interface to be able to leave the liquid.

It was stated by Krenkel and Orlob (1962) that the approach offers a reasonable explanation of the method of entry of gas molecules into the surface of the liquid, but it takes no account of the effect of turbulence on the ultimate mixing of the gas molecules within the bulk of the liquid.

They considered the absorption of gas molecules as being an energy controlled kinetic rate process and based on Arrhenius equation which states that the variation of reaction rates with temperature can be expressed by

$$k = A' \exp(-E_a/RT) \qquad (38)$$

where k is the reaction rate, A' is the collision factor, E_a is the activation energy, proposed that the gas transfer process could be described by:

$$K_2 = r \exp(-E_a/RT) \qquad (39)$$

where the group "$\exp(-E_a/RT)$" is a measure of the fraction of the total number of molecules that possess the requisite activation energy to enable them to take part in the reaction and r is the rate of surface renewal.

Another kinetic-theory model was presented by Tsivoglou (1967). Also based on the consideration of the difference between the rate of entry and the rate of loss of gas molecules from a surface layer of liquid, he obtained the following expression:

$$K_L = b.L_f.n_s \qquad (40)$$

where b is the proportion of available molecules in the surface layer that actually escape to the atmosphere, L_f is the thickness of the surface layer from which gas molecules can escape to the atmosphere, and n_s is the number of new surface layers exposed per unit of time.

According to Rainwater and Holley (1984), the assumption that molecular diffusion occurs in a thin surface layer that is continuously replaced from the bulk of the mixed fluid (implicit in the above equation) is contradictory to the assumptions of the theories previously described in this chapter. The main assumption of the renewal models is that the effects of molecular diffusion and turbulent mixing within the body of fluid are combined to distribute the concentration of gas throughout the fluid. Tsivoglou's assumption also requires the concentration gradient to be multi-directional, since neighbouring volume elements would not necessarily have the same concentration of gas, while the concentration gradient in the body of a fluid is generally considered to be only in the vertical direction.

Although none of the parameters on the right hand-side of equation (40) can be measured, some of the results obtained by Tsivoglou (1967) by manipulation of this model are of interest (see Bennett and Rathbun,1972 and also Rainwater and Holley,1984), and will be discussed later.

1.2.4 Recent Developments:

The development of reliable techniques for the measurement of turbulence at the gas-liquid interface (e.g. Davies and Lozano,1979 and Dickey et al.,1984) made possible a more accurate investigation of the energy dissipation effects on the transfer coefficient as well as a better understanding of the turbulence structure at this region (see Hunt,1984).

It has been generally agreed that K_L varies with the 1/2 power of the molecular diffusivity, and consequently with -1/2 power of the Schmidt number (see Ledwell,1984), which is in accordance with most of the renewal models described before.

However, controversy still exists in relation to the rate of energy dissipation effects upon the transfer coefficient K_L. As recently demonstrated by Shulz (1985), the usual approximation for the energy dissipation rate (E=USg) used by various authors (see Rathbun,1977) in open channel flows leads to a variation of K_L with the 1/3 power of the energy dissipated. It has been suggested (Roberts,1984 and Shulz,1985) that there is actually significant evidence that this exponent is different from 1/3. Roberts (1984) found it to be between 0.776 and 0.84, while Shulz and Giorgetti (1986) argue that it appears to be in the 0.0 - 0.5 range.

Based on the statistical theory of turbulence and on the turbulent mixer theory (Corrsin,1957,1964), Shulz and Giorgetti (1986) developed an interesting model by assuming stationary and isotropic turbulence and also uniform concentration distribution at the interface. The model is given by two equations. For low rates of energy dissipation, they obtained:

$$K_L = \frac{x'X}{5\ Sc^{1/2}} \qquad (41)$$

and for high rates of energy dissipation (also high values of Sc), the equation given is:

$$K_L = \left(\frac{x'}{Sc^{1/2}}\right) / \left[3 \left(\frac{5}{\pi}\right)^{2/3}\left(\frac{L_s^2}{E}\right)^{1/3} + \left(\frac{\nu}{E}\right)^{1/2}\ln(Sc)\right] \quad (42)$$

where x' can be a function of both Sc and the geometric scale, X is another constant depending on the energy distribution and on the kinematic viscosity, and L_s is the segregation scale (all parameters defined by Corrsin,1957,1964).

It is claimed by Shulz and Giorgetti (1986) that the combination of the above equations, when applied to situations of unbroken surface, leads to a variation of K_L with the rate of energy dissipated which includes all the exponents found in the literature. For very low values of Sc, K_L is apparently independent of the rate of energy dissipated (but still dependent on the energy distribution) at the interface, but as the energy dissipated increases, its exponent increases until a value of 1/2 and then starts to decrease until a value of 1/3. Their conclusion is similar to that presented by Kozinski and King (1966) where the exponent of the rate of energy dissipated was found to be between 0.2 and 0.4. The exponents greater than 0.5 are due to situations of broken surface where there is an increase in the surface area at the gas-liquid interface.

Despite the fact that the above model is a new and valid attempt to describe the process of gas absorption into turbulent liquids by applying the statistical theory of turbulence to a region near the interface, it is, as all other conceptual models are, limited by its own assumptions (ideal situation) and by the difficulty in measuring the parameters involved (Shulz and Giorgetti,1986).

As in all conceptual models described in this chapter, one is always left with the problem of determining and measuring parameters like the rate of surface renewal, film thickness, rate of energy dissipated and so on. It is questionable whether parameters measured in ideal situations (e.g. stirred cells, falling films, submerged jets) can be applied to open channel flow. The impossibility in measuring such parameters in natural conditions, leads in two different directions. One of them is to relate these parameters to measurable hydraulic variables so that the conceptual models can be applied to predict reaeration rates in natural streams. A possibility which has not been successful since the early work of O'Connor and Dobbins (1956). The other way, regarded as more realistic, is to limit the use of conceptual models to an explanatory role only, as mentioned before, and apply them for the development of reaeration rate measurement methods (e.g. Tsivoglou et al.,1965,1968).

1.2.5 Practical Applications:

It has been well recognised that for the case of diffusion of a gas into or out of a liquid, the interface between the gas and the liquid constitutes a resistance or barrier to gas transfer and that this is a controlling factor in gas transfer. In other words, the theories of absorption in which a chemical moves from air to liquid can be used equally well for desorption in which a chemical moves from liquid to air (Danckwerts,1970). The application of such theories led to the development of the gas tracer method for measuring reaeration in streams.

In their studies for the development of the radiotracer technique for the measurement of reaeration rates in streams, Tsivoglou et al. (1965) and Tsivoglou (1967) concluded that the values of rate coefficient ratios between two different gases were independent of temperature and mixing condition. A major assumption of the tracer method. He used his results to support his own model (equation 40) for relating the rate coefficients for different gases.

According to his model, the factor b in equation (40) varies with temperature according to the relation:

$$(b)_{T2} = (b)_{T1} \frac{(C_s)_{T1}}{(C_s)_{T2}} \tag{43}$$

where the subscripts indicate two different temperatures. The combination of the above equation with equation (40) yields:

$$\frac{(K_2)_{T2}}{(K_2)_{T1}} = \frac{(C_s)_{T1}}{(C_s)_{T2}} = \theta^{(T2-T1)} \tag{44}$$

in which θ is the temperature correction coefficient for the mass transfer coefficient. The values calculated by Tsivoglou for θ, for oxygen and water, between 0 and 30^oC, range from 1.018 to 1.026. But because this is another topic which has been subjected to much controversy (no single relationship between temperature and reaeration seems to best explain the data), the problem has been only briefly depicted here as an example of conceptual modeling application to practical situations. A detailed discussion is presented in Chapter 3.

As described by Rainwater and Holley (1984), Tsivoglou also showed from his studies that for the simultaneous transfer of two gases the following equation would apply:

$$\frac{(K_2)_1}{(K_2)_2} = \frac{(D_m)_1}{(D_m)_2} \qquad (45)$$

an equation which corresponds to Dobbins' results, equation (8) with the exponent n equals to one.

In further developing his model, Tsivoglou (1967) pointed out that if mass transfer through the gas-liquid interface is governed by Einstein's law of diffusion, the ratio of molecular diffusion coefficients becomes:

$$\frac{(D_m)_1}{(D_m)_2} = \frac{d_2}{d_1} \qquad (46)$$

where d is the molecular diameter of a particular gas. The predicted ratios for two different gases were found to be in good agreement with the observed ones, and according to Rainwater and Holley (1984), although some doubts exist about the soundness of Tsivoglou's theory, his experimental results are not inconsistent with the conclusion of his model.

The relation between K_2 and D_m (equation 45), as proposed by Tsivoglou, was further investigated by Rathbun et al.(1978) in developing a modified gas tracer technique for the measurement of reaeration rates in streams. They carried out an extensive laboratory tests to establish the ratios between the absorption rate of oxygen and the desorption rate of two hydrocarbon gases (ethylene and propane), which are as follows:

$$R_e = \frac{K_2}{K_e} = 1.15 \tag{47}$$

and

$$R_p = \frac{K_2}{K_p} = 1.39 \tag{48}$$

The ratio between the molecular diffusivities of the above gases, for different temperatures, calculated from the values available in the literature (Baird and Davidson,1962 and Wise and Houghton,1966) is about 1.29 for oxygen/ethylene and 1.3 for oxygen/propane. But considering the combined experimental errors in determining the molecular diffusivities and the absorption and desorption rate coefficients, Rathbun et al. concluded that the above ratios (equations 47 and 48) were consistent with Tsivoglou's theory and that they were independent of mixing and temperature conditions, a major assumption of the tracer method.

Rainwater and Holley (1984) presented a study made by Kyosai et al. (1980) who did an experimental and theoretical investigation of simultaneous transfer of volatile substance in water in sewers. Their results were used to support the validity of a relationship developed by the combination of Dobbins (1962) and Wilke and Chang (1955) studies. Their final conclusion was that the ratio between the transfer coefficients of two different gases is given by:

$$\frac{(K_L)_1}{(K_L)_2} = [\frac{(V_c)_2}{(V_c)_1}]^{0.629n} \tag{49}$$

where V_c is the volume occupied by one mole of a substance at its critical temperature and pressure and n is assumed to be 1/2 at sufficiently high renewal rates, as defined by them. The data of Rathbun et al.(1978) was applied to the above expression, resulting in theoretical R_e values equal to 1.19 and R_p values equal to 1.38, which do appear consistent with experimental results.

The acceptance of Dobbins' concept of a variable n and the related assumption that complete mixing corresponds to the condition of high mixing intensity required for n=1/2 is questioned by Rainwater and Holley (1984) in relation to Kyosai et al.(1980) studies. It is stated by them that this assumption contradicts the conclusion of Rathbun et al.(1978), whose data Kyosai et al. used to verify their model. According to Rathbun et al.(1978) their results are in agreement with those obtained by Tsivoglou, i.e. n=1. Using a simplistic comparison between the analysis of Kyosai et al. and of Tsivoglou, Rainwater and Holley (1984) provide a possible explanation for the use of n=1/2 by Kyosai et al. and bring different points of view into some agreement. If the critical molecular volume is proportional to the cube of the molecular diameter, for n=1/2, the following relationship is obtained:

$$\left[\frac{(V_c)_2}{(V_c)_1}\right]^{0.315} = \left(\frac{d_2}{d_1}\right)^{0.94} = \frac{(K_2)_1}{(K_2)_2} \qquad (50)$$

and a general consistency between equations (49) and (45) is then verified. Although this is being recognised as a rather simplistic explanation, it does have its merits since it brings some insights for obtaining a more generalised form of relationship for the gas absorption process in turbulent liquids from two apparently unreconcilable theories (Dobbins' and Tsivoglou's).

1.3 EMPIRICAL MODELS:

The first attempt to relate measurable hydraulic variables to the reaeration rate coefficient was made by Streeter and Phelps (1925). They found that the physical factors which change with river stage were the most significant upon reaeration rates, mainly velocity and depth. The following relationship was then obtained:

$$K_2 = C \frac{U^n}{H^2} \tag{51}$$

where C and n are constant which must be evaluated for a particular hydraulic situation.

Since then, a number of empirical equations has been developed based on regression-correlation analysis of the experimental data. The formulas that are shown in Table 1 are based on gas transfer theory, river mixing, dimensional analysis or a combination of the three. They are mainly meant as tools for design and management, rather than concerned with the oxygen absorption mechanism (Lau,1972).

As it has been pointed out by Bennett and Rathbun(1972) and many others who reviewed the various empirical formulations (e.g. Lau,1972, Zogorski and Faust,1973, Wilson and MacLeod,1974, Brown,1974, Kramer,1974, Holley,1977, and Rathbun,1977 among others), it is of upmost importance to

Table 1: Reaeration Rate Coefficient Predictive Equations for Rivers and Streams

Author(s)	K_2 (1/days)	Development Conditions						Observations
		Hmin	Hmax	Umin	Umax	K_2min	K_2max	
1.O'Connor and Dobbins (1956)	$3.72\ U^{0.5}\ H^{-1.5}$	0.30	11.0	0.06	1.30	0.02	5.80	shallow to deep streams oxygen balance applied to various data sources
2.Churchill et al. (1962)	$5.02\ U^{0.969}\ H^{-1.673}$	0.65	3.50	0.55	1.50	0.23	5.56	oxygen balance applied to various intermediate streams of the Tennessee valley
3.Krenkel and Orlob (1962)	$173.6\ (US)^{0.408}\ H^{-0.660}$	0.02	0.06	0.07	0.65	10.6	115.3	laboratory studies in a 0.30m wide flume with variable slope
4.Owens et al. (1964)	$6.92\ U^{0.73}\ H^{-1.75}$	0.12	0.75	0.03	1.50	0.31	49.2	disturbed equilibrium method applied to some shallow streams in England
5.Owens et al. (1964)	$5.33\ U^{0.67}\ H^{-1.85}$			0.03	0.55			
6.Dobbins (1964)	$55.4 \dfrac{1+F^2}{(0.9+F)^{1.5}} \dfrac{(US)^{0.375}}{H} \coth\left[\dfrac{4.75(US)^{0.125}}{(0.9+F)^{0.5}}\right]$	same as O'Connor and Dobbins						oxygen balance applied to various data sources as O'Connor and Dobbins
7.Langbein and Durum (1967)	$5.13\ U\ H^{-1.33}$	0.01	11.0	0.01	1.50	0.02	115.3	synthesis of various data sources (O'Connor-Dobbins, Churchill et al.,Krenkel-Orlob and Streeter et al.)
8.Isaacs and Gaudy (1968)	$4.75\ U\ H^{-1.5}$	0.15	0.40	0.17	0.50	1.34	13.4	laboratory studies in a recirculating cylindrical flume
9.Thackston and Krenkel (1969)	$24.92(1 + F^{0.5})u_*H^{-1.0}$	0.01	0.08	0.10	0.70	11.1	72.9	laboratory studies in a 0.60m wide flume with variable slope
10.Negulescu and Rojanski (1969)	$10.91\ U^{0.85}\ H^{-1.0}$	0.05	0.15	0.20	0.60	8.64	18.7	laboratory studies in a flume with variable width (0.07 to 0.20m)
11.Cadwallader and McDonnell (1969)	$185.4\ (US)^{0.5}\ H^{-1.0}$	0.06	3.50	0.03	1.50	0.26	40.0	multivariate analysis of reaeration data (Churchill et al.,Owens et al. and WPRL)

Author(s)	K_2 (1/days)	Development Conditions						Observations
		Hmin	Hmax	Umin	Umax	K_2min	K_2max	
12.Padden and Gloyna (1971)	$4.52\ U^{0.703}\ H^{-1.054}$	0.04	0.20	0.03	0.14	0.72	10.2	laboratory studies in a metal flume of 60m in length and 0.75m wide
13.Lau (1972)	$2514\ (u_*/U)^3\ (U/H)$	0.01	3.50	0.07	1.50	0.26	115.3	synthesis of data from Churchill et al.,Krenkel, and Thackston-Krenkel
14.Parkhurst and Pomeroy(1972)	$23.0(1 + 0.17F^2)(US)^{0.375}H^{-1.0}$	0.05	0.48	0.45	3.60			deoxygenation method used in 12 sewers in the Los Angeles County Sanitation District
15.Bennett and Rathbun (1972)	$32.81\ U^{0.413}\ S^{0.273}\ H^{-1.408}$	0.01	11.0	0.03	1.50	0.02	115.3	reanalysis of hystorical reaeration data
	$5.58\ U^{0.607}\ H^{-1.689}$	0.01	11.0	0.03	1.50	0.02	115.3	
17.Bansal (1973)	$1.80\ U^{0.6}\ H^{-1.40}$	0.30	11.0	0.06	1.50	0.02	5.80	synthesis of Churchill et al. and O'Connor and Dobbins field data
18.Tsivoglou and Wallace (1972)	$0.18\ \left(\frac{\Delta h}{t}\right)$	0.24	2.30	0.07	0.75	0.65	14.9	radioactive tracer technique applied to 5 different streams in the U.S.A.
19.Tsivoglou and Neal (1976)	$0.36\ \left(\frac{\Delta h}{t}\right)$ for $0.03 \le Q \le 0.30$ $0.18\ \left(\frac{\Delta h}{t}\right)$ for $0.70 \le Q \le 85.0$	very wide range of hydraulic conditions, with flow varying from 0.006 to 85.0 m^3/s and reaeration rates from 0.0 to 360.0 $days^{-1}$						data collected in 24 different streams in six states of the U.S.A. using radioactive tracer method
20.Foree (1976)	$0.30 + 595.8\ S^{0.75}$	-	-	0.02	0.24	0.34	20.7	radioactive tracer technique used on small streams in the state of Kentucky, U.S.A.
21.Grant (1976)	$0.27\ \left(\frac{\Delta h}{t}\right)$	0.03	0.45	0.10	0.35	1.83	49.0	radioactive tracer data collected from 10 small streams in Wisconsin,U.S.A.
22.Grant (1978)	$0.18\ \left(\frac{\Delta h}{t}\right)$	0.30	3.00	0.06		0.01	0.70	radioactive tracer data collected from the Rock River, Wisconsin and Illinois,U.S.A.

Author(s)	K_2 (1/days)	Development Conditions						Observations
		Hmin	Hmax	Umin	Umax	K_2min	K_2max	
23.Shindala and Truax (1980)	$0.26 \left(\frac{\Delta h}{t}\right)$ for $Q \le 0.30$ $0.19 \left(\frac{\Delta h}{t}\right)$ for $0.30 \le Q \le 8.0$	0.70	13.0	0.01	0.35	0.11	49.5	based on statistical analysis of reaeration coefficients in 7 states of the U.S.A. where the radioactive tracer method was used to measure K_2
24.Iberall and Cardon (1966)	$C \frac{Re^{1/8}}{H^2 Sc^{2/3}}$ for $10^5 \le Re \le 10^7$	0.02	11.0	0.06	1.50	0.02	115.3	synthesis of various data sources (Streeter-Phelps, Streeter et al., O'Connor-Dobbins, Churchill et al., and Krenkel)
25.Roberts and Demond (1982)	$0.023 \frac{D_m}{H^2} Re^{4/5} Sc^{1/3}$	0.01	11.0	0.03	1.50	0.02	129.6	synthesis of 121 field data points and 118 laboratory data points from various sources
26.Eloubaidy and Plate (1972)	$5.0\times10^{-5} \frac{V_w^{1.5} U_*}{\nu}$	0.05	0.15	0.17	0.36	16.2	76.8	laboratory studies in a wind-wave tunnel facility to investigate wind effects on K_2
27.Mattingly (1977)	$\frac{K_{2w}}{K_2} - 1 = 0.2395\, V_w^{1.643}$							laboratory studies of the effects of wind on the reaeration rate coefficient

where,

C = constant of proportionality

D_m = molecular diffusivity in cm^2/s

F = Froude number

g = acceleration due to gravity in m/s^2

H = average stream depth in metres

Δh = change in stream bed elevation between two points in metres

K_2 = reaeration rate coefficient (base e) at 20°C in $days^{-1}$.

K_{2w} = reaeration rate coefficient under wind conditions in $days^{-1}$

Q = stream flow rate in m^3/s

R = hydraulic radius in metres

Re = Reynolds number

S = slope in m/m

Sc = Schmidt number

S_c = pressure-adjusted channel slope (dimensionless)

t = travel time between two points where h was measured (days)

U = average stream velocity in m/s

u_* = shear velocity = $(gRS)^{1/2}$ in m/s

U_* = water shear velocity = $(gHS_c)^{1/2}$

V_w = wind speed in m/s

W = average stream width in metres

ν = kinematic viscosity of water in m^2/s

Obs.:this table is adapted from Bowie et al.(1985)

consider the conditions under which a particular predictive equation was derived (also listed in Table 1) and not to apply it out of its range of applicability. Most of these equations were developed from data collected for specific ranges of those hydraulic and physical characteristics which have a bearing on the gas transfer process, and outside of its range, they often give widely differing estimates of the reaeration coefficient, as it can be seen in Figures 1 and 2.

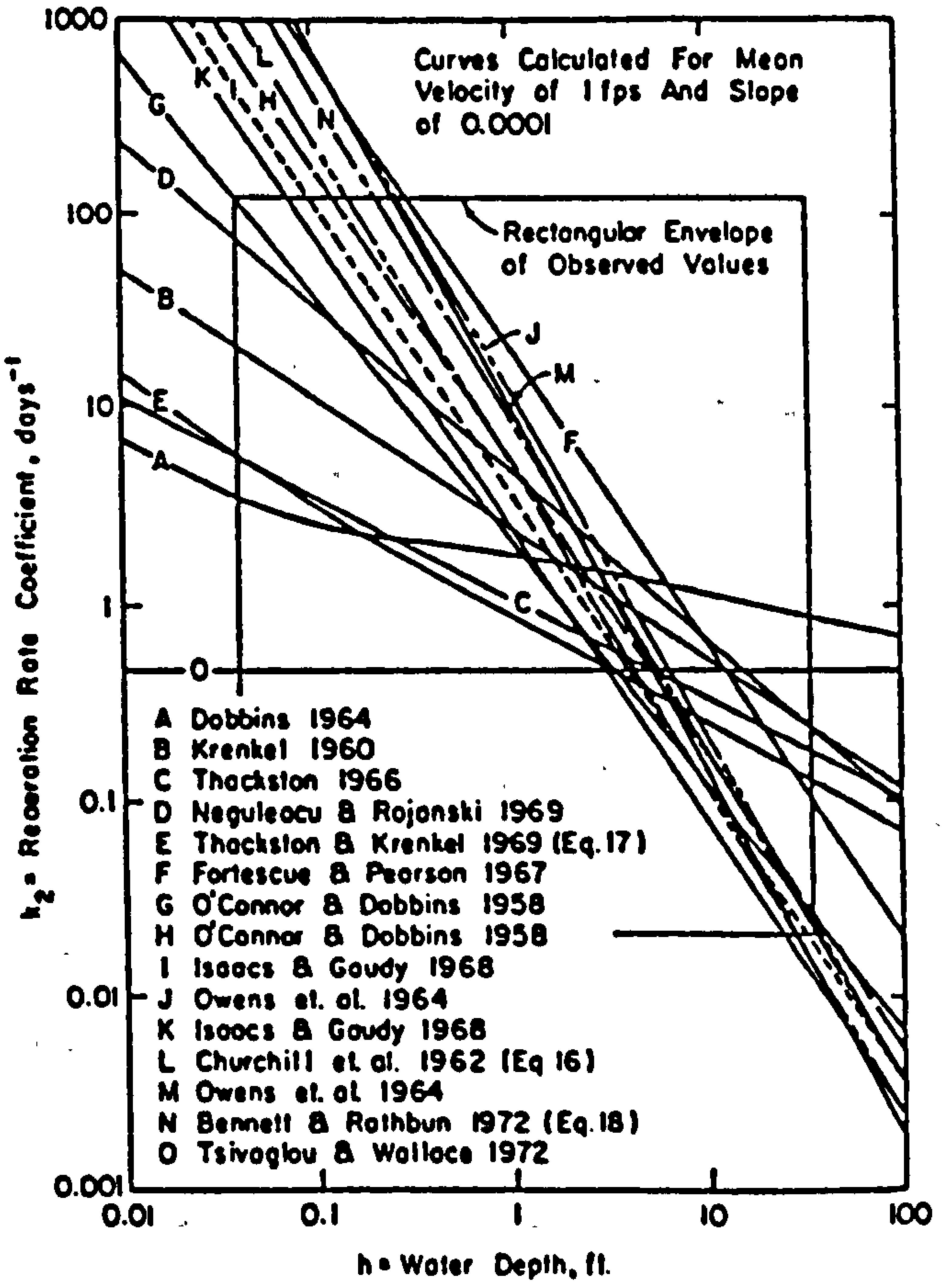


Figure 1:Comparison of reaeration prediction equation for a constant slope and mean velocity (1ft=0.3048m) (after Bennett and Rathbun,1972)

These differences can seriously affect the calculation of the oxygen balance, lead to a misinterpretation of the effects of the waste water discharge on the oxygen resources of a stream, and result in an improper determination of the required degree of waste treatment (St.John et al.,1984).

This problem gave rise to the development of procedures and rational methods to guide the engineer in the selection of a proper predictive equation. Covar (1976), as discussed by Zizon et al.(1978) and Wilcock (1982), was the first to realise that the research of O'Connor and Dobbins(1956), Churchill et al.

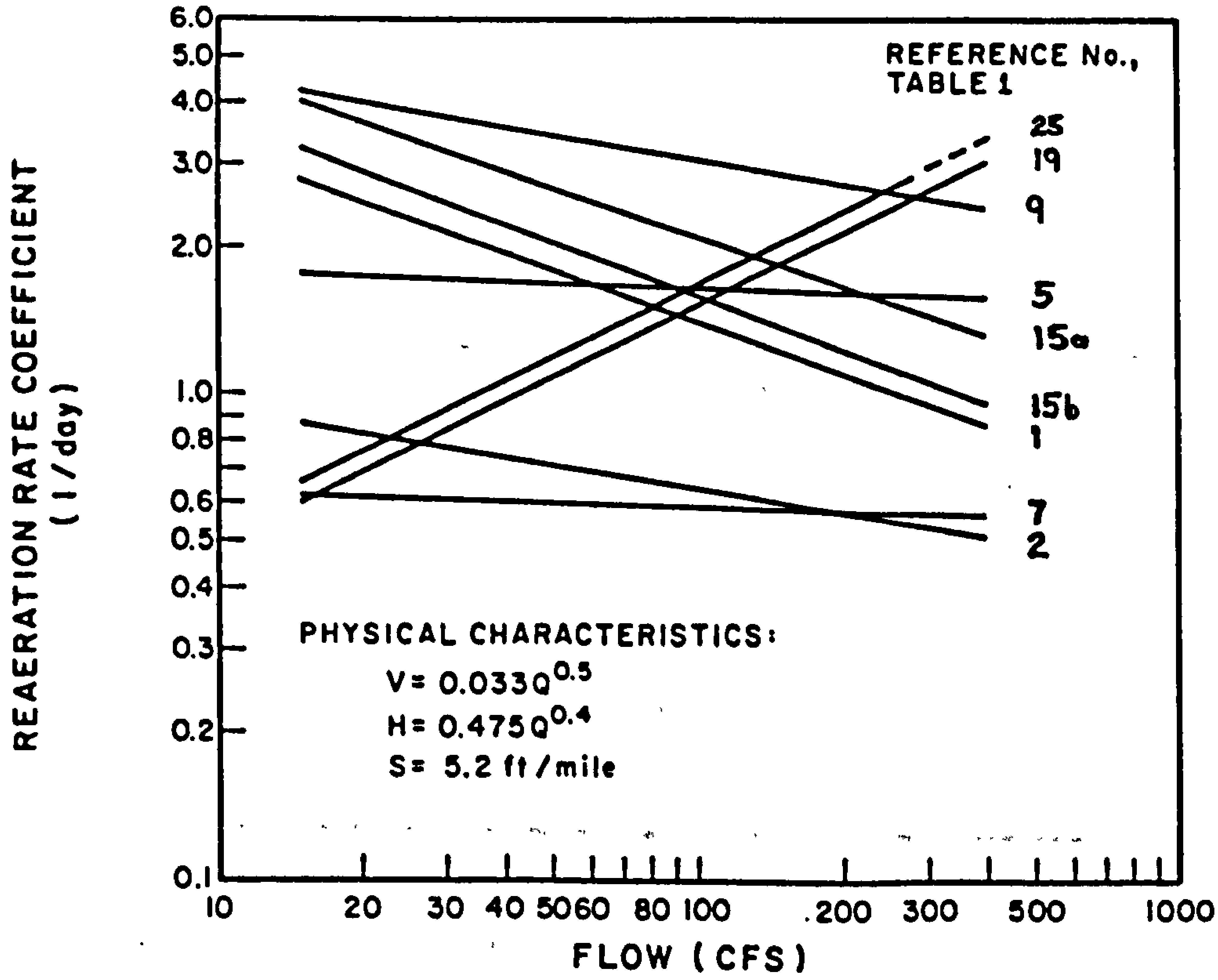


Figure 2:Reaeration rate - flow Relationships (where 1cfs is 0.02832 m^3/s) (after St.John et al.,1984)

(1962), and Owens et al.(1964), could be used jointly to predict stream reaeration coefficients for a certain range of depth and velocity combinations. Figure 3 shows the data points collected by each investigator and the regions Covar chose to divide the applicable formulas. Figure 4 shows the plot of reaeration predictions.

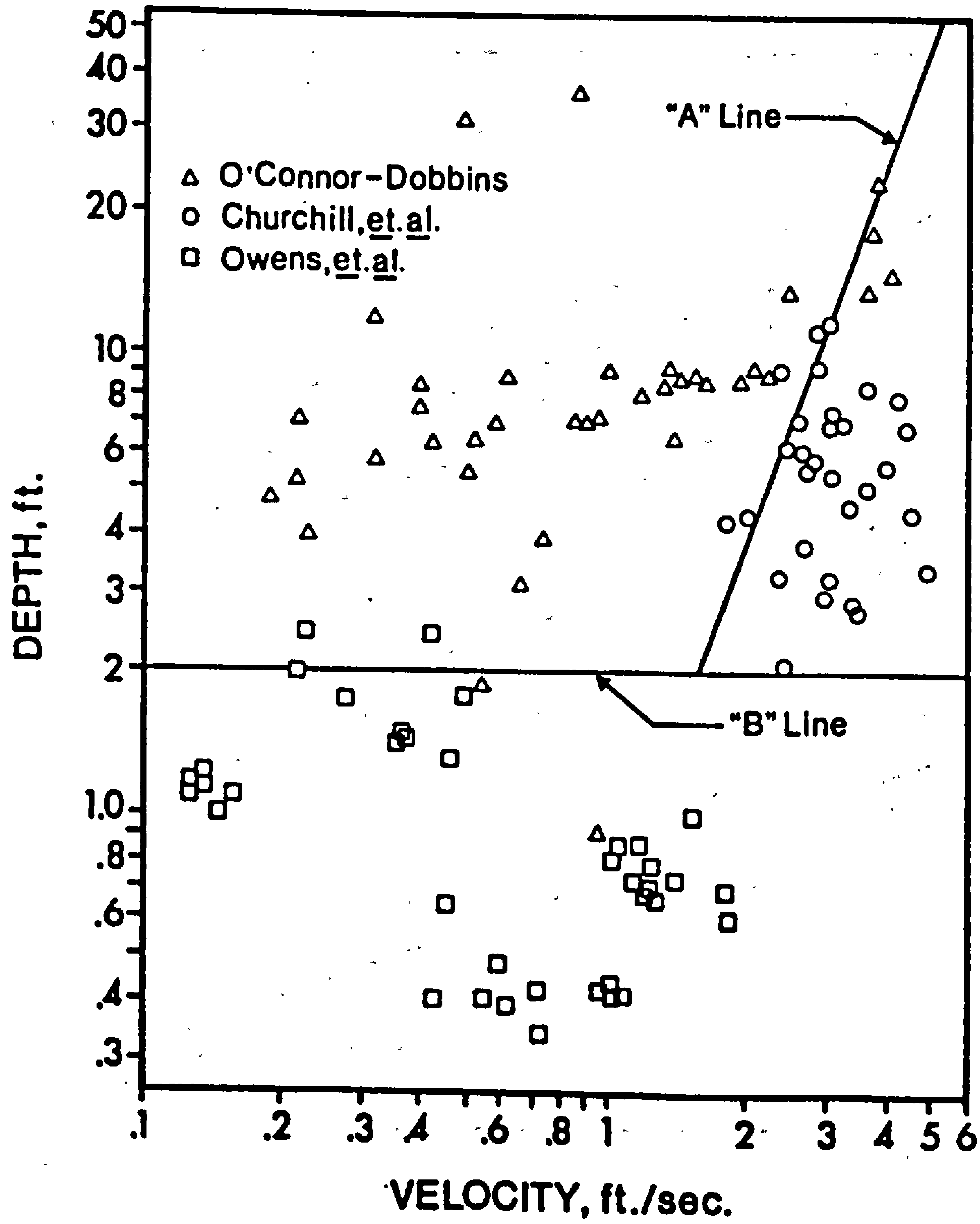


Figure 3:Field data considered (1ft=0.3048m) by three different investigations (after Covar,1976)

With the advent of fairly reliable techniques for the measurement of reaeration in streams (e.g. tracer methods), a better selection of empirical models used in the analysis of stream quality data can be made. The current procedure (as described by St.John et al.,1984) is to "first conduct a field determination of K_2 for the stream flow and hydraulic

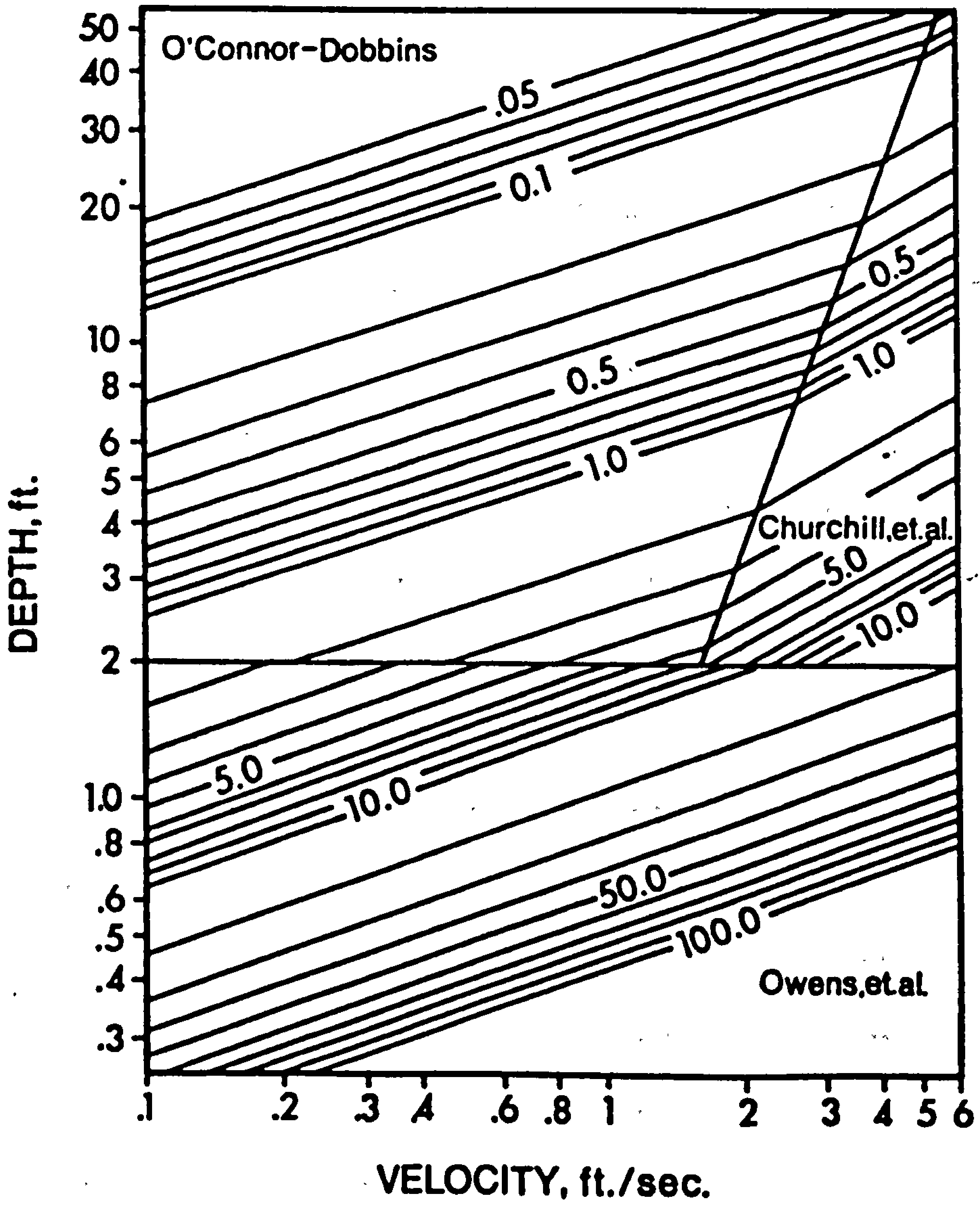


Figure 4:Reaeration coefficient (1/day) versus depth and velocity (1ft=0.3048m) using the suggested method of Covar (1976)

characteristics during the survey. This value is then compared to estimates produced by the various predictive equations for the same conditions for selection of the most applicable formulation (see for example, Bauer et al.,1979, Kwasnick and Feng,1979, Grant and Skavroneck,1980, House and Skavroneck,1981 and NCASI,1982). This equation is then used to project the reaeration coefficient for other flow conditions at which stream water quality data were collected for mathematical analysis. In addition, the selected equation is used to estimate reaeration coefficients with which to project stream water quality at critical summer low flow and other conditions of interest".

However, problems still exist when projecting water quality for other flow conditions using the selected empirical equations. As it was already shown, this is due to the markedly different estimates of K_2 produced by these formulas, and the consequences can be substantial from a wastewater point of view. It has been therefore recommended that multiple field measurements be encouraged to relate reaeration to flow conditions, employing, preferably, one of the tracer methods. Various examples of such kind of approach are reviewed by Bowie et al.,1985.

In applying empirical models to natural streams, one has to consider not only the limitations of the formulas but also the fact that the understanding of the reaeration process and the development of empirical models are not complete. The often deliberate use of empirical predictive models in water quality analysis is neither an advisable nor an accurate procedure.

Natural streams are generally different from each other and unique in their hydraulic characteristics. It is therefore, highly unlikely that any predictive model can be an entirely satisfactory substitute for direct measurement of stream reaeration, especially in those situations where the economics of waste treatment dictate a need for the greatest accuracy (Tsivoglou and Neal,1976). On the other hand, as mentioned by Holley and Yotsukura (1984), the impossibility of making direct measurements of K_2 for every river and every flow condition for which reaeration information is needed, certainly leave a place for prediction equations.

CHAPTER 2

The Methods of Measurement of K_2

Dissolved oxygen has been widely used as one of the main indicators of water quality conditions in streams, rivers, lakes and estuaries. Sufficient levels of oxygen are necessary to maintain a balanced biological community.

Stimulated by the need to control pollution of the major sources and to ensure protection of public health, sanitary engineers were probably among the first to quantitatively examine the physical, chemical and biological responses of streams to loading of nutrients (Orlob,1983).

Most countries have adopted water quality standards which must be satisfied in order to protect the aquatic environment. All such standards contain specific numerical requirements for dissolved oxygen. Advanced wastewater treatment technologies have been developed due to the rising public concern for protection and improvement of the natural environment. Seeking to evaluate the economical benefits of such measures in terms of quantitative response of the aquatic environment, engineers started to perform calculations in order to relate the effect of specific wastewater discharges to dissolved oxygen conditions in the receiving waters. The most common procedure consists of the application of an appropriate water quality model which incorporates relevant transport, transfer and kinetic terms associated with the dissolved oxygen balance, to determine the specific level of treatment necessary to maintain the required

DO standard in the receiving water bodies.

It has been generally agreed that a particularly important factor, characteristic of such models, is the atmospheric reaeration coefficient. Misinterpretation or poor estimation of reaeration can seriously affect the calculation of the oxygen balance and result in an improper determination of the required degree of waste treatment. Accurate knowledge of the reaeration coefficient as representative of the gas transfer process is required for proper environmental and economical decision making (St.John et al.,1984).

The purpose of this review is therefore to critically discuss the three primary methods that have been developed for the reaeration measurement. Namely the oxygen balance, the disturbed equilibrium technique and the tracer techniques. The related assumptions, degree of applicability, general procedure and errors involved in each method will be discussed and a new method, called the floating soluble solid technique, is introduced.

2.1 THE OXYGEN BALANCE TECHNIQUE:

The general DO balance technique for the measurement of K_2 in natural streams is based on the concept of a one-dimensional model developed by Streeter and Phelps (1925), given by:

$$\frac{dD}{dt} = K_1L - K_2D \qquad (52)$$

where D is the oxygen deficit written as (C_s-C), C is the observed oxygen concentration, C_s is the oxygen saturation concentration, L is the biochemical oxygen demand, K_1 is the deoxygenation coefficient, K_2 is the reaeration coefficient and t is the time.

This basic approach was later extended to take into account not only bacterial oxidation of the organic matter and atmospheric reaeration, but also numerous other processes which take place in natural streams. Some of them had already been recognised by Streeter (1926,1930,1935), but were summarised by Dobbins only in 1964, as follows:

(i) reduction of BOD by sedimentation or adsorption;

(ii) increase of BOD from scoured bottom deposits or from the diffusion of partly decomposed organic products from the benthic layer into the water above;

(iii) increase of BOD along the stream from runoff;

(iv) removal of oxygen from the water by diffusion into the benthic layer to satisfy the oxygen demand in the aerobic portion of this layer;

(v) removal of oxygen from the water by the purging action of gases rising from the benthic layer;

(vi) addition of oxygen by the photosynthetic action of plankton and fixed plants;

(vii) removal of oxygen by respiration of plankton and fixed plants;

(viii) continuous redistribution of both BOD and DO by longitudinal dispersion;

The approximate range of the effects of the main processes affecting the distribution of DO in British rivers were summarised by Downing (1967) and are as follows:

Table 2: Examples of approximate ranges of the main processes affecting distribution of DO in British rivers (Downing,1967)

Processes	Rate of change of dissolved oxygen (mg/l day)					
	Depth 0.50 m			Depth 2.0 m		
	Velocity (m/s)			Velocity (m/s)		
	0.03	0.15	0.30	0.03	0.15	0.30
Reaeration from the air	*Supply*					
(DO concentration is 50% of saturation at 14°C)	8	23	37	0.6	2	3
Photosynthesis						
Rooted plants (max)	40	40	40	10	10	10
Phytoplankton (max)	40	40	40	10	10	10
BOD_c in water	*Demand*					
20 per cent 30:20 effluent	1.3	1.3	1.3	1.3	1.3	1.3
50 per cent 30:20 effluent	3.2	3.2	3.2	3.2	3.2	3.2
Nitrification						
20 per cent effluent	2.2	2.2	2.2	2.2	2.2	2.2
50 per cent effluent	5.5	5.5	5.5	5.5	5.5	5.5
Respiration						
Mud	2.4-19.2+	2.4-19.2+	(0)	0.6-4.8+	0.6-4.8+	(0)
Slimes (max)	16	16	16	4	4	4
Rooted plants (max)*	30	30	30	7.5	7.5	7.5
Phytoplankton (max)	15	15	15	3.75	3.75	3.75

* varies with dissolved oxygen content, velocity and temperature

\+ in exceptional circumstances can be up to 43 mg/l day in water 0.5 m deep and 11 in mg/l day in water 2 m deep

( ) uncertain

Since the work of Dobbins (1964), numerous solutions for the BOD and DO profiles have been given (e.g. Camp,1965, O'Connell and Thomas,1965, Di Toro and O'Connor,1968, Bella and Dobbins,1968, Dresnack and Dobbins,1968 and O'Connor and Di Toro,1970 among others). These have been summarised and discussed by Bennett and Rathbun (1972), by Krenkel and Novotny (1980) and by Orlob (1983).

Considering the case of non-dispersive steady-state distributions and also factors such as reaeration, carbonaceous nitrogenous and benthal oxygen demand, photosynthetic production, plant respiration and non-point sources, the general 1-D equation, given by Fisher et al.(1979), is:

$$\frac{\partial c}{\partial t} + U \frac{\partial c}{\partial x} = \frac{1}{A} \frac{\partial}{\partial x} (A\, D_L \frac{\partial c}{\partial x}) + S \qquad (53)$$

where A is the stream cross-sectional area, D_L is the coefficient of longitudinal dispersion, S represents all other source and sink terms, and x is the longitudinal distance. This is solved to give (Holley and Yotsukura,1984):

$$\begin{aligned} D_t = D_0 \exp(-K_2 t) &+ \frac{K_1 L_0}{K_2-(K_1+k_3)} \{\exp[-(K_1+K_3)] - \exp(-K_2 t)\} + \\ &+ \frac{K_n L_0{}^n}{K_2-K_n} [\exp(-K_n t) - \exp(-K_2 t)] + \\ &+ \frac{S_b-P+R_p}{K_2} [1 - \exp(-K_2 t)] \qquad (54) \end{aligned}$$

where L_0 and $L_0{}^n$ are the ultimate carbonaceous and nitrogenous biochemical oxygen demand, respectively, D_0 is the initial oxygen deficit, K_1 is the deoxygenation coefficient, K_2 is the reaeration coefficient, K_3 is the coefficient for the removal of BOD by sedimentation into an anaerobic benthal layer, K_n is the nitrification rate coefficient, S_b is the benthal oxygen demand, P is the photosynthetic production and R_p represents plant respiration.

The oxygen balance approach then, consists of measuring the change in the DO along a reach with steady state conditions, measuring or calculating all sources and sinks of DO except reaeration, and obtaining the reaeration coefficient as the residual between the measured DO change and the evaluated sources and sinks.

The Water Pollution Research Laboratory group at Stevenage, England (Edwards and Owens,1962, Edwards and Owens,1965, Owens and Edwards, 1963), has used a somewhat different approach. An integral form of the DO balance, based on Odum's (1956) analysis of oxygen metabolism in flowing waters, is used instead of equation (54). The various coefficients are assumed to be independent of time and longitudinal position within the reach, and the stream flow is also assumed to be constant and uniform over the reach of interest. The change in DO concentration in water between two points is assumed to be dependent upon the following factors:

(i) the release of oxygen into the water as a result of photosynthesis by plants;

(ii) the uptake of oxygen from the water as a result of respiration by plants, animals and aerobic bacteria;

(iii) the exchange of oxygen with the air in a direction which depends upon whether the water is super or under saturated with oxygen.

These processes are then expressed as follows:

$$Q = P \pm D - R \qquad (55)$$

where Q is the rate of gain or loss of oxygen per unit area of surface between the upstream and downstream sampling stations, P is the rate of photosynthetic production per unit area, R is the rate of respiration per unit area, and D is the rate of oxygen uptake by diffusion per unit area. The above equation can then be modified as needed to meet the conditions in the stream under study (Owens and Edwards,1963).

Q is calculated from:

$$Q = (C_2 - C_1) \frac{F}{S} \tag{56}$$

where C_1 and C_2 are DO concentrations at the upstream and downstream stations, respectively, at times t_1 and t_2, F is the volumetric rate of flow, and S is the surface area between stations.

The rate of diffusion depends on the degree of saturation of the water and is defined by

$$D = f\ (C_s - C) \tag{57}$$

where f is the exchange coefficient and (C_s-C) is the average oxygen deficit of the reach. The reaeration or exchange coefficient is then calculated from the rate of change of DO in a body of water flowing downstream at different times (during the hours of darkness if plants are present) and at different saturation deficits. This change in oxygen content is determined by diffusion through the water surface at a rate depending on the magnitude of the coefficient and on the saturation deficit, and by the rate of community respiration.

The measurement of photosynthetic production, community respiration and diffusion rates by diurnal oxygen analysis, light and dark bottles, respiration chambers, floating plastic domes and so on, have been thoroughly studied and discussed by many authors (Odum,1956, Edwards and Owens,1962, Hull,1963, Copeland and Duffer,1964, Camp,1965, O'Connel and Thomas,1965, Duffer and Dorris,1966, Vollenweider,1969, Bailey,1970, Bennett and Rathbun,1972). A summary of such methods is given by Bowie et al. (1985), including numerical and analytical techniques which have been recently developed (e.g. Hornberger and Kelly,1975, Erdmann,1979, Gulliver et al.,1982, Terry et al.,1983,1984). Gulliver et al. (1982) provide a review of Odum's method and reports numerical and graphical procedures for the estimation of community respiration and photosynthesis in streams. Terry et al. (1983,1984) have conducted an interesting study of the water quality assessment of the White River and of the Illinois River Basin, Arkansas, U.S.A., and describe the various methods used for data collection and measurement of physical (suspended and dissolved solids, water temperature), chemical and biochemical (chlorides, sulphates, pH, DO, BOD, benthal oxygen demand, net photosynthetic DO production and nutrients), and biological (phytoplankton, periphyton, total coliform bacteria) characteristics.

Because the discussion and description of these methods are beyond the scope of this literature review, the reader should refer to some of the above references for more detailed information.

As it has been generally agreed, the oxygen balance approach is subjected to potentially large errors associated with the many sources and sinks of oxygen which must be evaluated. According to Bennett and Rathbun (1972), because of the complexity of the general DO balance equation, the number of parameters involved, and the difficulty in reproducing field conditions for replications of K_2 determinations, a rigorous statistical analysis of the effect of errors on the calculated K_2 cannot always be performed. Actually, there has been little attention given to a quantitative analysis of errors in K_2 obtained from oxygen balances.

Holley and Yotsukura (1984), based on the studies of Hovis et al. (1982), listed and discussed the sources of errors in experimentally determined gas transfer coefficients, which are classified as follows:

(i) Procedural errors (may arise from):

(i.1) poor selection or inadequate number of sampling points (e.g. the assumption of 1-D conditions when they do not exist);

(i.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;

(i.3) failure to adequately preserve samples between collection and analysis;

(i.4) selection of a test reach which is not representative of the entire reach of interest;

(i.5) failure or inability to account for all sources and sinks of the gas within the test reach;

(ii) Parameters errors (may arise from):

(ii.1) uncertainty in evaluating or determining the value of C_s, the oxygen saturation concentration;

(ii.2) uncertainty in evaluating or selecting the appropriate temperature correction factor, θ;

(iii) Random errors:

these are present in all measurements, and, according to

Holley and Yotsukura (1984), if they can be quantified, it is possible to analyse the propagation of the errors through the calculations and obtain error bounds on results. Based on standard techniques for the analysis of propagation of errors, the following equation was written:

$$\mathrm{Var}(x) = \mathrm{Var}(u)\left(\frac{\partial x}{\partial u}\right)^2 + \mathrm{Var}(v)\left(\frac{\partial x}{\partial v}\right)^2 + \mathrm{Var}(w)\left(\frac{\partial x}{\partial w}\right)^2 + \ldots \quad (58)$$

where the expected value of a variable, x, is a function of the mean values of other variables, such that $x=f(u,v,w,\ldots)$. It is assumed that the errors in $u,v,w,\ldots,$ are small relatively to the mean values and independent of each other.

Relative error terms can be obtained by dividing the square root of the above equation by $\bar{x}$. If the variable (u,v,or w) is A mean value, then its standard error is given by:

$$\sigma(\bar{u}) = \frac{\sigma(u)}{n^{1/2}} \quad (59)$$

where n is the number of measurements.

It was pointed out by Holley and Yotsukura (1984) that equation (58) demonstrates that "if one of the variables has a large measurement error, this error will dominate in the calculation of $\mathrm{var}(\bar{x})$ and little may be gained by obtaining extremely precise values for all of the other variables. If the standard deviation for any of the variables is expected to contribute a major part of the standard deviation of $\bar{x}$, then $\sigma(\bar{x})$ can be reduced according to equations (58) and (59) if repeated measurements of that variable are feasible".

The result of applying equation (58) to the oxygen balance equation would be that the potential error in K_2 would be some type of non-linear combination of the errors in all of the other terms in the equation (Holley and Yotsukura,1984). However, the application of equation (58) for situations of many variables may become impractical. It was therefore concluded, in a qualitative sense, that the resulting K_2 values should not be expected to be very precise since:

(i) some of the biochemical and physical processes have a lot of inherent variations and corresponding uncertainty;

(ii) many of the processes have strong spatial variations but can only be measured at relatively few points so that there is uncertainty concerning whether the measured values are representative of averages for the study reach (see Churchill et al.,1962 conclusions);

Bennett and Rathbun's (1972) sensitivity analysis gives an indication of the input parameters which, because of the combination of sensitivity and possible input errors are likely to cause the greatest error in K_2. Their results show that if photosynthetic oxygen production is present, its neglect is probably the most serious source of error in the calculation of K_2. Following, in decreasing order of effects, are errors in the upstream and downstream DO deficit, K_1 and the BOD_c at the upstream end of the study reach.

It has been recommended by both Bennett and Rathbun (1972) and Holley and Yotsukura (1984), that the use of Monte Carlo simulation (see Kothandaraman and Ewing,1969, Brutsaert,1975 and

Hornberger,1980) to determine possible errors in DO concentrations is a feasible alternative. This would give the distribution function of the reaeration coefficient calculated from the DO balance equation for known distributions of the other parameters. However, it does not appear that the Monte Carlo simulation leads to any realistic improvement in the determination of the errors associated with the estimation of K_2 from the oxygen balance technique. The approach is often subjected to limitations such as the assumption of 1-D transport situation (uniform BOD and DO distributions, steady and uniform flow) which may not always be true. In most cases the exact distribution of BOD and DO at each point along the stream is not known. The initial BOD and DO distributions may be assumed (based on the fitting of observed values) and then, various techniques may be used to predict the probability distribution downstream (see Loucks and Lynn,1966, Thayer and Krutchkoff,1967 and Padgett and Rao, 1979).

2.2 <u>THE DISTURBED EQUILIBRIUM TECHNIQUE</u>:

The disturbed equilibrium technique for measuring reaeration rates in small streams requires measurement of the upstream and downstream DO concentrations and the respiration rate in the reach at two different values of the upstream deficit. These values may be produced by diurnal variations in photosynthesis and respiration or in BOD inflow, or by the addition of a reducing chemical.

Churchill et al. (1962) presented an approach where the calculated reaeration coefficient was measured from changes in oxygen concentration which occurred when partially deoxygenated water drawn from the hypolimnion of reservoirs, flowed down river channels. However there are some conditions which must be satisfied in order to apply the method:

(i) a dissolved oxygen deficit exists;

(ii) the rate of reaeration is large enough so that a measurable difference in DO deficit can be easily detected between two sampling stations;

(iii) the water is free from organic pollution;

In effect, as discussed by Zogorski and Faust (1973), the method applies only where all sources and sinks of dissolved oxygen are minimum in comparison with the DO change due to atmospheric reaeration, a situation very difficult to be satisfied.

Edwards and Owens (1963) used an opaque plastic sheet suspended on a nylon net about 0.60 m above the water surface, and measured the change in oxygen concentration down the covered reach throughout 24 hours. The method makes use of naturally occurring changes in oxygen concentration brought about by photosynthesis upstream and, according to them, can be applied to small productive streams.

Copeland and Duffer (1964) introduced the use of a clear, floating plastic dome with surface transfer being determined from changes of oxygen in the air trapped under the dome. Duffer and Dorris (1966) and Juliano (1969) made limited use of the method, which was originally developed to obtain information on surface transfer as part of primary productivity.

According to Holley and Yotsukura (1984), there are many problems with the method. The turbulence under the dome may not be the same for natural conditions, potentially large and uncertain temperature corrections may be needed, and the method gives only one-point measurement, which would be of limited value in rivers and estuaries.

Based on the difficulty in observing large natural changes in oxygen content of rivers, Gameson et al.(1955) devised a method where the oxygen concentration may be reduced by the controlled addition of sodium sulphite and a cobalt catalyst. The method is a modification of Churchill's et al.(1962) approach in that a measurable deficit is artificially created between two sampling stations. If all sources and sinks of DO (except atmospheric reaeration) are constant and not affected by the sulphite for the reach during the period of measurement, then by manipulation of equation (55), and for steady state conditions,

$$K_2 = \frac{1}{\Delta t} \ln \left(\frac{C_1 - C_1'}{C_2 - C_2'}\right) \tag{60}$$

and if the flow rate (Q) changes due to distributed inflow,

$$K_2 = \frac{1}{\Delta t} \ln \left[\frac{Q_1 (C_1 - C_1')}{Q_2 (C_2 - C_2')}\right] \tag{61}$$

where C_1 and C_1' are the upstream DO concentrations at the two levels of concentration, C_2 and C_2' are the downstream DO concentrations measured at a time t after the upstream concentrations, and Δt is the time of travel between the two sampling stations. Gameson et al.(1955) have also discussed several aspects related to the method of deoxygenation, injection procedure and choice of stream. They have originally used a constant rate injection device of a strong aqueous solution, catalysed with 40 mg/l of cobaltous chloride, which would give a concentration in the stream ranging between 0.025 and 0.050 mg/l. It was later observed that on adding the concentrated cobaltous chloride solution to a strong solution of sodium sulphite should be avoided in order to prevent any precipitation of cobaltous hydroxide. They also recommended that nitrogen gas be bubbled through the sulphite solution, thus minimising the premature oxidation of sulphite by the contact with atmosphere.

In interpreting the disturbed equilibrium method in terms of the 1-D mass balance equation for DO, Holley and Yotsukura (1984) wrote the following equation:

$$\frac{\partial (C-C')}{\partial t} + U \frac{\partial (C-C')}{\partial x} = D_L \frac{\partial^2 (C-C')}{\partial x^2} - K_2 (C-C') \qquad (62)$$

The depleted DO concentration can then be viewed as a quantity which is being transported by advection and dispersion, and which is desorbing through the free surface. They further stated that the transport of the depleted concentration is similar to that for tracer gases, but in this case it may be affected by sources and sinks of dissolved oxygen, and also by residual sulphite. For steady state conditions, the time derivative in equation (62) is zero and the transport by longitudinal dispersion is negligible so that the above equation is reduced to equation (60) or (61).

In 1959, Gameson and Truesdale found that the degree of longitudinal mixing in a stream would be of importance when the effects of sudden changes were to be examined. Besides the difficulties experienced in maintaining a steady-state injection of sulphite, they found that the region of concentration had been eroded by longitudinal mixing at some cross sections. They then decided to modify the method, but limited the analysis to short reaches so that linear variations of (C-C') could be assumed. With measurements at two cross-sections, for constant Q, the following equation can be obtained:

$$K_2 = \frac{1}{\Delta t} \ln \frac{N_1}{N_2} \qquad (63)$$

and if Q increases with x in such a way that the DO concentration profile remains one dimensional (i.e. in accord with the general 1-D transport equation), an approximate analysis shows that it is possible to write (Holley and Yotsukura, 1984):

$$K_2 = \frac{1}{\Delta t} \ln \frac{N_1 Q_1}{N_2 Q_2} \qquad (64)$$

where N is the area under the (C-C') versus time curve at a sampling station, given by:

$$N = \int_0^\infty (C - C')\, dt \qquad (65)$$

and the subscripts 1 and 2 refer to the upstream and downstream sampling stations, respectively.

In 1961, Edwards et al. observed that the assumption of constant respiratory demand during the period of observation, might prove invalid in situations where plant growth occurs. Based on the relation between the oxygen content and oxygen consumption of each major component of the biological community, and on the relative oxygen amounts consumed by each component at any oxygen tension, they suggested that the disturbed equilibrium be conducted after the sunset, when the photosynthetic production is negligible. The following modification for the calculation of K_2 was also suggested:

$$K_2 = \frac{1}{H} \frac{q' - x'q}{(C_s - C)' - x'(C_s - C)} \qquad (66)$$

where q and q' are the rates of change of oxygen per unit area in the study reach before and during the passage of the deoxygenated water, x' is the ratio of oxygen consumption of the biological community during the passage of sulphite to that before its addition, (C_s-C) and $(C_s-C)'$ are the DO deficits before and during the passage of deoxygenated water, respectively. They have also stated that unless all sulphite is oxidised, the Winkler method cannot be used for the determination of the DO concentration, otherwise very low oxygen concentrations are obtained. They also performed laboratory studies to verify the effect of temperature and different cobaltous concentrations on the oxidation of sulphite. The conclusions obtained were that temperature has a large effect on the rate of sulphite oxidation, that cobalt catalyses sulphite oxidation more effectively at high pH values (at about 9.0), and that the Winkler method is not interfered with by 1 mg/l of cobaltous chloride.

Bennett and Rathbun (1972) also included the variation of respiration rates in their analysis of the disturbed equilibrium technique. The equation derived by them gives an integral reaeration coefficient rather than one based on the average DO deficit for the reach and must be solved by trial and error:

$$K_2 = \frac{1}{\Delta t} \ln \left[\frac{(D_1 - D_1') + \dfrac{p - p'}{K_2}}{(D_2 - D_2') + \dfrac{p - p'}{K_2}} \right] \qquad (67)$$

where D and D' are the DO deficits before and during the passage of the deoxygenated water, p and p' are the net production of oxygen by photosynthesis before and after the passage of the deoxygenated water, and subscripts 1 and 2 refer to upstream and downstream sampling stations, respectively.

In discussing the disturbed equilibrium technique, Zogorski and Faust (1973) summarised the major criteria which must be satisfied before applying the method, as follows:

(i) the rates of all processes (except atmospheric reaeration) affecting the DO concentration do not alter during the reduction of the oxygen level by the addition of a reducing chemical;

(ii) the existing DO profile is such that the driving force (C_s-C) of the atmospheric reaeration process can be increased by the addition of reducing chemicals;

(iii) the sodium sulphite is completely oxidised before the first sampling station is reached;

(iv) complete horizontal and vertical mixing is obtained before the first sampling station;

(v) the same body of water is measured at the two sampling stations;

It has been reckoned by them that the last three requirements are operational difficulties which can be satisfied by employing sophisticated injection equipment in order to ensure complete mixing and by properly selecting river reaches and sampling sites.

Zogorski and Faust (1973) have successfully applied the disturbed equilibrium technique as modified by Gameson and Truesdale (1959), in two streams in the U.S.A. with average velocities ranging from 0.17 to 0.83 m/s, average depths from 0.15 to 0.34 m, and reaeration coefficients (at 20°C) from 7.19 to 43.4/day. A complete discussion about dosing equipment and requirements, DO monitoring and K_2 computation is also given by them.

According to Bennett and Rathbun (1972), a rigorous statistical analysis of the method is not always possible for the same reasons that such an analysis is impractical for the DO balance technique. Again, very little attention has been given to a quantitative analysis of errors in K_2.

Holley and Yotsukura (1984) made use of propagation of errors techniques to analyse the errors involved in the method, as they did for the oxygen balance technique. If equation (58) is applied to the disturbed equilibrium equations, we have:

(i) for steady state conditions:

$$\frac{\sigma(\bar{K}_2)}{\bar{K}_2} = \frac{1}{\bar{K}_2 \Delta t} \left[2 \left(\frac{\sigma(\bar{Q})}{\bar{Q}}\right)^2 + \frac{\sigma^2(\bar{C}_1) + \sigma^2(\bar{C}_1')}{(\overline{C_1 - C_1'})^2} + \frac{\sigma^2(\bar{C}_2) + \sigma^2(\bar{C}_2')}{(\overline{C_2 - C_2'})^2} + \bar{K}_2^2 \sigma^2(\Delta t)\right]^{1/2} \tag{68}$$

(ii) for transient distributions:

$$\frac{\sigma(\bar{K}_2)}{\bar{K}_2} = \frac{1}{\bar{K}_2\,\Delta t}\left[\,2\left(\frac{\sigma(\bar{Q})}{\bar{Q}}\right)^2 + \frac{\sigma^2(\bar{C}_1) + \sigma^2(\bar{C_1}')}{(C_1 - C_1')_{avg}{}^2} + \frac{\sigma^2(C_2) + \sigma^2(C_2')}{(C_2 - C_2')_{avg}{}^2} + \bar{K}_2{}^2\sigma^2(\Delta t)\right]^{1/2} \qquad (69)$$

where the $(C-C')_{avg}$ term is N/t_b, (with N given by equation (65)) and t_b is the time base of the (C-C') distribution.

It is agreed by them that certain aspects of the above equations are somewhat cumbersome, but they do provide a basis for at least an approximate evaluation of $\sigma(\bar{K})/\bar{K}$, and reveal the following general observations concerning the effect of the various factors on the accuracy of K_2:

(i) the importance of errors in C and C' must be considered in relation to (C-C'), not relatively to C or C' separately;

(ii) C' is a measured quantity, but C, during the cloud passage, must be estimated by interpolation from C values before and after the cloud, and any errors involved in the estimation of C have a direct effect on the calculation of K_2;

(iii) for 1-D transport it is necessary that reaeration be very rapid or that the test be conducted when natural temporal variations of C are small;

Bennett and Rathbun (1972) gave some general qualitative conclusions based on sensitivity analysis about the errors involved in the measurement of reaeration rates by the disturbed equilibrium method:

(i) error in all parameters of the disturbed equilibrium technique are significant in the calculation of K_2; the most significant is the error in the downstream deficit, followed by errors in the net photosynthetic production parameter, upstream DO deficit, and time of travel;

(ii) neglecting a respiration rate difference of 1.0 mg/l per day causes about 12% error in the calculation of K_2; therefore, neglecting the effect of DO concentration on the respiration rate may be significant;

(iii) use of equation (67) for disturbed equilibrium calculations is preferred;

In 1973, Zogorski and Faust pointed out that the lack of precision of the method is due to the following reasons:

(i) failure to comply exactly with the assumptions inherent when applying the disturbed equilibrium method for measuring K_2;

(ii) error in calculating K_2 from the given equations;

(iii) error due to the variability in the stream's hydraulic characteristics at low flow;

They felt that the second and third reasons are the most important since any error in monitoring the altered oxygen profile or in planimetering areas will be magnified in the computation of K_2. It was also suggested that a number of experiments should be conducted under the same hydraulic conditions and an average K_2 value should be used rather than a single observation.

In summarising all the aspects discussed above, Holley and

Yotsukura (1984) concluded that the application of the disturbed equilibrium technique may be limited to streams with no temporal variation of the natural DO concentration and no sources and sinks which depend on DO concentration, if it can be verified that there is no residual sulphite. In other words, several requirements must be satisfied before the disturbed equilibrium method can be employed, and if careful consideration of its main assumptions and inherited limitations are taken into account, the method can be successfully applied to directly measure K_2 in small streams ($Q < 1.5\ m^3/s$), as it has been demonstrated by Zogorski and Faust (1973).

2.3 THE TRACER TECHNIQUES:

The use of tracers for the determination of the reaeration coefficient is generally accepted as the most accurate of all direct tracer methods. Tsivoglou et al.(1965,1968) were the first to perform a series of radioactive gas tracer experiments which eventually led to an independent method of determining K_2 under field conditions. Although the method appears to produce the most accurate results, its use has been limited by a rising public concern on the potential hazards of using radioactive substances in natural streams. Another tracer technique (modified gas tracer technique) was then developed and is still under investigation. A hydrocarbon gas tracer and a fluorescent dye, as the dispersion-dilution tracer, are used instead of the radioactive tracer. The method was originally developed by Rathbun et al.(1975,1978), and although it has been improved in the last few years, there are still some doubts about its accuracy.

2.3.1 <u>The Radioactive Tracer Technique</u>:

In 1965, Tsivoglou et al. carried some laboratory tests in an attempt to develop an independent and direct tracer method of determining K_2 under natural conditions. Their first step was to select a suitable gaseous tracer and establish its gas transfer behaviour or its capability relative to that of oxygen in a turbulent system. If this was satisfactorily accomplished, the gaseous tracer could then be directly used in the field together with a non-gaseous tracer that would be indicative of dispersion alone. For the laboratory phase of the work, Kr_{85} and Rn_{222} were selected for trials as oxygen tracers, and the rates of decay of the two radioactive tracers, as well as the rate of oxygenation of the system, were measured at a wide range of turbulent conditions and temperature (10 to 30°C). The gas transfer capability of the two tracer gases relative to oxygen was reported to be:

$$\frac{K_2}{K_{Kr}} = 1.22 \pm 0.06 \qquad (70)$$

and

$$\frac{K_2}{K_{Rn}} = 1.43 \pm 0.07 \qquad (71)$$

The above results were then further analysed by Tsivoglou (1967), who concluded that the ratios of gas transfer coefficients can be assumed to be constant within the limits of experimental error, and independent of temperature (between 10 and 30^{o}C) and mixing conditions (see equations (45) and (46) in Chapter 1). This turned out to be the major assumption of the tracer techniques, and as already discussed, it appears that Tsivoglou's experimental results are not inconsistent with the conclusions of his model (Rainwater and Holley,1984).

In outlining the method, Tsivoglou (1967) further assumed that:

(i) the non-gaseous dispersion tracer (tritiated water) undergoes only dispersion in the stream, and is not adsorbed on the stream bed or otherwise lost in any significant amount;

(ii) the dissolved tracer gas undergoes dispersion to the same degree as the non-gaseous dispersion tracer, and in addition is lost to the atmosphere; it is not otherwise lost by adsorption or other processes in any significant amount;

No assumptions are made regarding the uniformity of channel, the uniformity or non-uniformity of mixing, the frequency of mixing length or rate of surface renewal. It is not either necessary to assume that reaeration takes place as a simple first order process with a single constant value of K_2.

However, as discussed by Rathbun et al.(1980) and Rainwater and Holley (1984), there is no indication that the assumption of the conservancy of the tritium has been verified. Lau (1977), in a series of experiments in which the evaporation of water and tritium took place simultaneously, found that, other conditions being constant, turbulence in the water does not affect the water evaporation rate but significantly affects the tritium evaporation rate. Horton et al. (1971) presented laboratory and field results indicating that tritium in water was lost to the atmosphere preferentially to the water. The assumption of physical inertness of the radioactive gas tracer Kr^{85} has also been questioned by Gordon (1977). His studies of the oxygen transfer capabilities of mechanical surface aerators showed that the effect of biological active suspended solids on the krypton transfer rate is significantly different from the effect exerted on the oxygen transfer rate. His data indicate that oxygen transfer rates decreases at about 19% due to the effect of biologically active suspended solids, while Kr^{85} transfer rate decreases at about 10%.

The technique was first applied in the Jackson River, Virginia, U.S.A., by Tsivoglou et al.(1968). It uses an instantaneous injection of three tracers at a point upstream from the reach over which the reaeration coefficient is to be measured. The first tracer is a fluorescent dye which indicates the movement of the other two tracers and provides an accurate measure of the time of flow between sampling stations. The second, tritiated water, is used as a conservative dispersion tracer, and the third, the radioactive tracer gas Kr^{85}, is used to measure the gas transfer capability of the flow. The two radioactive tracers are injected by breaking an ampoule completely filled with a homogeneous water solution of tritiated water and fully dissolved Kr^{85} gas under the water to provide an instantaneous release. The dye tracer is also released at the same time. By using a field fluorometer to monitor the dye tracer (usually Rhodamine-WT 20%) concentration, water samples are collected in the vicinity of the tracer peaks and analysed for concentrations of krypton and tritium (by liquid scintillation counting). A typical flow-through sampling system using portable generation is shown in Figure 5.

The transfer capacity of the flow for the tracer gas is obtained from the relative concentrations of the gas and tritiated water tracers at two ends of the study reach. It was shown by Tsivoglou et al.(1968), on the basis of an argument involving the number of atoms of krypton and tritium and an exponential expression for gas exchange that (Bennett and Rathbun,1972):

$$\left(\frac{C_G}{C_T}\right)_2 = \left(\frac{C_G}{C_T}\right)_1 \exp[-K_T(t_2 - t_1)] \qquad (72)$$

where C_G is the concentration of the tracer gas, C_T is the concentration of the conservative tracer, K_T is the tracer gas rate coefficient, t is the time of flow between stations 1 (upstream) and 2 (downstream) in the study reach. It is common to take t_1 and t_2 at the peaks of the conservative tracer

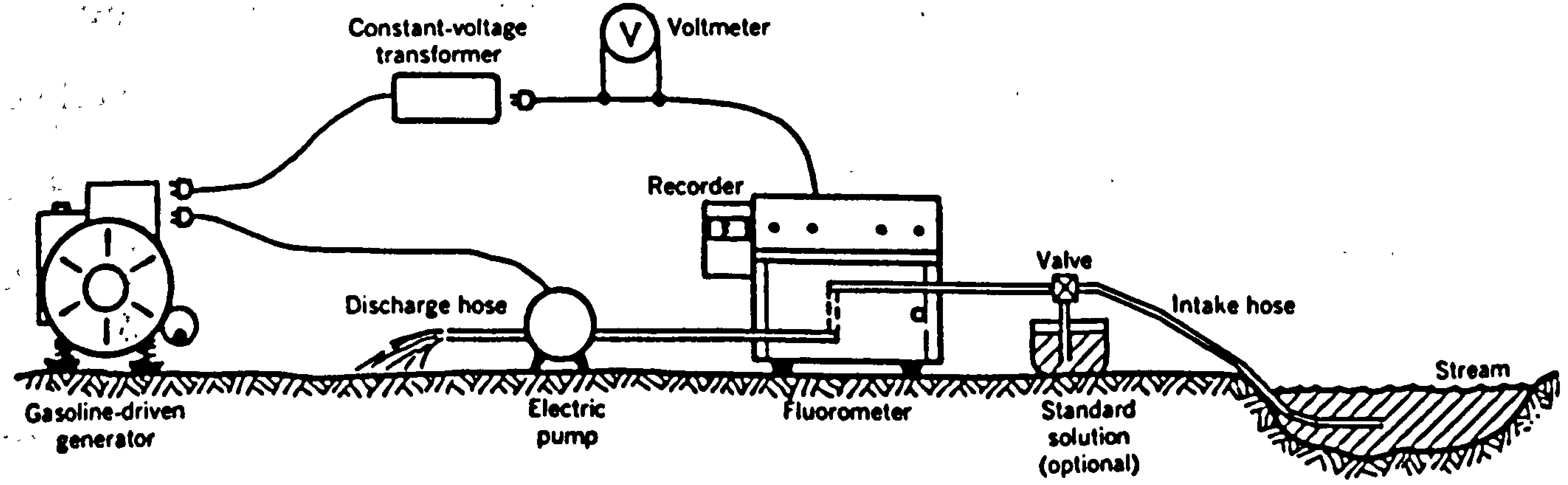


Figure 5: A Flow-Through Sampling System (after Wilson,1968)

distributions at the upstream and downstream locations, respectively, so that $(t_2 - t_1)$ is approximately the flow time (Holley and Yotsukura,1984). Field procedures for the measurement of time of travel by dye tracing are described by Hubbard et al.(1981), and fluorometric procedures are described by Wilson (1968).

It has been recommended by the NCASI (1982) that a pollutant effect factor (also reported by Neal,1984), α, be considered for the adjustment of measured gas transfer rates in polluted water to a pure water base, defined by:

$$\alpha = \frac{K_{Kr} \text{ (polluted water)}}{K_{Kr} \text{ (pure water)}} \qquad (73)$$

The reaeration coefficient is then obtained by multiplying the observed K_{Kr} by α and then substituting it in equation (70).

Holley and Rainwater (1983) and Holley and Yotsukura (1984) described a somewhat different approach leading to the derivation of equation (72) above. It is stated by them that since the hydraulic transport is a linear process (refer to Fischer et al.,1979), 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, e.g. for two conservative tracers, a and b, with identical initial conditions, $C_a/M_a = C_b/M_b$ for all x,y,t. If it is assumed that the surface transfer is a first-order process so that the tracer gas concentration decays exponentially with time while it is also changing due to mixing, then:

$$\frac{C_G\ (x,y,t)}{M_G} = \frac{C_T\ (x,y,t)}{M_T} \exp\ (-K_T t) \qquad (74)$$

where G and T are the subscripts for the gas tracer and conservative tracer respectively. For field applications, values of K_T calculated from data at any two cross sections must be considered an average value for the reach. Equations (72) and (74) are therefore valid for uniformly mixed (1D) clouds whether the discharge is steady or unsteady, as long as K_T can be considered constant. Holley and Yotsukura (1984) recommended that situations where transverse uniformity is not verified, be further studied in order to devise appropriate sampling schemes and analysis of data.

In 1970, Tsivoglou and Wallace reported the results of field studies of the reaeration capacities of three streams in the U.S.A., Flint River, South River and Patuxent River. The results were used to develop an adequate mathematical explanation of the hydraulic properties of the stream, which eventually led to the development of the energy dissipation model (see Table 1), reported two years later by Tsivoglou and Wallace (1972). In these studies, Tsivoglou and Wallace (1972) report a total of 323 measurements of K_2 in about 70 miles of stream (Flint, South, Patuxent, Jackson and Chattahoochee Rivers) including rapids, waterfalls, shoals, pools and relatively uniform reaches (see tabulated values in Zizon et al.,1978). The objectives of such studies were to evaluate the degree of accuracy and the range of error normally associated with the various predictive models for reaeration capacity, define and evaluate the basic relationships between stream reaeration and measurable stream hydraulic properties, refine the field methodology for the use of radioactive tracers in large river flows, and also evaluate the effects of pollutants on K_2.

Tsivoglou and Neal (1976) summarised the information obtained in 10 years of study using the radioactive tracer technique. Accurate field measurements of K_2, and associated hydraulic parameters, were made in more than 400 km of 24 different streams in the U.S.A. The observed results provided the basis for thorough testing of the available predictive models at that time, as well as for the development of new models. These studies have led to a considerably improved understanding of stream hydraulic properties that are associated with reaeration.

Also in 1976, radioactive tracer measurements were made by Foree (1976) in small streams of the State of Kentucky, U.S.A. and by Grant (1976), who employed the method for the characterisation of the reaeration capacity in 10 small streams in Wisconsin, U.S.A.

The technique has also been reported by Grant (1978), who measure the reaeration capacity of the Rock River, in Wisconsin and Illinois, U.S.A., by Shindala and Truax (1980) who performed a statistical analysis of in-situ measured reaeration coefficients with data collected from seven different states in the U.S.A., by NCASI (1982) which reported the measurement capacity for the Ouachita River (at low flow velocities), in Louisiana and Arkansas, U.S.A., in an attempt to identify the limitations of the radioactive tracer technique. In this study, the precision of the measurements was directly related to the amount of gas lost during the experiment. It was concluded that the precision of a measurement is ultimately limited by the ability to follow the dye and conservative tracers, the precision of the K_2/K_{Kr} ratio, and the temperature correction factor θ (also refer to section 2.1 and to Hovis et al.,1982). Whittemore and Hovis (1984) have summarised these results in terms of the uncertainty of K_2 measured by the radioactive tracer technique as a function of the percentage of gas lost during the measurement as shown in Table 3 below:

Table 3: Uncertainty of K_2 as measured by the radioactive tracer technique and percentage of gas lost during measurement (Whittemore and Hovis,1982)

Source (rivers in the U.S.A.)	$K_{2,20}$ (base e) 1/day	95% confidence interval for K_2 (%)	% of gas tracer lost	theoret. precision of K_2 (%)
Ouachita River				
Louisiana	0.02	±1000*	4	±200
Arkansas	0.17	±777	2.8	±300
Dudgemona River				
condition 1	0.13	±18	29	±27
condition 2	0.34 - 0.37	±14	28 - 30	±30 to ±25
condition 3	0.91 - 1.06	±6	54 - 89	±12 to ±4

*interference due to partial withdrawal of tracer material by power plant water intake

The uncertainties displayed in this table were calculated by propagating the uncertainties of the individual C_G/C_T ratios for each measurement station. The error is propagated using the following general formulation:

$$f(X_1,X_2) = f(A,B) \pm [(\frac{\partial f(A,B)}{\partial X_1})^2 a^2 + (\frac{\partial f(A,B)}{\partial X_2})^2 b^2]^{1/2} \qquad (75)$$

where A ± a and B ± b are the confidence intervals on the variables X_1 and X_2. The NCASI(1982) report also demonstrated that the percentage of gas tracer lost could be related to the precision of the calculation of K_{Kr}, as shown below:

Table 4: Theoretical Precision of K_{Kr} (NCASI,1982)

R_d/R_u	% of gas tracer lost	precision of K_{Kr}
0.1	90	±4%
0.5	50	±13%
0.9	10	±90%

where R is the ratio C_G/C_T and the subscripts d and u refer to the downstream and upstream measurements, respectively.

Table 5 below gives the theoretical length of time a given tracer study must be followed in order to achieve a desired precision in the measurement.

Table 5: Length of time a tracer study must be followed to achieve a desired precision (NCASI,1982)

K_2 to be measured (base e) 1/day	time necessary to achieve a precision ±50%	time necessary to achieve a precision ±10%
1.0	3.9 hours	22.0 hours
0.5	7.8 hours	1.8 days
0.1	1.6 days	9.2 days
0.05	3.2 days	18.4 days

Since the bias (any systematic error associated with the measurement technique) in the temperature correction factor θ, and in the K_2/K_{Kr} ratio at low rates, has not yet been established, the accuracy of any low rate radioactive tracer measurements of K_2 is still in question. Further research into θ and K_2/K_{Kr} is recommended in order to perform any calculation of the complete accuracy or uncertainty associated with the calculation of K_2 (NCASI,1982, Whittemore and Hovis,1984).

The most recent studies employing the radioactive tracer technique include the work of Hren (1983) who measured K_2 in the

North Fork Licking River, Ohio, U.S.A., and the studies of reaeration in swamp streams made by Neal (1984). He examined the potential relationship between reaeration characteristics and secondary flow, made some recommendations concerning reaeration predictions for swamp-like streams and also pointed out for future research needs in the area. An active research which involves the substitution of a non-radioactive isotope of krypton is being carried out at Tufts University and organised by R.C.Whittemore, but results have not yet been published (Barnwell, written communication,1987).

Comparative studies between the radioactive and the modified tracer techniques have been also carried out and will be discussed later.

In 1972, Bennett and Rathbun pointed out for the two major disadvantages of the radioactive tracer technique. The first is concerned with radiation exposure received by the personnel conducting the study and the public along the stream, which may be significant for rivers with discharge greater than 5 m^3/s. The second is concerned with the nuclear counting equipment necessary for tritium and krypton, which is expensive and not field-type equipment. Some other points could also be added to the above, such as the requirement of licenses to use radioactive material in a public waterway and the employment of qualified personnel leading to high costs.

2.3.2 The Modified Gas Tracer Technique:

Because of the hazardous nature of radiation and the strict controls on the use of radioactive tracers in the natural environment, the U.S.Geological Survey undertook an effort to find acceptable non-radioactive tracer gases.

Based on a gas-chromatographic technique for measuring extremely small quantities of low molecular weight hydrocarbon gases in water samples developed by Swinnerton and Linnenbom (1967), Rathbun et al.(1975) devised the possibility of using one of these gases as the gaseous tracer and reported preliminary experiments on a reach of West Hobolochitte Creek, Missouri, U.S.A. The method substitutes the Kr^{85} gas tracer by low weight hydrocarbon gases and tritiated water by rhodamine-WT. The gases selected were ethylene and propane (see Rathbun et al.,1978) which are inexpensive and readily available, fairly soluble in water (with saturation concentrations of 131 and 62 µg/l respectively, under 1 atm of the pure gas), detected in very small quantities (µg/l range) and have molecular diffusivities comparable to that of oxygen (see Rainwater and Holley,1984).

The assumptions of the modified gas tracer technique are similar to those of the radioactive tracer technique, with the difference that the dilution-dispersion tracer (rhodamine-WT) is not assumed to be conservative. Field measurement and data analysis techniques were therefore modified to measure the total mass of dye that passed each cross-section rather than just the peak-concentration (see Rathbun and Grant,1978). Rathbun et al.(1980) demonstrated that the error introduced by neglecting the dye correction factor averages at 6.7%, and therefore has relatively little effect on the computed K_2, as it has been questioned by Tsivoglou (1979). If the entire gas concentration curve is used in the area method, the rhodamine dye is used only to determine time of travel and correction for losses is not necessary (Rathbun and Grant,1978). In this case, K_T is given by:

$$K_T = \frac{1}{t_2 - t_1} \ln \frac{A_1}{A_2} \qquad (76)$$

or, if the flow (Q) increases with x in such a way that the concentration remains one-dimensional, then:

$$K_T = \frac{1}{t_2 - t_1} \ln \frac{A_1 Q_1}{A_2 Q_2} \qquad (77)$$

where t is the time of travel of the centroids of the tracer masses and is defined by:

$$t = \int t.C(t)dt \,/\, \int C(t)dt \qquad (78)$$

and the subscripts 1 and 2 refer to the upstream and downstream sampling stations respectively.

The assumption of constant ratios between the desorption rate coefficients for ethylene and propane and the reaeration coefficient was verified by Rathbun et al.(1978) and the resulting values are:

$$R_e = \frac{K_2}{K_e} = 1.15 \qquad (79)$$

and

$$R_p = \frac{K_2}{K_p} = 1.39 \qquad (80)$$

These experiments were carried out in an open rectangular stainless steel mixing tank at temperatures 20, 25 and 30°C. A total of 84 tests were made for several combinations of mixing intensity and temperature. Hydrocarbon concentrations were measured by gas chromatography as described by Shultz et al.(1976). Briefly, the ethylene and propane gases are stripped from the water samples using a stripping line and cold trap apparatus followed by analysis with a gas chromatograph equipped with a flame ionisation detector (Rathbun et al.,1977). In 1984, Rainwater and Holley carried an independent laboratory assessment of hydrocarbon gas tracers and measured oxygen, ethylene and propane ratio coefficients for three different mixing speeds (100, 150 and 200r.p.m.) and for three different temperature conditions (4,20 and 32°C). They found R_e and R_p values equal to 1.14 and 1.36, respectively, which compared favourably with the values originally reported by Rathbun et al.(1978). A detailed description of the gas stripping apparatus as well as hydrocarbon analysis procedure is also given by them. Bales and Holley (1986) carried laboratory studies of the modified gas tracer technique in a tilting recirculating flume at different hydraulic conditions. Inspection of their data reveals that both the R_e and R_p mean and standard deviation values agree well with previous studies, except for one test series where the results were considered to be inconsistent when compared with the other two test series. A similar condition can also be observed for some of the tests reported by Rainwater and Holley (1984) which could not be explained.

The field procedures were originally described by Rathbun et al.(1975) and Rathbun and Grant (1978). Rathbun (1979) describes how the gas and dye quantities are estimated for the use of the modified gas tracer technique. Generally, the two tracer gases are simultaneously injected into the stream by bubbling through porous tube diffusers placed on the stream bed. The tracer gases must be injected over a period great enough to produce detectable concentrations at the downstream end of the reach. The dye tracer is released in a manner to simulate the source configuration and duration of the gas tracer. The sampling procedure at two stations downstream of the injection site is similar to that used for the radioactive tracer technique and it is usually better to employ a flow-through system.

In the peak method, the entire rhodamine concentration (C_T) curve is obtained to determine the amount of dye recovery. This data is then used to correct C_T to an equivalent conservative concentration as follows:

$$C_T = C_c \exp(-K_D t) \qquad (81)$$

where K_D is the dye loss rate coefficient and C_c is the corrected dye concentrations. Tracer gas measurements at the peak of the C_T curve at two or more cross-sections are then used to obtain (C_G/C_T) and by a combination of equations (73) and (81), K_T can be computed from:

$$\left(\frac{C_G}{C_T}\right)_2 = \left(\frac{C_G}{C_T}\right)_1 \exp[-(K_T - K_D)(t_2 - t_1)] \qquad (82)$$

The reaeration coefficient can then be obtained from equations (79) or (80).

Bauer et al.(1979) measured reaeration coefficients for low flow conditions in the Yampa River, Colorado, U.S.A. They calculated the K_2 values using both the peak and area methods, and typical concentration versus time curves are presented in Figure 6, as well as the results showing the different K_2 values obtained by the two methods (Table 6). The percentage differences between the area and peak methods for ethylene and propane are 6.96 and 3.84%, respectively. A similar study was reported by Grant and Skavroneck (1980) where the same percentage differences are 12.35 and 4.95% for ethylene and propane, respectively, clearly indicate that the differences between the area and peak methods are two or more times greater for ethylene than for propane.

The peak method is probably more accurate than the area

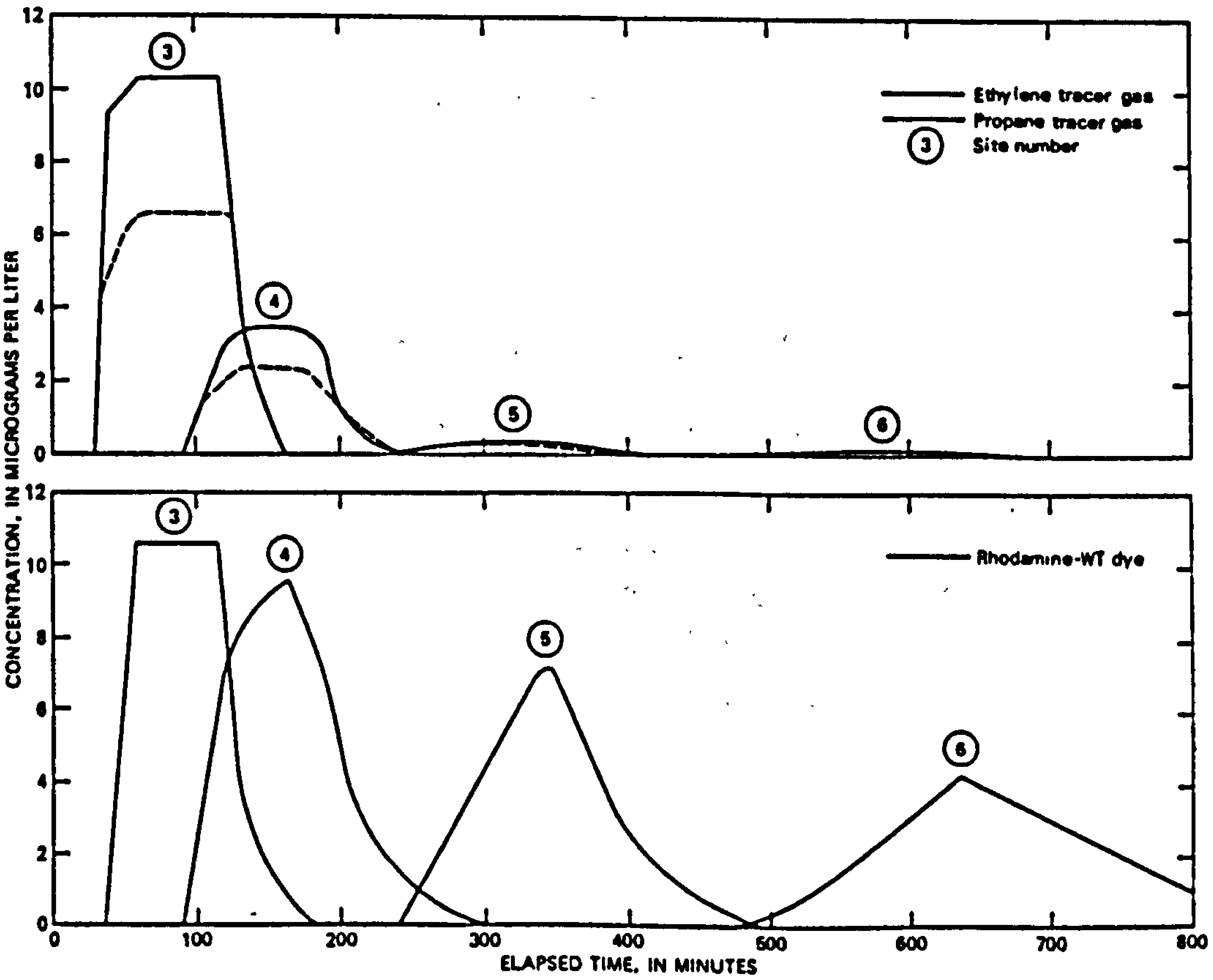


Figure 6: Concentrations of ethylene and propane tracer gases and rhodamine-WT dye at Yampa River, river mile 191.0 to 185.2, September 1976 (Bauer et al.,1979)

method because the peak concentrations are the largest and therefore the most accurately determined. The area method requires the measurement of much smaller concentrations on the leading and trailing edges of the tracer distributions, thus requiring a larger number of samples to be collected and analysed. From a statistical point of view, the results could then be considered more reliable , but economic considerations may limit the analysis of a large number of samples. Both methods require discharge measurements at each cross-section.

The results of the preliminary field studies, summarised by Rathbun et al.(1977), suggested that the modified technique was a promising procedure which could be an acceptable alternative to the use of radioactive tracers for the measurement of reaeration in streams. However, as it has been pointed out by Tsivoglou (1979), tracer gas losses due to biouptake, degradation or adsorption is an important factor to be considered, and Rathbun and Grant (1978) results strongly indicate that such losses were indeed real and did create a

Table 6: Reaeration coefficients for ethylene and propane determined using area and peak concentration methods, Yampa River, September 1976 (Bauer et al.,1979)

Subreach as defined by site numbers indicated	Water temperature degrees Celsius	Reaeration coefficient based on measured water temperatures (day^{-1})				Reaeration coefficient adjusted to 20 degrees Celsius (day^{-1})			
		Peak method		Area method		Peak method		Area method	
		Ethylene	Propane	Ethylene	Propane	Ethylene	Propane	Ethylene	Propane
3-4	13.3	23.1	26.8	25.6	28.5	27.1	31.4	30.0	33.4
4-5	16.2	20.8	20.6	-----	-----	22.8	22.6	-----	-----
5-6	18.0	-----	10.9	-----	-----	-----	11.4	-----	-----
3-6	15.1	-----	16.1	-----	-----	-----	18.1	-----	-----
8-9	13.8	8.93	8.78	9.71	9.69	10.4	10.2	11.2	11.2
9-11	14.4	7.56	7.01	7.82	6.60	8.64	8.01	8.94	7.54
8-11	14.0	8.05	7.65	8.56	7.79	9.29	8.83	9.87	8.99
13-14	14.8	7.00	5.34	7.67	5.85	7.92	6.04	8.68	6.62

substantial error in the derived K_2 values.

Rathbun et al.(1980) acknowledged that both ethylene and propane may be susceptible to adsorption, but assumed that adsorptive losses would be negligible since the ability of bacteria to attack hydrocarbons is highly specific, with the susceptibility to attack depending greatly on the size and type of hydrocarbon molecules. It was further stated that there was no reason to believe that the hydrocarbon gases were any more or any less susceptible to physical adsorption on sediments and debris in the stream than other simple molecules. Rainwater and Holley (1984) presented a review of hydrocarbon adsorption studies and also results showing that adsorptive losses of ethylene and propane on five different types of soil were negligible within the accuracy of the concentration measurement technique. Holley and Yotsukura (1984) and Holley (written communication,1986) have indicated that ethylene may be lost due to chemical reactions and is not recommended for field studies downstream of wastewater treatment plant discharges. Further investigation of this question is required.

In 1979, Kwasnick and Feng carried out laboratory and field studies to determine the ratio between the ethylene and oxygen transfer rates and to measure reaeration in two different streams, the Mill and the North Rivers ($Q=0.70\ m^3/s$), Massachusetts, U.S.A. The ratio K_2/K_e found of 1.14 was in good agreement with the previous reported value of 1.15 reported by Rathbun et al.(1978). The measured reaeration values of 4.14/day for the Mill River ($H=0.70$ m, $W=13.0$m) and 12.02/day for the North River ($H<0.30$ m, $W=12.0$ m) were considered to be consistent with the values estimated for the study reaches by various equations. A somewhat different gas chromatography technique (described by Bellar et al.,1976) from that presented by Shultz et al.(1976), has been employed for the analysis of ethylene samples.

In 1980/81 the U.S.Geological Survey made comparative studies between the modified tracer technique and predictive equations in five small streams in Wisconsin. These studies have been described by Grant and Skavroneck (1980) and House and Skavroneck (1981). Since the tracer techniques are still subjected to limitations, such as difficulties of implementation and expense, a selection of the best predictive models based on direct measurements can always be useful for less accurate requirements in water quality analysis. Both studies report the energy-dissipation model of Tsivoglou and Neal (1976) as the best predictive model for the selected reaches, based on the measurement of K_2 with the modified gas tracer technique. Also in 1980, Goddard carried a one year study to calibrate and demonstrate the use of a steady state water quality model for a 42 mile reach of the Arkansas River in Pueblo County, Colorado, U.S.A. Using ethylene gas and rhodamine-WT as tracers, he determined reaeration rates ranging from 5.04 to 12.1/day with discharge varying from 3.5 to 11.3 m^3/s, velocity varying from 0.50 to 0.75 m/s and depth from 0.34 to 0.60 m.

In 1983, Yotsukura et al., in an attempt to examine reproducibilities of tracer data and of the propane desorption coefficient as well as to evaluate the effect of wind shear on the desorption coefficient, developed and tested a steady-state method for the measurement of reaeration rates in natural streams. The method combines an instantaneous injection of dye tracer with a long duration injection of propane gas tracer. They demonstrated that for 1-D situations (see Fisher et al.,1979) where negligible effects from longitudinal mixing may be assumed for steady-state conditions ($4D_LK_T/U^2 << 1$), the gas tracer concentration distribution is a function of x only and may be adequately approximated by:

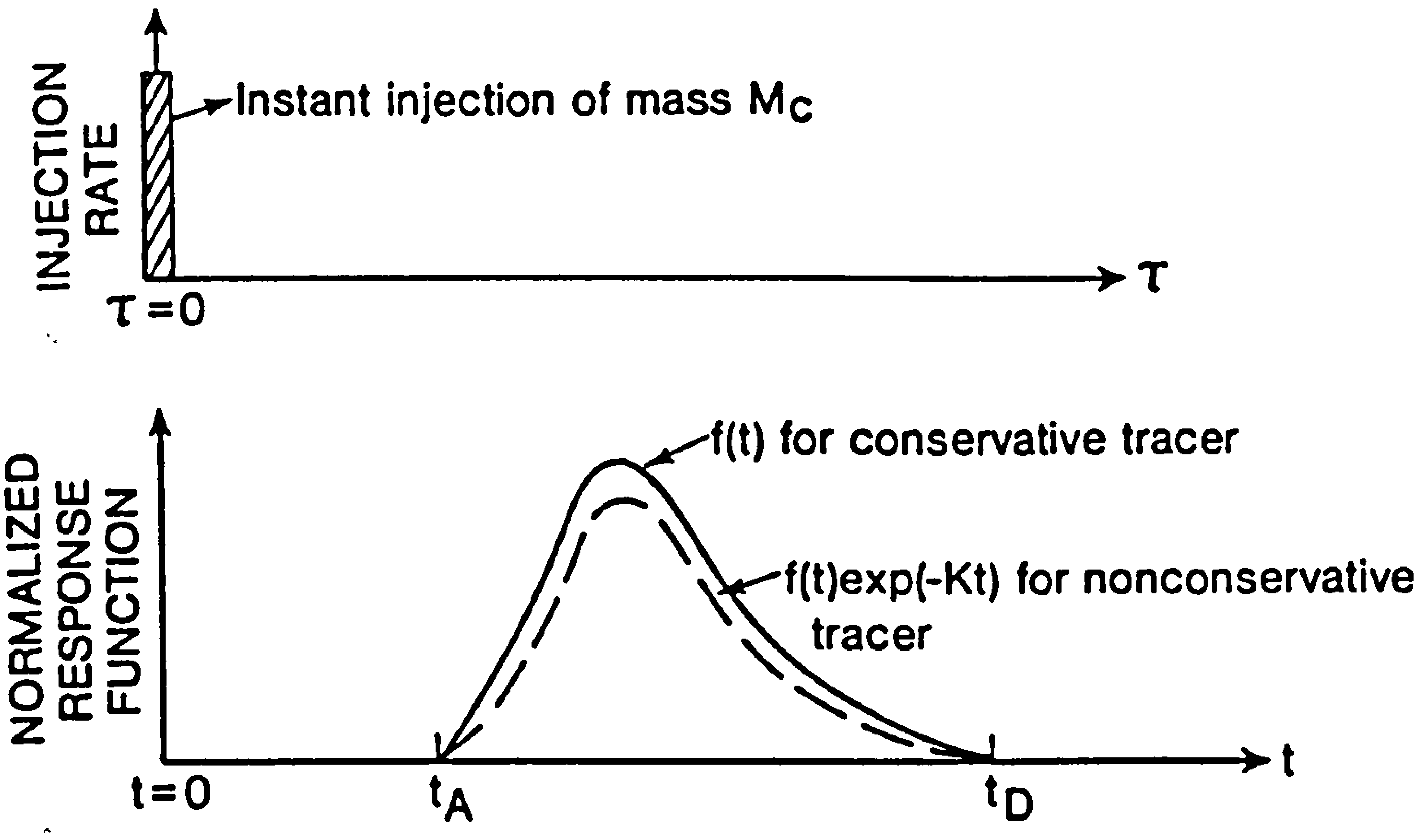
$$C_G(x) = \frac{m}{Q(x)} \exp(-K_T\,\Delta t) \qquad (83)$$

where m is the flux of dissolved gas at the injection site, Q is the river discharge, and Δt is the flow time. It is assumed that Q is constant and does not decrease with x due to seepage loss from the channel. If equation (83) is applied at two cross-sections, then:

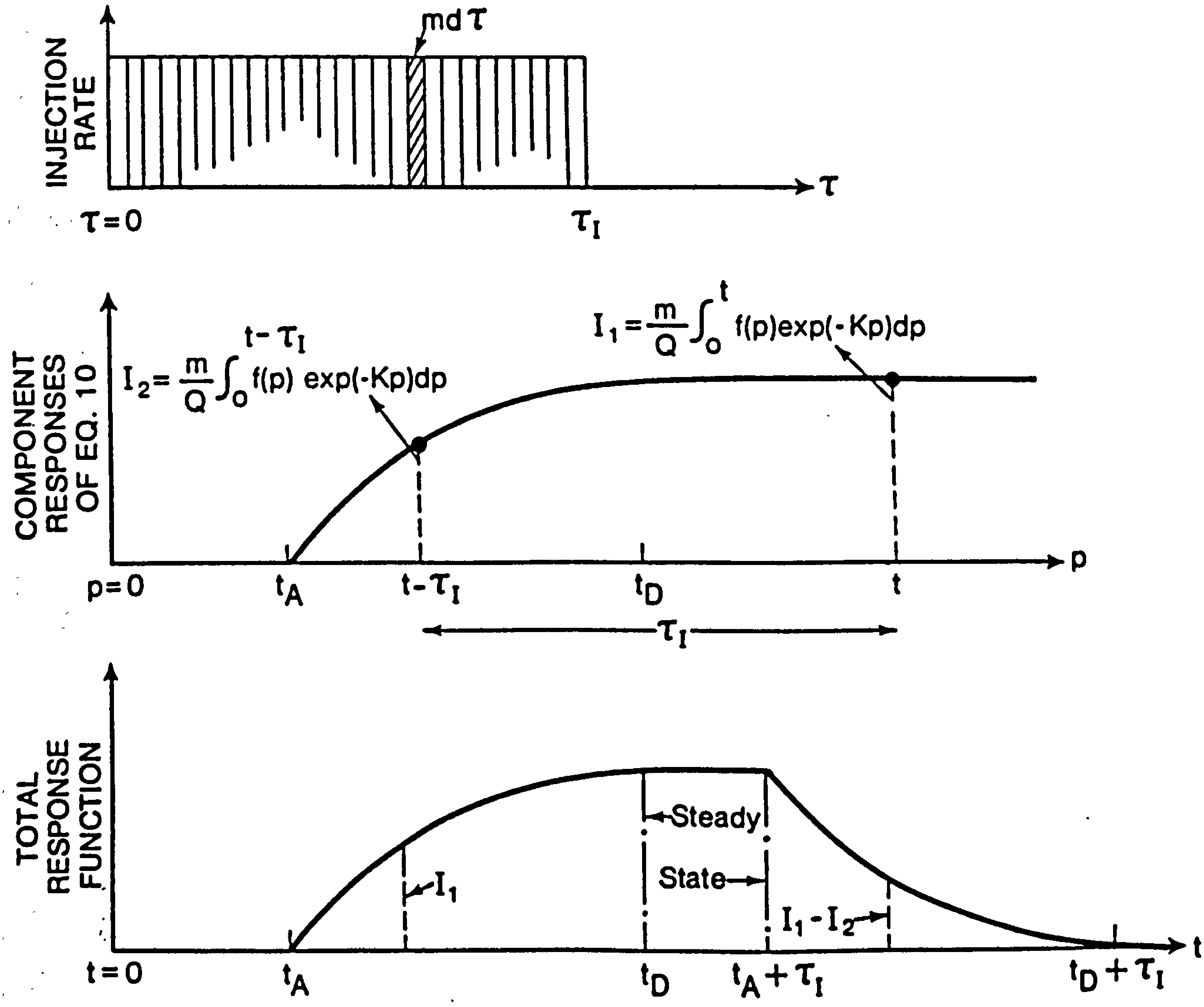
$$(C_GQ)_2 = (C_GQ)_1 \exp[-K_T(t_2 - t_1)] \qquad (84)$$

where the subscripts 1 and 2 refer to the upstream and downstream sampling stations, respectively. The above equation is the result of using linear superposition (Yotsukura and Kilpatrick,1973) with the 1-D version of equation (74), i.e. equation (83).

The field procedure uses an instantaneous injection of a conservative tracer (rhodamine-WT) at t=0 and the resulting concentration curve is obtained at a given downstream location, as is shown in Figure 7A. Referring to Figure 7B, for a continuous injection of the gaseous tracer between $0 < \tau < \tau_I$, and using linear superposition of the instantaneous injection



A) Input-output relation for an instantaneous injection



B) Input-output relation for a continuous injection

Figure 7: The principle of linear superposition for long duration gas tracer injection (Yotsukura et al.,1983)

and response of the conservative tracer, it can be demonstrated (refer to Yotsukura et al.,1983) that a steady-state gas concentration will exist for $t_D < t < t_A + \tau_I$. Only dye concentrations are determined while the dye cloud is passing. When the dye concentration declines to approximately 2% of the peak concentration, the gas concentration will be essentially at steady state (see Figure 7). The dye measurements are then stopped and gas sampling is initiated and continued as long as desired during the steady-state period. The reach averaged desorption coefficient K_T is then calculated from equation (84) and the reaeration rate coefficient is obtained from equations (79) or (80).

Yotsukura et al.(1983) conducted 1-D steady-state tracer gas tests in a 5.2 km straight reach of the Cowaselon Creek, New York, U.S.A. (see Figure 8). The reproducibility of desorption data and coefficients was considered to be satisfactory, and the long duration injection method was considered to be a reliable and feasible technique. Concerning the accuracy of the determination of K_T, it was concluded that equation (84) can be used with confidence for a steady natural stream for the steady-state method. It was difficult to establish the absolute level of accuracy of calculated K_T values from field data, but based on the propagation of error analysis, from where the following relationship can be derived

$$\frac{\sigma(\bar{K}_T)}{\bar{K}_T} = \frac{1}{\bar{K}_T\,\Delta t}\left[\frac{\sigma^2(\bar{C}_1)}{\bar{C}_1^{\,2}} + \frac{\sigma^2(\bar{C}_2)}{\bar{C}_2^{\,2}} + \bar{K}_T^{\,2}\sigma^2(\Delta t)\right]^{1/2} \qquad (85)$$

it was established that the non-dimensional group $(\bar{K}_T\,\Delta t)$, is the single parameter which controls the propagation of error from concentration measurements to calculation of desorption coefficients or reaeration coefficients. It was further stated that the planning of a tracer study should be made so that an estimated non-dimensional number is equal or larger than unity for the test reach, i.e. ($K_T \Delta t$) ≥ 1. For values greater than unity, the errors from the individual variables are attenuated in calculating K_T, while for values less than unity, the errors are amplified. Apparently, this simple relationship has never been clarified in the literature, even though the empirical

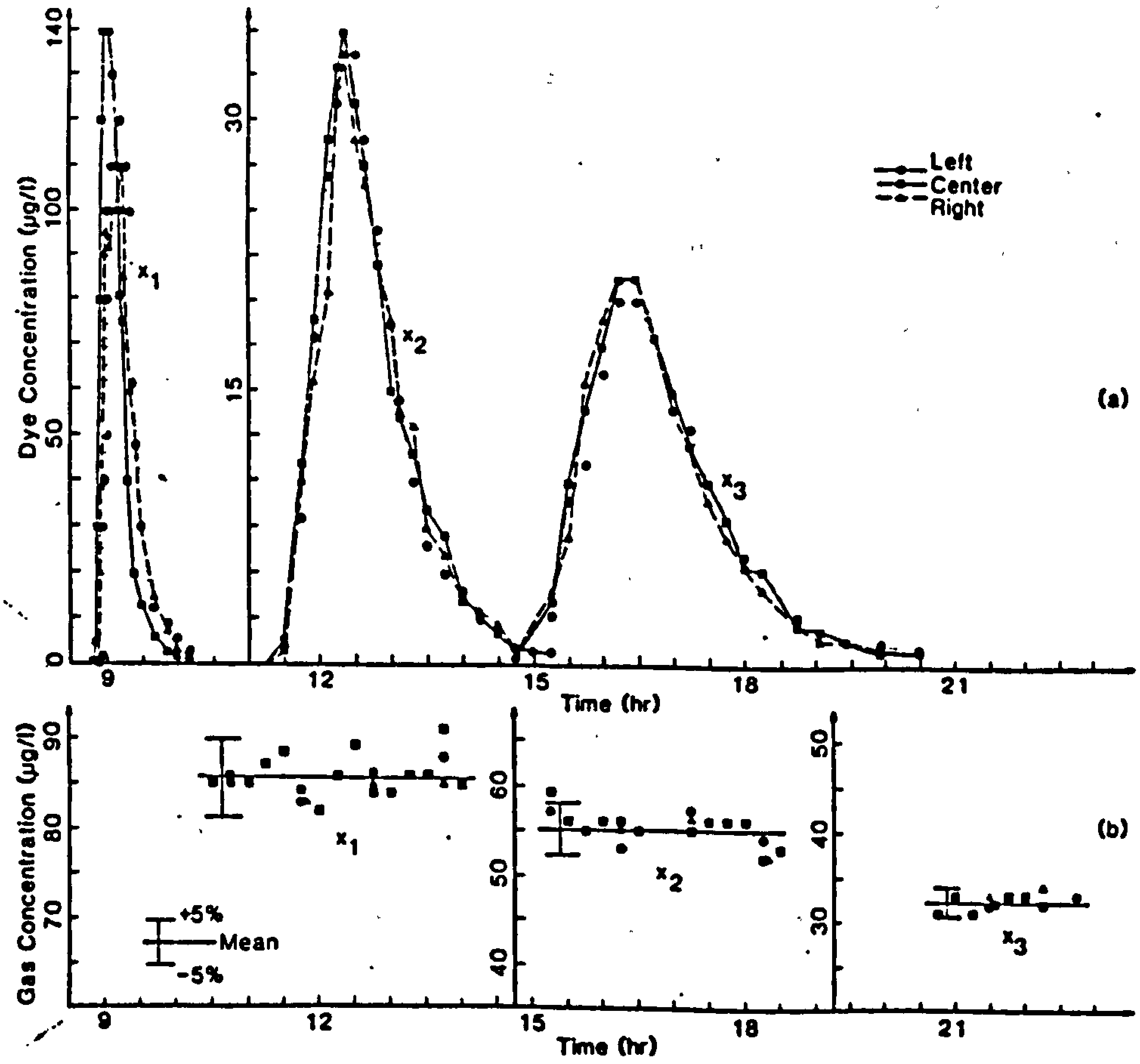


Figure 8: Data from Cowaselon Creek long duration injection gas tracer study (Yotsukura et al.,1983)

knowledge existed for some time that the reach length or residence time must be large enough to make the ratio Q_1C_1/Q_2C_2 larger than 2.72, which correspond to the above non-dimensional number of unity (Yotsukura et al.,1983). This is an important consideration which has not been recognised in planning some experimental programs (Holley and Yotsukura,1984).

In the case of wide rivers, the distance required for achieving transverse uniformity may be longer than the study reach for gas transfer measurements. A non-uniform plume method has then been developed by applying the principle of linear superposition. It was first described by Holley and Rainwater (1983), and later by Holley and Yotsukura (1984). Actual tests have been carried out by Yotsukura et al.(1984) in a 10 km meandering reach of the Chenango River, New York, U.S.A.

The field procedure, as described by Holley and Yotsukura (1984), uses an instantaneous injection of rhodamine-WT at the beginning of a continuous injection of gas tracer at some fixed source location in a cross-section. At several transverse locations in the measurement cross-sections, measurements are made only for dye concentrations while the dye cloud is passing and then switched to gas concentration, as for uniformly mixed plumes. The current practice is for transverse locations to be chosen on the same depth-averaged streamline determined from discharge data. Also, enough dye data must be collected to provide the transverse distribution of mass passing each cross-section. The reach averaged desorption coefficient $K_T(j)$, for the j-th streamline is calculated from:

$$\left(\frac{C_G(j)Q}{\phi(j)}\right)_2 = \left(\frac{C_G(j)Q}{\phi(j)}\right)_1 \exp[-K_T(j)(t_2(j) - t_1(j))] \qquad (85)$$

where the quantities x(j) are measured on the j-th streamline. The non-dimensional distribution factor, $\phi(j)$, is defined by:

$$\phi(j) = \frac{Q \int_0^\infty C_T(j)dt}{\int_0^B \left(\int_0^\infty C_T(j)dt\right) u\ h\ dy} \qquad (86)$$

where u is the local depth-averaged velocity, h is the local depth and B is the channel width. Results obtained by Yotsukura et al.(1984) at the Chenango River with discharge of 14.2 m^3/s and width varying from 70 to 90 m, were as follows:

(i) for the 10 and 30% streamlines, K_T was steady at about 0.16/hour;

(ii) for the 50% streamline, K_T varied between 0.17 and 0.12/hour, with the variation corresponding with high and low wind periods, respectively;

The tracer injection location was on the 30% streamline and the duration of the gas injection was about 21 hours.

Although these studies appear to provide an operationally feasible method utilising a relatively short reach of a wide river, it is limited, as for the uniform plume situation, to essentially steady flows. A point to be verified is whether the same $K_T(j)$ would be obtained with injections at different transverse locations (Holley and Yotsukura,1984).

Terry et al.(1984) made a water quality assessment of the Illinois River Basin, Arkansas, U.S.A., and reported reaeration measurements by the modified gas tracer technique. Ethylene gas was used as the gaseous tracer and the peak method was employed for K_T calculation. Reaeration rates ranging from 0.40 to 24.60/day were found for low flow velocities (at about 0.05 m/s) in four different rivers (Muddy Fork, Spring Creek, Osage Creek and Illinois River). Sensitivity tests indicted that DO profiles were most sensitive to stream depth and atmospheric reaeration in almost all situations.

Wilcock (1984a,1984b) developed a modified gas tracer technique by using methyl-chloride as the gaseous tracer. Laboratory experiments and field measurements in five rivers in New Zealand were reported and summarised by Wilcock (1984c).

Laboratory experiments have been conducted in order to establish the relationship between the mass transfer coefficients of oxygen and methyl chloride over a range of temperature between 5 and 35^oC. This was found to be temperature dependent and given by:

$$\frac{K_{CH3Cl}}{K_2} = 4.323 \exp(-530.97/T) \qquad (87)$$

A gas chromatographic analytical technique using electron capture detection was used in order to determine the methyl-chloride concentrations in water samples and is described by Wilcock (1984a).

Field measurements have been described by Wilcock (1984b) and the procedure is similar to that of Rathbun and Grant (1978). Methyl chloride masses required for each experiment were roughly estimated using the Fickian model for longitudinal dispersion, modified for loss of tracer by volatilisation:

$$C_T^p = \frac{W \exp(-K_{CH3Cl} t)}{A (4 \pi D_L t)^{1/2}} \qquad (88)$$

where W is the initial mass of tracer added, A is the mean cross-section area of the stream, D_L is an estimate of the longitudinal dispersion coefficient, and t is the time of travel between two sampling stations, having a hypothetical peak concentration C_T^p of 1 mg/m^3.

In summarising the results of field studies in New Zealand rivers, ranging in discharge from 0.3 to 36 m^3/s and having measured K_2 values over the range 0.3 to 16.6/day, Wilcock (1984c) found the possible sources of error in the gas tracer technique to be:

(i) analytical errors arising from low levels of tracer (or high background concentrations);

(ii) unequal mixing of the dye and methyl chloride;

(iii) non-conservancy of the tracer dye;

(iv) uncertainties in the estimates of peak dye and methyl chloride concentrations;

The main error came from estimating the values of the dye and gas concentrations at each site, and especially where the tracer profiles were very sharp or where concentrations were extremely low. In fact, if the non-dimensional group ($K_T \Delta t$) is calculated for the data given by Wilcock (1984c), an average value of 0.70 is found for all measurements, suggesting a good accuracy for the measured K_2. As it has been recognised by Wilcock (1984c), the results obtained for the Waipa River are the least accurate due to significant analytical errors ($K_T \Delta t$ = 0.06), and problems associated with differential mixing of dye and methyl chloride.

It has been concluded by Wilcock (1984c), and it has been generally agreed, that rivers in which the measured value of K_2 is greater than 1.0/day are likely to yield results having the best precision. For rivers in which $K_2 < 1.0$/day, the small changes in peak concentrations between sites yields uncertainties in K_2 values comparable with those obtained with predictive models.

Rutherford (1986) has also measured reaeration rates using methyl chloride as a gas tracer. Reaeration coefficients ranging from 5.5 to 7.5/day were reported for two uniform reaches of the Tarawera River, New Zealand, with mean velocity of 0.70 m/s, mean depth of 2.1 m and annual mean flow of 30 m^3/s.

2.3.3 Radioactive vs. Modified Techniques:

A few comparative studies between the two tracer techniques have been reported and a general agreement concerning the difference of results has not yet been obtained.

The first of these studies was reported by Rathbun and Grant (1978). The radioactive and modified tracer techniques were used to measure the reaeration coefficients of two reaches each of Black Earth Creek and the Madison Effluent Channel, Wisconsin, U.S.A. The coefficients measured with the modified technique were from -8.96 to +3.61 and from +15.7 to +32.2 percent different from the coefficients measured with the radioactive tracer technique at two different reaches of the Black Earth Creek. The larger coefficients measured with the modified technique were attributed to increased wind conditions (wind speed may have been about 3 m/s greater during the modified technique test) during the latter part of the modified technique experiment. On two other reaches of the Madison Effluent Channel, reaeration coefficients measured with the modified tracer technique ranged from +25.3 to 57.9, and from -4.74 to 2.94 percent different from the values measured by the radioactive tracer technique. The larger differences observed on one of the reaches were attributed to an unsteady flow condition in the channel resulting from increased discharges from a sewage treatment plant during the modified tracer experiment. However, as it has been pointed by Tsivoglou (1979), such speculations would have been eliminated had the comparative tests been performed simultaneously. He believes that tracer gas losses due to biouptake, degradation or adsorption must have caused the modified K_2 values to be larger than those found with radioactive tracers.

In 1980, Grant and Skavroneck carried out a study of four modified tracer techniques and 20 predictive equations for the determination of K_2 compared with the radioactive tracer method in 3 small streams (0.05 to 0.50 m^3/s) in Wisconsin, U.S.A. The propane area method gave the least absolute mean difference of 11% compared with the radioactive tracer method. Propane-peak, ethylene-peak and ethylene-area methods gave absolute mean differences of 18, 21 and 26%, respectively, compared with the radioactive tracer method results. It has been also concluded that the propane-area method is more accurate and more consistent than any of the predictive equations evaluated for the three streams, and that it may be as accurate as the radioactive tracer method since experimental errors inherent to both methods may prevent the measurement of K_2 with zero error.

NCASI(1982) carried out a comparison of reaeration estimation techniques for the Ouachita River Basin, Arkansas, U.S.A., and obtained rather different conclusions in respect to the accuracy of the modified tracer technique. Variability aside, the measurement of reaeration by the two methods produced considerably different reaeration rates. In the case of the radioactive tracer method, reaeration at 20°C was 0.17/day whereas in the case of the hydrocarbon method, the rates were 0.44 and 1.0/day depending on the method of calculation (ethylene-peak and area methods, respectively). The measured variability of K_2 obtained by the radioactive tracer technique does not encompass either of the hydrocarbon derived values. Had variability been determinable for the hydrocarbon method, the wide difference between K_2 determined by these methods could at least be attributed to variability in the hydrocarbon method or bias between the methods.

Liu and Fok (1983) in assessing water quality capacity of the Canandaigua Outlet, New York, U.S.A., concluded that the modified tracer technique could provide results within 5% error by comparing survey results using propane and ethylene as the tracer gases, with results obtained by Tsivoglou, using radioactive tracers in the same stream reaches.

As it is shown, either low or high percentage differences between the two methods have been reported. Although it appears that the modified gas tracer technique is an acceptable alternative to the use of radioactive tracers, there are still some doubts concerning its accuracy and reproducibility of field data. Since both methods are subjected to their own limitations, its selection should be primarily dependent upon the accuracy required and on the capital available. Several questions concerning the utility of direct tracer measurements in low transfer environments have been raised by Hovis et al.(1982). "The uncertainty of the hydrocarbon tracer measurement from poor and insufficient sampling and of the radioactive tracer measurement from the inherent analytical precision demonstrates the need to calculate potential errors prior to the conduction of such studies. If it is impossible to improve experimental procedures to reduce these errors to an acceptable range, then consideration should be given to not conducting the studies. In such situations empirical equations may produce comparable precision to those from direct tracer measurements."

2.4 <u>THE FLOATING SOLUBLE SOLIDS TECHNIQUE</u>:

Both the modified and radioactive gas tracer techniques require sophisticated equipment for reaeration measurement, but recently, another method has been developed by Giorgetti and Giansanti (1983) which is based on the dissolution of solids floating on the water surface. This does not need any equipment other than an anlytical balance and appears to offer a simple and reliable method for measuring reaeration rates.

The floating soluble solids technique was initially proposed by Giorgetti and Giansanti in 1983. It was developed under the assumption that the dissolution of the solid is increased by turbulent eddies which are randomly renewed at the water surface. These first studies were conducted in a turbulent agitation tank where the water was recirculated and could produce the desired level of turbulence. Sugar pellets, supported by a polysterene ball was used as the floating soluble solid, as shown in Figure 9. It was assumed that the dissolution process could be described by a first order reaction model of the type (Giorgetti and Giansanti,1983):

$$\frac{W}{W_0} = \exp(-K_s t) \qquad (89)$$

where W_0 is the initial weight of the solid at time t=0, W is

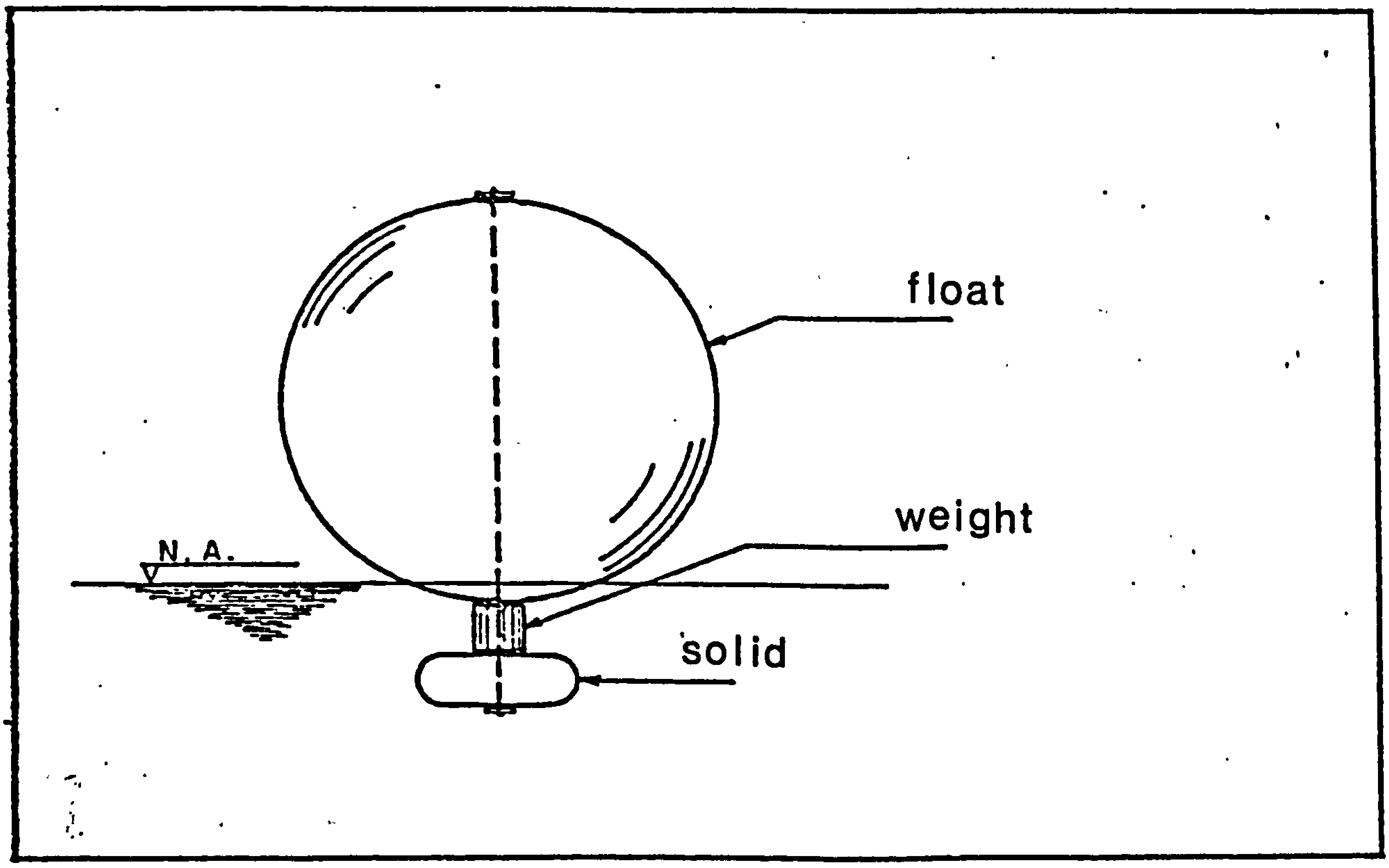


Figure 9: The first floating soluble solid (Giorgetti and Giansanti,1983)

the weight of the solid after a time of exposure t, K_s is the solids dissolution rate coefficient, and t is the time of exposure.

The conclusions drawn from these first studies were that both K_s and K_2 are strongly dependent on the level of turbulence, but there were insufficient data to attempt the development of a relationship correlating the two rate coefficients.

In an extension of these preliminary studies, Giansanti and Giorgetti (1986) reported experimentally measured values of K_2 and K_s on a straight and uniform recirculating flume (12.0 m long, 15.0 cm wide and 20.0 cm deep), at various hydraulic

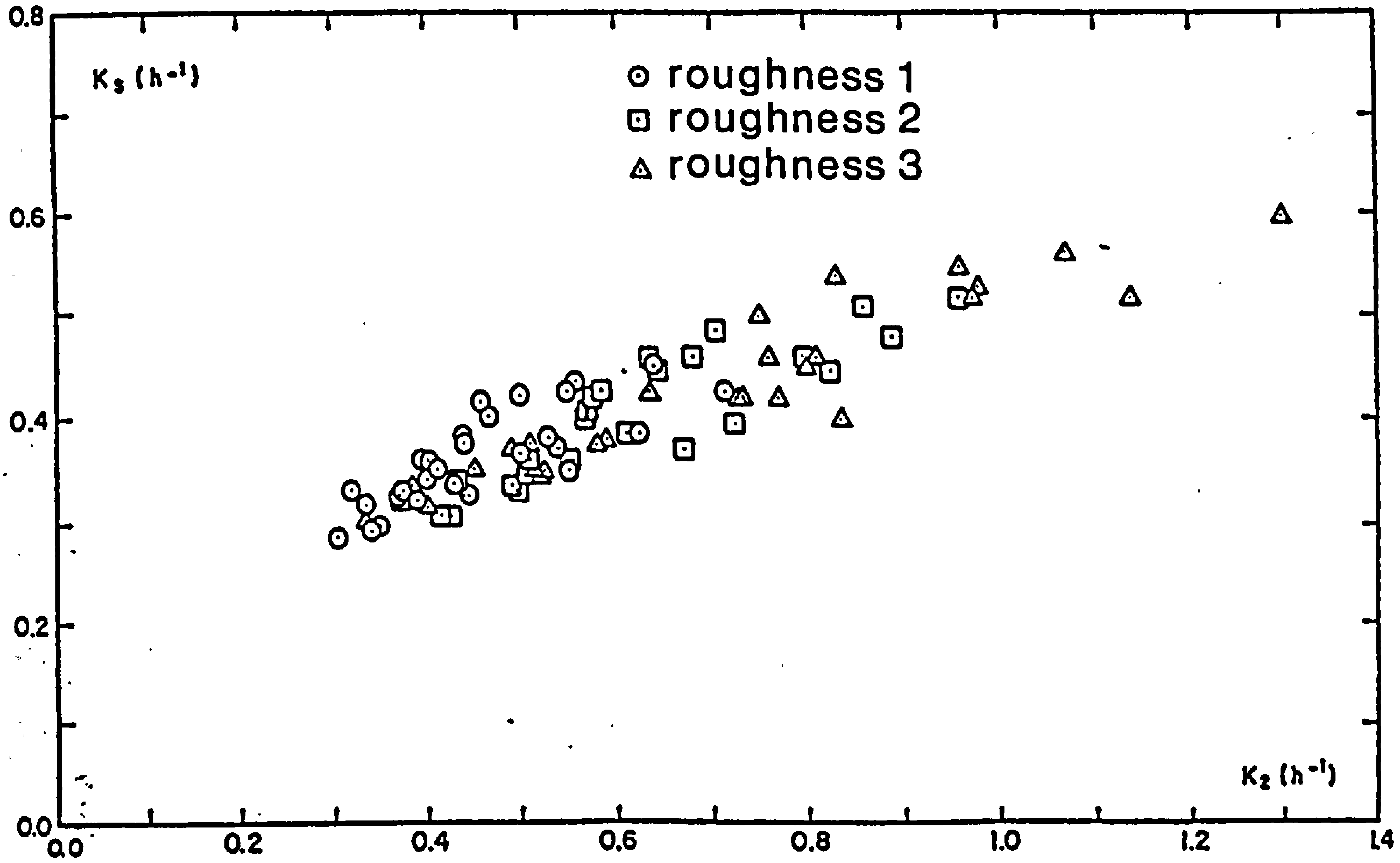


Figure 10: The relationship between the reaeration and dissolution processes at three different roughnesses (Giansanti and Giorgetti,1986)

conditions, with velocity ranging from 0.26 to 0.56 m/s. The results, as shown in Figure 10, clearly indicate a strong correlation between the reaeration and the solids' dissolution processes. It can be also concluded that there are no significant differences among the values obtained at three different roughnesses, thus indicating that roughness is equally affecting the two processes.

However, as it was later demonstrated by Shulz (1985), the first order reaction model is not adequate in describing the dissolution process. He argued that it is only valid for short exposure times, where the dissolved portion is small compared with the initial weight of the solid, and thus incompatible with the experimental needs when reliable measures of $W-W_0$ are desirable (Giorgetti and Shulz,1986).

A cubic model was then developed by Shulz (1985), where the change of weight of the solid (sodium chloride monocrystals supported on a metal framework with three polystirene floats; see Figure 11) is related to the cube of time as follows:

(i) the mass transfer between the solid and the water is proportional to the surface area of the solid and can be mathematically expressed by:

$$\frac{dW}{dt} = -\alpha . L^2 \tag{90}$$

or

$$\rho \frac{dL^3}{dt} = -\alpha . L^2 \tag{91}$$

where W is the weight of the solid, ρ is the specific weight of the solid, L is the characteristic linear dimension, and α is a proportionality constant.

(ii) the characteristic linear dimension was averaged for the six faces of the cubic solid and is given by:

$$L_0 = (a_0 . b_0 . c_0)^{1/3} \qquad (92)$$

where a_0, b_0, c_0 are the three characteristic dimensions of the cube.

(iii) the velocity of dissolution could then be defined as:

$$\frac{dL}{dt} = \frac{-1}{3} . \frac{\alpha}{\rho} = V_s \qquad (93)$$

(iv) integration of equation (93), between 0 and t, led to the following model:

$$\frac{W}{W_0} = (1 - \frac{V_s}{L_0} t)^3 \qquad (94)$$

where V_s/L_0 has the same dimensions as the reaeration rate coefficient.

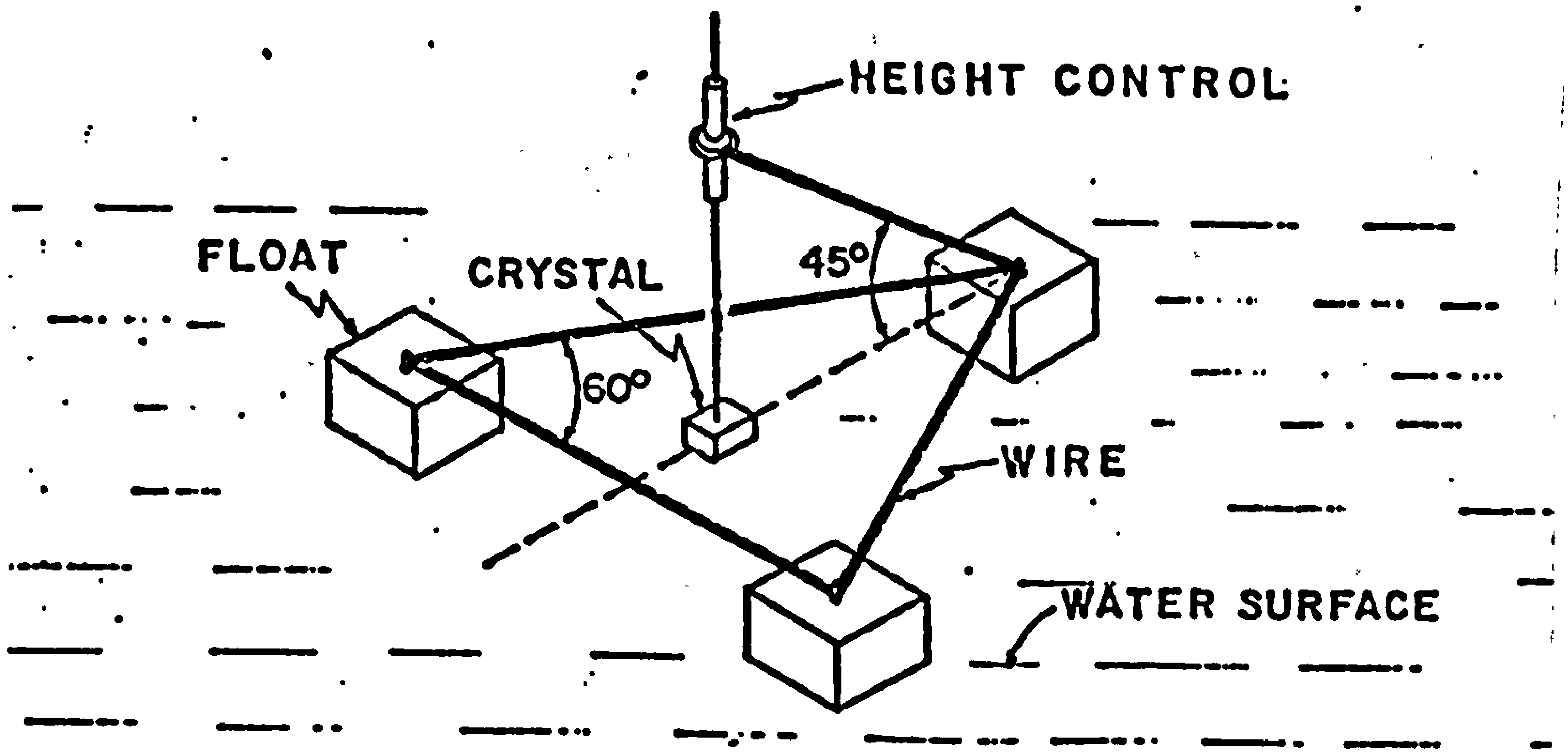


Figure 11: The sodium chloride monocrystal floating framework as used by Shulz(1985) and Giorgetti et al.(1986)

It has been shown by Shulz (1985) that the cubic model expressed by equation (94) was an adequate means of describing the dissolution process, and that the rate of dissolution could be correlated with discharge at high turbulent levels in his turbulent agitation tank. He verified that at low turbulence the main physical process responsible for the solids dissolution is natural convection, and that the cubic model cannot describe the process in these situations. He could thus, qualitatively express K_2 as a function of V_s (velocity of dissolution), based on equations (41) and (42), developed from the statistical theory of turbulence (see Chapter 1), for a flow range between 1.3 to 2.0 l/s, in the form:

$$K_2 = \alpha . V_s^{0.60} \qquad (95)$$

where K_2 is the reaeration rate coefficient, V_s is velocity of solids dissolution, and α is a proportionality constant.

It was later reported by Giorgetti et al.(1986) that the solids dissolution could not be considered uniform throughout the surface of the cubic solid and that the characteristic linear dimension could not be averaged as it was before.

The following model was then developed to describe the dissolution process, where the change in the surface area as a function of time was described by a Taylor's series:

$$\frac{W_0 - W}{W_0} = -2.\frac{(a_0.b_0+b_0.c_0+a_0.c_0)}{a_0.b_0.c_0}.(V_s.t) + 4.\frac{(a_0+b_0+c_0)}{a_0.b_0.c_0}.(V_s.t^2)$$

$$-8.\frac{1}{a_0.b_0.c_0}.V_s^2.t^3 \qquad (96)$$

where (W_0-W) is the change in weight due to dissolution after a time of exposure t, W_0 is the initial weight of the solid at time t=0, a_0,b_0,c_0 are the lateral dimensions of the solid at time t=0, V_s is the velocity of solids dissolution, and t is the time of exposure.

Experimental studies carried out in a concrete channel with gradually varied flow, of approximately 4.0 km in length, 2.50 m wide, showed that the velocity of dissolution of sodium chloride monocrystals remained constant for three different hydraulic situations (Giorgetti et al.,1986) as it is shown in Table 7, below:

Table 7: Velocity of solids dissolution (sodium chloride monocrystals) values measured in a concrete lined channel at different hydraulic conditions (Giorgetti et al.,1986)

Test Number	Average velocity (m/s)	Average depth (m)	Average discharge (m_3/s)	Velocity of solids dissolution (cm/min)
1	0.74	0.49	0.72	0.01517
2	0.73	0.46	0.65	0.01539
3	0.49	0.38	0.36	0.01474

Although these results were not sufficient to prove the inadequacy of sodium chloride monocrystals as floating soluble solids, they revealed that its dissolution process is mainly caused by natural convection, which, in this case, is the predominant process at either low or high turbulent conditions. It was suggested that a less soluble solid would be more appropriate for future research (Giorgetti,1987; personal communication).

Further experiments have then been planned on the basis of the conclusions drawn from the above studies, i.e. despite its initial drawbacks, it appears that there is a strong correlation between the reaeration and the dissolution processes, and that the technique shows considerable promise for the measurement of reaeration rates in small streams.

CHAPTER 3

The Effects on Reaeration

The reaeration rate coefficient is often interpreted as a function of hydraulic variables, such as velocity, depth and slope of the channel. But in addition to that, K_2 can also be affected by certain special factors, including:

(i) water temperature

(ii) wind

(iii) surfactants

(iv) suspended particles

(v) channel geometry

(vi) hydraulic structures

In respect to the water temperature effect, much controversy still exists and no single relationship between temperature and reaeration seems to best explain the data. The effect of wind is not always taken into account in reaeration prediction of streams (Frexes et al.,1984), although there is evidence that at high wind speeds, the reaeration rates can be significantly increased (e.g. Rathbun and Grant,1978). Effects such as those caused by surfactants and suspended particles are never included in water quality models, and are still subjected to much discussion. It has also been recognised that channel characteristics, such as meandering, can produce different effects on the reaeration coefficient, but very little information is available in the literature. The effect of hydraulic structures (small weirs, dams and spillways) on K_2 is another important factor and a subject in its own right. The reader should refer to Bowie et al.(1985) for a review.

3.1 TEMPERATURE EFFECTS:

The experimental work of Streeter et al.(1936) led to the development of the commonly used K_2-temperature dependence given by:

$$K_2(T) = K_2(20).\theta^{T-20} \tag{97}$$

where T is the water temperature in ^{o}C and θ is the temperature correction factor. Typically, values of 1.022 to 1.024 are used in most modelling applications. The above equation has since been widely used and although many studies appear to support its validity (refer to Zizon et al.,1978), a wide range of temperature correction factor values have been reported in the literature, as shown in Table 8. According to Zizon et al. (1978), the range of the temperature coefficient (1.006 to

Table 8: Reported values of temperature correction factor for equation (97); (adapted from Bowie et al.,1985)

temperature coefficient(θ)	aeration system	temperature range(^{o}C)	reference
1.047	channel	0 - 30	Streeter et al.,1936
1.0241	stirred	5 - 30	Elmore and West,1961
1.0226	stirred	5 - 30	Elmore and West,1961
1.020	stirred	0 - 35	Downing and Truesdale,1955
1.024	stirred	0 - 35	
1.016	stirred	0 - 35	
1.016	stream	0 - 30	Streeter,1926
1.018	channel	2 - 40	Truesdale and Van Dyke,1958
1.015	channel	2 - 40	
1.008	channel	2 - 40	
1.024	stream	5 - 30	Churchill et al.,1962
1.022	stirred	10 - 30	Tsivoglou,1967
1.036	stirred	28 - 38	Kozinski and King,1966
1.0192	stirred	10 - 30	Bewtra et al.,1970
1.021	stirred	4 - 20	Rainwater and Holley,1984
1.006	stirred	20 - 32	

1.047) produces reaeration rate ratios of 146 and 68% at 30 and 10°C respectively, when a base temperature of 20°C is used. Therefore, by using an incorrect θ for a particular system, the DO resource estimates for the system can be quite inaccurate, as already discussed in Chapter 2.

In 1956, O'Connor and Dobbins, based on the Stokes-Einstein equation (Wilke and Chang,1955),

$$D_m = F \frac{T}{\mu} \tag{98}$$

where D_m is the molecular diffusivity, T is the absolute temperature, μ is the coefficient of viscosity and F is the diffusion factor, determined the effect of temperature on the reaeration coefficient by substituting equation (98) above into equation (7), so that:

$$K_2 \propto (D_m)^{1/2} \propto \left(\frac{T}{\mu}\right)^{1/2} \tag{99}$$

The ratios of the reaeration coefficient at 20°C to that at other temperatures, as computed by equation (97) with $\theta = 1.016$, indicated that the divergence between the two formulae is in the order of 2%.

In an extension of Dobbins (1964) studies, Metzger and Dobbins (1967) and Metzger (1968) observed that the absorption of helium (D_m=4.45x10^{-5}cm^2/s) was affected more by temperature than the absorption of nitrogen (D_m=1.88x10^{-5}cm^2/s). They then stated that equation (97) is not necessarily correct when the film penetration is used because θ would have to be a variable with constant values being applicable only over certain ranges of turbulence. The value of θ would have to be different for each gas, in addition to the dependence on turbulence. The computed values of θ for oxygen in these tests ranged from 1.036 for very gentle mixing to 1.006 for rapid mixing characterised by surface distortion, and were considered to be in agreement with the predictions of equation (6). Metzger (1968) presented his results in the form of a diagram (Figure 12), where the computed θ values are shown as smooth curves plotted against the 20°C absorption coefficient. According to him, Figure 12 in addition to illustrate the effect of turbulence at one temperature, shows the variation in temperature at a given level of turbulence. Rainwater and Holley (1984) pointed out for the fact that the assumption that values of D_m follow the relation defined by the Stokes-Einstein equations was not verified by Metzger and Dobbins (1967) and that no comparisons with measured diffusivities at different temperatures were either made, since such data were not available at that time.

Issacs and Gaudy (1965) showed that the generally accepted value of $\theta = 1.0241$ is related to the fluid properties by:

$$\frac{\left(\frac{D_m^{1/2}}{\nu^{1/6}}\right)_T}{\left(\frac{D_m^{1/2}}{\nu^{1/6}}\right)_{20}} = (1.0241)^{T-20} \qquad (100)$$

and Fortescue and Pearson (1967) used a temperature correction of the type:

$$K_2(T) = K_2(20)\,\frac{(C_s D_m^{1/2})_T}{(C_s D_m^{1/2})_{20}} \qquad (101)$$

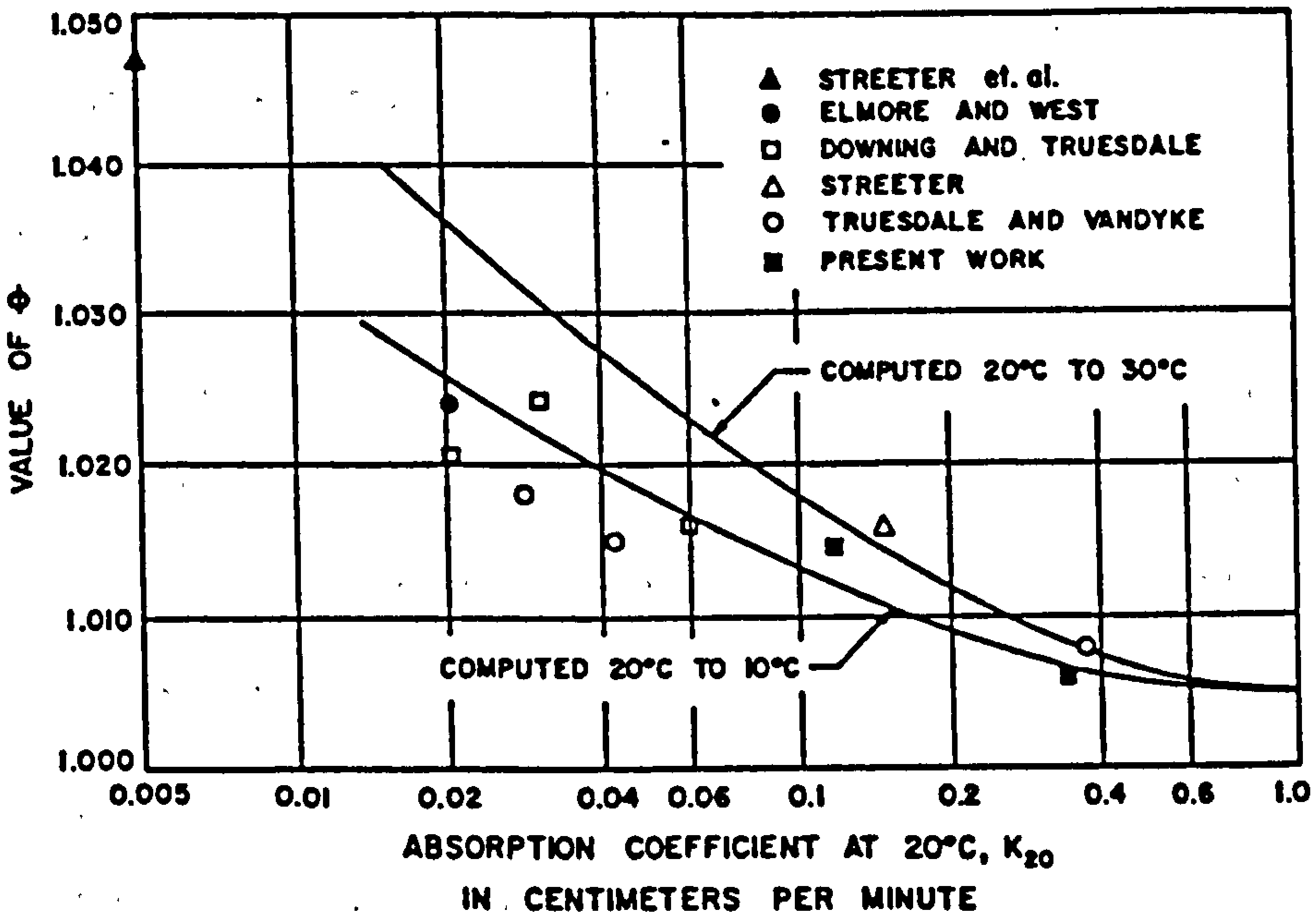


Figure 12: Effect of K_L (20^{o}C,base e) on reported and computed values of θ (Metzger,1968)

As already discussed in Chapter 1, Tsivoglou (1967) demonstrated, based on his kinetic-theory model, that the value of θ for oxygen and water, for temperatures from 10 to 30^{o}C, range between 1.018 to 1.026, which has eventually led credence to his model.

In 1977, Howe questioned the validity of equation (97) based on experimental studies, and proposed an inverse temperature dependence for the reaeration coefficient. His results have been entirely refuted by Brown and Stenstrom (1980) for lack of theoretical considerations and justifications.

Rathbun et al. (1978) carried out experimental studies to verify the relationship between gas transfer ratios of oxygen and hydrocarbon gases (ethylene and propane) at temperatures of 20, 25 and 30^{o}C. They have used the Arrhenius equation (as did Davies,1964 and Krenkel and Orlob,1962 using the available data for D_m and E_a) to calculate the dependence of temperature on the gas transfer ratios, as follows:

$$D_m = B \exp\left(\frac{-E_a}{RT}\right) \tag{102}$$

where E_a is the activation energy for the gas, R is the ideal gas constant, T is the absolute temperature and B is a constant relating the molecular diffusivity D_m to temperature. They then performed a linear least squares regression analysis on $\ln(D_m)$ from the data of Baird and Davidson (1962) and Wise and Houghton (1966) as a function of temperature to determine the values of B and E_a for each gas. These constants were then used to compute the oxygen to ethylene and oxygen to propane transfer ratios over a range of 10 to 25°C. The effect of temperature on these rates was found to be negligible (as it had been originally observed by Tsivoglou,1967) based on both experimental evidence and approximate analytical methods.

Schneitter and Grenney (1983) developed a mathematical model that provides a temperature correction factor for biological reaction rate coefficients over a temperature range from 4 to 30°C. Their approach effectively allows θ to vary as a function of temperature, but it has not been widely used (Bowie et al.,1985).

In conducting hydrocarbon studies for reaeration measurement, Rainwater and Holley (1984) concluded that their results do not support either the use of a single value of θ for correction of K_2 values for different temperatures, or the prediction of Metzger and Dobbins (1967) that θ would have different values for gases with different molecular diffusivities. It was further stated that the results obtained tended to support the proposal of temperature independent models such as those proposed by Tsivoglou (1967) and Kiosay et al.(1980) for predicting ratios of gas transfer coefficients, as well as the experimental observations of Rathbun et al.(1978).

The most recent studies on the effect of temperature on oxygen transfer have been conducted by Chao et al.(1987). They have presented an additional interpretation of the equation of O'Connor and Dobbins (1956) where the tangent hyperbolic term $[(r.L_y{}^2/D_m)^{1/2})]$ may not be always assumed to be 1 and therefore neglected. By using a combination of Stokes-Einstein equation and the Lewis-Whitman (1924) film thickness formula given by

$$L_T = \frac{14.652 - 0.4011T + 0.007991T^2 - 0.0007774T^3}{452} \qquad (103)$$

where L_T is the film thickness for a given temperature T, and substituting into O'Connor and Dobbins' (1956) model, they could simulate the variations of K_2 at different levels of temperature (10 to 30°C) and different levels of surface renewal rates (100/s for mechanical aerators to 0.1/s for sluggish rivers). They demonstrated that for a F value (refer to equation 98) equals to 0.714×10^{-7} g.cm/s^{2}K, the hyperbolic tangent term is close to unity only for surface renewal rates (r) greater than 50/s. When r is 10/s or less, the hyperbolic term is much less than unity and thus cannot be neglected when equation (6) is used to calculate the oxygenation coefficient. Consequently, the reaeration rate constant increases at higher water temperatures for r being 100/s and decreases at higher temperatures for r equals to 0.1/s. For the intermediate r value of 10/s the relationship between the logarithmic value of K_2 to temperature is shown to be non-linear. When different F values are used, the same observations can be verified, except that the region of r values corresponding to the non-linear relationship between $\log(K_L)$ and temperature is shifted. It has been therefore concluded that the effect of temperature on oxygen transfer depends on the magnitude of the F and r values.

Laboratory measurements of surface oxygen transfer rates at increasing temperature (9 to 30°C) made by Chao et al. (1987) appear to support their interpretation of O'Connor and Dobbins (1956) model.

3.2 WIND EFFECTS:

The basic concepts and mechanisms of oxygen absorption into flowing streams where the turbulence is a result of the shear at the channel boundaries, are equally applicable to turbulence and mixing generated by wind blowing over a water surface. The shear stresses exerted by the wind at the surface induce surface currents which can be turbulent, and cause wind waves which stretch the surface into a larger area at which oxygen can be absorbed (Eloubaidy and Plate,1972). According to Holley (1977), neglecting the influence of wind may have caused a significant part of the deviations amongst the available reaeration data, especially in the case of large bodies of water where the flow velocities are small.

Kramer (1974) and Holley (1977) present a general review of

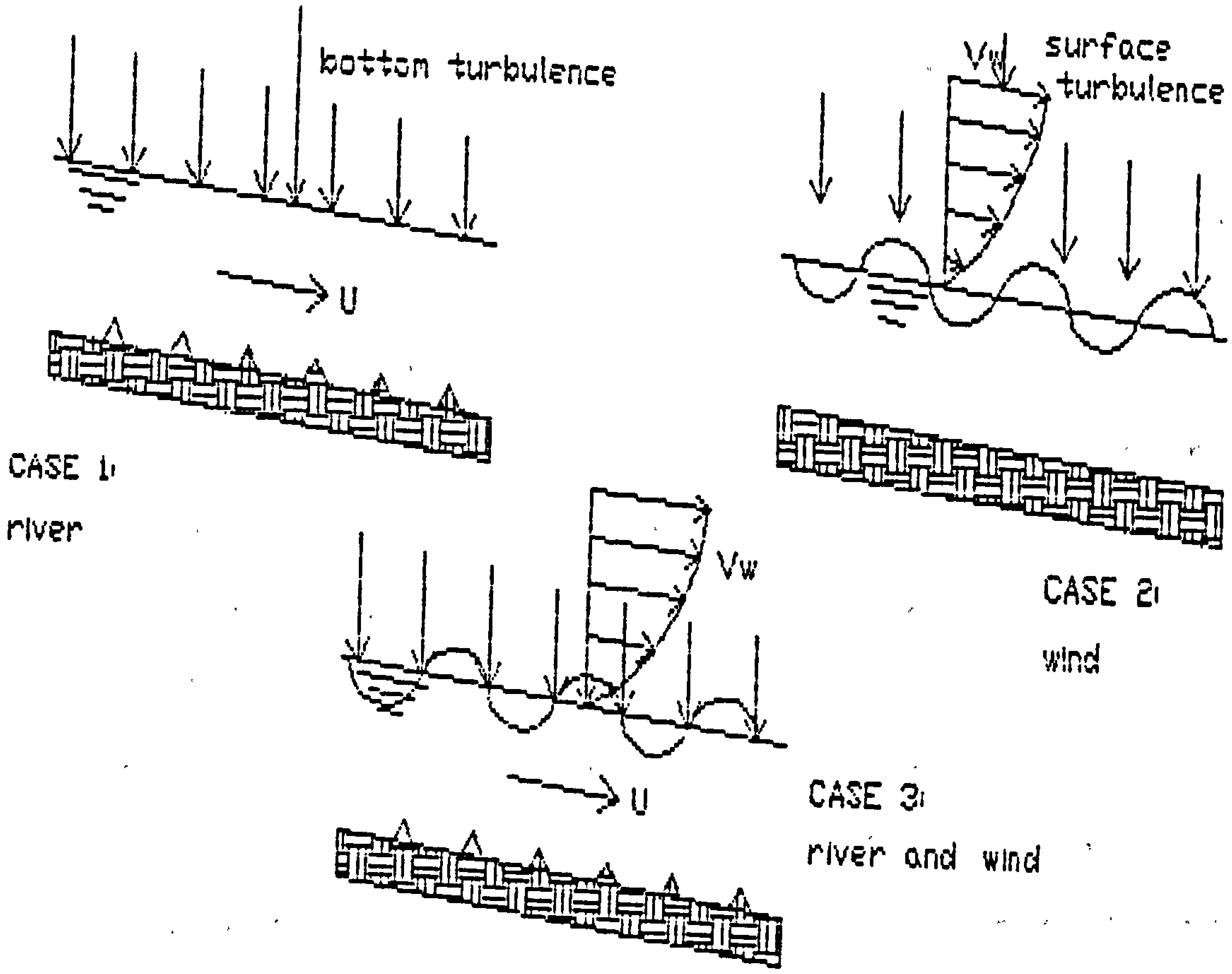


Figure 13: Schematic representation of reaeration processes (Plate and Friedrich,1984)

the studies on the effects of wind upon the reaeration coefficient, with further discussion by Frexes et al.(1984).

The first investigation on such effects has been conducted by Downing and Truesdale (1955). They performed a laboratory study using a small tank and fan to generate wind currents, with speeds between 0 and 9 m/s. Their data indicate that below a wind velocity of about 3 m/s, there are no significant increase in the reaeration rate. However, they have stated that the laboratory results were not in total agreement with estimates of the effect of the wind obtained from the results of direct measurements of the rate of reaeration in an estuary, due to the more turbulent nature of wind generated by the fan as compared with "normal" wind. Reaeration rates in the Thames estuary were reported to vary from 1.22 m/day under calm conditions to approximately 6.1 m/day under conditions which produced 0.5 m wave heights.

Since then, relatively few important additional studies have been carried out. Juliano (1969) reported oxygen transfer rates in a California, U.S.A., estuary, at 0.5 to 3.0/day, apparently depending upon wind velocity. However, as discussed by Kramer (1974), these data are scattered, indicating that wind direction has not been considered. A general and somewhat obvious conclusion which can be drawn from these first studies is that the dependence of the reaeration process (as represented by the magnitude of K_L) depends on both the wind speed and the fetch of the wind. Wind speeds of about 5 to 7 m/s at 10 m height are normally quoted as the critical value above which the wind begins to influence reaeration (Holley,1977).

Eloubaidy (1969) conducted reaeration experiments in a wind-water tunnel 15.8 m long and 0.61 m wide with water depth of 0.12 m. His results were later reported by Eloubaidy and Plate (1972) and published by Plate and Friedrich (1984). Increases of up to 20% in K_L with increasing fetch have been reported, and an empirical model has been developed for the surface transfer coefficient, as given in Table 1. The extremely high wind velocities used in the experiment (above 7 m/s) limit the validity of the approach when applied to lesser wind speeds, typically found in the natural environment (Bowie et al.,1985). But according to Holley (1977), Eloubaidy and Plate's (1972) data showed a dependence of K_L on the hydraulic conditions of the channel flow as well as on velocity speed and shear stresses, and thus have its merits.

Mattingly (1977) used a wind-water tunnel 8 m long, 0.55 m wide, with both air and water flows 0.27 m deep, to measure the reaeration coefficient. Air velocity varied between 0 and 15 m/s, and average water velocities were 4.5, 9.0 and 18.0 cm/s. He formulated the results of his experimental study into an empirical equation which relate a slight but definite dependence of K_L on water velocity in addition to the primary dependence on wind speed (Holley,1977):

$$\frac{K_{2w}}{K_2} - 1 = 0.2588\ (V_w - U)^{1.618} \qquad (104)$$

where K_{2w} is the reaeration rate coefficient under wind conditions, K_2 is the reaeration rate coefficient under normal conditions, V_w is the average wind speed and U is the average stream velocity.

O'Connor (1983) developed a relationship between the transfer coefficient of soluble gases and wind velocity in terms of the liquid film and surface renewal concepts. The parameters of these models have been related to the hydrodynamic characteristics of the air-water interface as induced by wind velocities under smooth and rough conditions. The derived relationships are as follows:

(i) for smooth surfaces:

$$K_L = [\frac{D_m}{\nu}]^{2/3}[\frac{\rho_a}{\rho_w}]^{1/2}\frac{K^{1/3}}{\Gamma_0} U_* \quad (105)$$

(ii) for rough surfaces:

$$K_L = [\frac{D_m U_*}{\kappa Z_e} \cdot \frac{\rho_a \nu_a}{\rho_w \nu_w}]^{1/2} \quad (106)$$

where K_L is the mass transfer coefficient, D_m is the molecular diffusivity, ρ is the mass density, ν is the kinematic viscosity, κ is the Von Karman's constant (usually 0.4), U_* is the shear velocity, Γ_0 is a dimensionless parameter related to the thickness of the viscous sub-layer with values ranging from 5 to 7, Z_e is the equilibrium roughness, and the subscripts a and w refer to air and water, respectively.

The transfer coefficients calculated by the above equations show reasonable agreement with observed values. Significant variations for a given wind were verified due to the characteristics of the individual systems, especially in the large scale ones, as well as a marked difference between laboratory and field data (also verified by Holley,1977).

Plate and Friedrich (1984) present and discuss results from reaeration experiments for three different cases: reaeration by bottom generated turbulence in open channels, reaeration by surface generated turbulence due to wind on water, and reaeration by wind on channel flow, in which the effects of the first two cases are combined (refer to Figure 13). The main results have been presented in the form of curves showing the reaeration transfer coefficient as a function of the root-mean-square value of the horizontal component of the velocity near the surface. In attempting to find a more generalised relationship, they have also plotted K_L as a function of dissipation velocity, which can be approximated by:

$$u_\varepsilon = 0.207\ V_W^{4/3} \qquad (107)$$

where V_W is the wind speed in m/s and u_ε is the dissipation velocity in cm/s. It has then been concluded, based on Figure 14, that there exists two basic regimes. Regime 1 corresponds to high winds, for which all data tend to approach the extreme case of full wind shear controlled flows. Regime 2 is controlled by water turbulence, and for low winds all data on open channel flow fall on the curve given by Eloubaidy and Plate's equation (refer to Table 1).

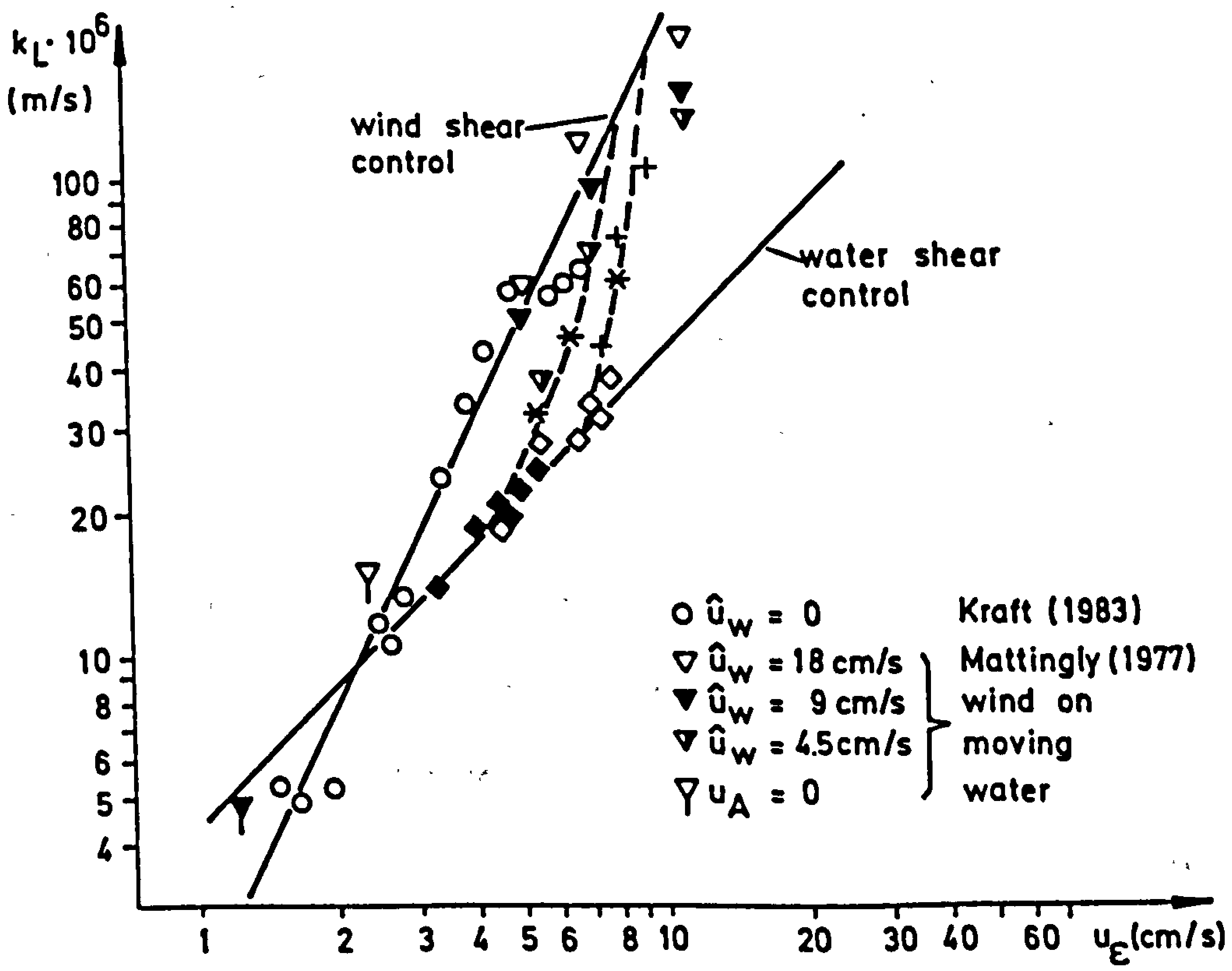


Figure 14: Summary of reaeration data as a function of dissipation velocity (Plate and Friedrich,1984)

There has also been some studies on the effect of wind on gas transfer processes for enclosed bodies of water, such as lakes and reservoirs, and the reader should refer to either Holley (1977) or Brutsaert and Jirka (1984) for more detailed information since it is a subject which is beyond the scope of the present review.

As it has been generally agreed, it appears that further experiments are needed to obtain more significant and definite field data (very little exists about wind effects measurements in natural streams) on the dependence of the transfer coefficient on wind speed and direction, and to further evaluate the significance of combined wind-wave effects on gas transfer. But because wind effects are typically neglected in river and stream reaeration modeling, a reasonable approach is to assume a zero wind velocity for most water quality applications (Bowie et al.,1985). In regard to field measurements of the reaeration rate coefficient, temporal variation monitoring of wind speed and direction should be conducted (Yotsukura et al.,1983) in order to identify any significant effect, and to avoid speculation due to the variability of measured values of K_2 (refer to Tsivoglou,1979 and Rathbun et al.,1980). In fact, Yotsukura et al.(1984), in assessing a steady-state propane gas tracer method for determining K_2 in the Chenango River, New York, U.S.A., found that the increase of the propane gas desorption coefficient due to high wind was substantial and consistent with the measurements from laboratory and field of gas desorption under purely wind controlled situations. They described an approximated method for estimating wind effects on gas desorption from the measurement of temporal variation of tracer concentration at a single station. But because the absolute steadiness of both water and air flows will never be realised in field measurements, the condition of steady-state for wind speeds is considered on the basis of averaged wind speeds utilising different time intervals of averaging, and defined as:

$$\bar{V}_w(x,q,t_s) = \frac{1}{t} \int_{ts-t}^{t} V_w(x,q,t)\, dt \qquad (108)$$

where $\bar{V}_w$ is the wind speed averaged over the mean travel time, q is the cumulative discharge, t_s is the time of gas sampling and V_w is the instantaneous wind speed. As for the increased gas desorption due to $\bar{V}_w$, an empirical wind function $\varnothing$, is defined as follows:

$$K = K_T + \varnothing \qquad (109)$$

where K represents the total gas desorption coefficient, K_T is the desorption coefficient generated by the steady-state channel flow turbulence, and $\varnothing$ is such that it is zero when $\bar{V}_w$ is low and finite when $\bar{V}_w$ is high. The expression which gives the steady-state gas concentration (see Chapter 2) is then modified by substituting equation (109) into it, and thus allowing the calculation of the desorption coefficient under windy conditions.

The results obtained by Yotsukura et al.(1984) showed that the wind function was found to be as much as 30% of K_T when the 3-hr averaged wind speed was approximately 2.5 m/s, and in agreement with the conclusions drawn by Jirka and Brutsaert

(1984) on the wind effects at the Chenango site, even though the interpretation of data was different.

3.3 CONTAMINANT EFFECTS:

Most of the studies of the contaminant effects upon the reaeration coefficient of flowing waters were conducted by the Water Pollution Research Laboratory, at Stevenage, England, during the mid and late 50's.

Downing and Truesdale (1955) investigated the effects of oil films and soluble surface active agents (SAA) on the rates of reaeration. The results indicate that the effect of oil films depends considerably on their thickness and on the degree of agitation of the water surface. Large effects on the rate of solution were not obtained under any conditions until the thickness of the oil film exceeded 10^{-4}cm. It seemed that the effect of oil films is mainly due to the additional resistance to the diffusion of oxygen molecules into the water which the films impose at the interface, although they may also tend to damp out surface disturbances where these occur. Tsivoglou and Wallace (1972) found that the reaeration capacity was increased more than double as mineral oil concentration was increased from zero to 400 mg/l. For a fixed concentration of 230 mg/l, the reaeration capacity decreased as the intensity of mixing increased, but the authors did not make any comment about these changes. Downing and Truesdale (1955) have also observed that the addition of small concentrations of SAA caused considerable reduction in the rate of solution of distilled, tap, and saline water, which increased with increasing concentration, but tended towards a limiting value.

Gameson et al. (1955) carried out similar experiments with water flowing under natural conditions. A mixed detergent and ABS were discharged into the stream at various different concentrations (between 0.6 to 3.5 mg/l). Their results show a considerable reduction in K_2 at lower rates of reaeration, and a slight reduction in K_2 at higher rates of reaeration.

Gameson et al.(1956), Downing et al.(1957) and Ogden et al.(1959), extended the original work of Downing and Truesdale and Gameson et al.(1955) by studying the effects on the rate of absorption of oxygen that are produced by changing the discharge in a channel, and by the addition, both separately and together, of settled sewage, sewage effluent, and SAA in water of varying salinity. It has been generally agreed that the effects of a particular contaminant (such as surface active matter) depend not only on its concentration, but also on the presence or absence of other contaminants (such as settled sewage or sewage effluent) on the particular rate of aeration being used, and also on the aeration system being employed. The lowering of the rate of aeration in saline water is quite pronounced but the proportional reductions produced by other factors do not appear to be dependent, to any great extent, on the presence of salt water. Wen et al.(1984) presented an experimental study indicating that the reaeration coefficient is actually increased with increasing chloride concentrations, and thus appear to be in conflict with the WPRL findings.

In 1964, Davies et al. measured the rates of absorption of various gases into turbulent stirred water, both with cleaned and SAA covered surfaces. The results obtained were similar to those presented by the WPRL, and it was concluded that the rate of reduction of gas absorption due to the SAA is somewhat dependent on the way the water is agitated and on the intensity of turbulence in the liquid. The rate of surface renewal and the dependence of the mass transfer coefficient on the molecular diffusivity have been evaluated from experimental evidence and compared with the predictions of the various conceptual theories (see discussion in Chapter 1).

Mancy and Okun (1965) performed studies on the effect of SAA on oxygen transfer in aeration vessels of different geometry in which the water was stirred at various speeds. It has been concluded that traces of SAA caused marked changes in the physico-chemical properties of the water surface, accompanied by a sharp increase on the resistance of water surface to oxygen transfer. The effect of SAA on oxygen transfer is also dependent on the hydrodynamic properties of the aqueous phase. At laminar flow mixing conditions, the bulk resistance is very high and it masks any changes in the surface resistance caused by the SAA. At turbulent flow mixing conditions, oxygen transfer is mainly dependent on surface renewal. Under these conditions there is no apparent effect of SAA on oxygen transfer.

Gas absorption experiments employing helium and nitrogen were conducted with water to obtain surface renewal rates and film frequencies in the presence of 0.5 mg/l of ABS by Metzger (1968). He reports similar results to those presented by Mancy and Okun (1965), indicating that the major effect of surface active substances is on the frequency of surface renewals and not on the diffusivity of the gas being absorbed into the liquid. With ABS present, the surface renewal rate is lower and the film thickness larger than in distilled water. His findings were also in agreement with the conceptual model developed by Dobbins (1962) and extended by Metzger and Dobbins (1967) (see discussion in Chapter 1).

Conflicting results have been obtained in the few studies which examine the effects of suspended solids on reaeration rates. It appears that part of the apparent inconsistencies are no doubt due to the fact that various types of suspended materials affect the reaeration processes in different ways, especially if the suspension results from sewage or industrial wastes are to be considered (Holley,1977). These conflicting results prompted Alonso et al.(1975) to perform a study of the effect of suspended sediments on reaeration rates in open channel flows in the laboratory. Their results are rather scattered but give an indication that the reaeration rate decreased about 35% over the sediment (0.115 mm sand) concentration range used, up to 3562 mg/l. This decrease in K_2 was attributed to the decrease in intensity of turbulent mixing at higher suspended sediment loads, which, in turn, decreased reaeration (Zizon et al.,1978). However, it has been concluded by Holley (1977) that there is significant evidence that the presence of suspended material can significantly change the value of the oxygen transfer coefficient, and most of this evidence points to an increase in K_2 due to the physical presence of suspensions. This has been generally attributed to the fact that the suspended material causes a redistribution of the turbulent energy so that most of the energy occurs in the lower frequency components.

CHAPTER 4

Preliminary Tests

Preliminary laboratory studies were planned in order to verify the existence of a relationship between the reaeration and solids dissolution processes over a range of hydraulic conditions. It was also intended to select the most appropriate methodology for the reaeration and dissolution rates measurement and estimation.

4.1 EXPERIMENTAL EQUIPMENT:

4.1.1 The Annular Channel:

An annular channel made from perspex, with 62.0 cm of outside diameter, 32.0 cm of inside diameter, and 20.0 cm of height, was chosen for the laboratory studies. It provided a wide range of turbulence and mixing by varying the depth and the power of a recirculating pump, and also a recirculation pattern which would not be achieved in the commonly used stirred tanks. The main disadvantage of using such a channel is the totally different hydraulic regime developed when compared with that of a natural stream. As the interest lay not in the hydraulic regime itself, but in the different turbulent scales it can provide, it was thought that the shape and geometry of the flume would not interfere with the main objective of these tests.

The water was circulated by an electrical pump (Totton, model DP 35/3 with maximum flow of 35 l/min). A Zenith voltage variometer, commonly called variac, with a 10-300 Volts range, was used to vary the power of the pump, and consequently control the water velocity within the flume. The complete laboratory equipment used in all tests is shown in Plate 1.

4.1.2 Velocity and Depth Monitoring:

The depth of the water in the annular channel was measured by a point gauge which gave readings to the nearest 1/10 mm. The gauge was moved to four different positions alongside the flume and the computed depth was the average between the four measurements obtained in the middle of the flume width.

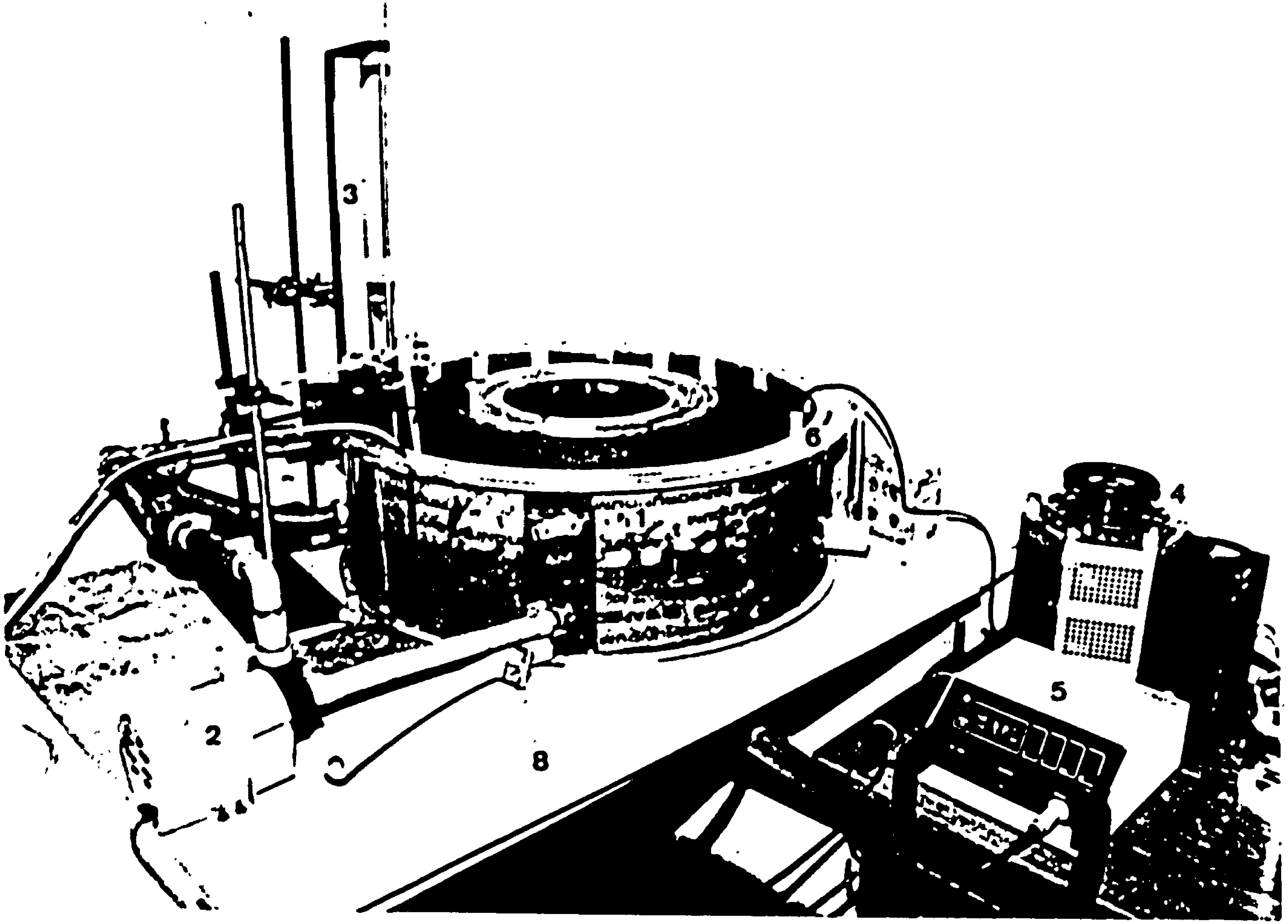
Velocity of flow was measured by a 9 mm current meter (Nixon Instrumentation Ltd., type 403, no.1094) which was also moved alongside four different positions in the channel. In order to ascertain the average velocity in the tank, sixteen point measurements were made at the four different positions, regardless of depth, totalizing 64 points. The average velocity in each of the four cross-sections was determined by computing the arithmetic mean of the 16 point velocity observations, and the average velocity in the flume was similarly determined by computing the mean value of the four different cross-sections.

The velocity range covered in all experiments was from 0.20 m/s to 0.38 m/s, approximately a two fold change in velocity.

4.1.3 Dissolved Oxygen Monitoring:

The dissolved oxygen concentration was measured by two different methods, namely,

(i) an azide modification of the Winkler method, according



1. ANNULAR CHANNEL
2. RECIRCULATING PUMP
3. DEPTH GAUGE
4. VOLTAGE VARIOMETER
5. DO METER
6. DO PROBE
7. THERMOMETER
8. FLOATING SOLUBLE SOLID

PLATE 1: THE EXPERIMENTAL EQUIPMENT

to the procedure described by the Standard Methods (1985);

(ii) the membrane electrode method;

in order to identify the potential errors involved in each method, and devise an accurate procedure for the measurement of DO concentration changes within the experimental system.

Water samples were collected at 30 minutes intervals during a reaeration experiment, by siphoning the water in the tank through a 1/8 inch teflon tubing into 250 ml standard bottles. The water was allowed to overflow for a period of 20 seconds, approximately corresponding to the volume of one bottle. The samples were immediately fixed and the DO concentration determined according to the procedure described in the Standard Methods (1985).

Usually, about 2.5 litres of water, or 10% of a certain water volume in the tank, was removed from it using the sampling procedure described above, during each reaeration test. This removal caused a decrease in depth of about 10% of the original depth, and was considered unacceptable for the sake of the accuracy of the DO measurements. It has thus been decided to follow the procedure described by Rathbun et al.(1978) where make-up water is introduced to keep the depth constant. The added water was saturated with oxygen and a volume of 500 ml was siphoned into the tank after each sample collection. According to Rathbun et al.(1978), the change in DO concentration of the water in the tank as a result of the addition of make-up water is near or less the limit of detectability of the Winkler technique. It has been verified herein that the same applies for the membrane electrode method.

As it will be shown later, the membrane electrode method proved to be at least as accurate as the Winkler technique for the measurement of DO concentration changes in the annular channel, and even more accurate at low DO concentration levels.

The instrument employed in all experiments was a portable digital oxygen meter model 7130 used with an oxygen sensor model 7131, manufactured by Kent Industrial Measurements. It measures two parameters of oxygen (% saturation and concentration) and also temperature in degrees centigrades. The measuring ranges given by the manufacturer are:

(i) oxygen: 0 - 199 % saturation (± 1%)
0 - 19.9 mg/l (± 0.1 mg/l)
(ii) temperature: -5 to +50°C (± 1°C)

The oxygen sensor model 7131 comprised a cylindrical body housing an oxygen sensor capsule (silver/lead galvanic cell) together with two thermistors and a Pt100 temperature probe providing automatic temperature compensation and measurement.

The calibration of the DO meter was made following the procedure recommended by the manufacturers and was as follows:

(i) a solution of 5% sodium sulphite was prepared by mixing 25 g of analytical grade sodium sulphite in 500ml of distilled water;

(ii) the membrane end of the capsule, with either the stirrer attachment or the working shield in place, was immersed in the solution;

(iii) few minutes were allowed for the sensor to stabilise, then using a screwdriver, the SET ZERO control was adjusted on the front panel until the LCD read zero;

(iv) the sensor was removed from the sodium sulphite solution and thoroughly rinsed with distilled water;

(v) meanwhile, the water in the tank was fully aerated as follows:

the pump was switched on and the water was circulated at a certain velocity such that the water surface was continually agitated but without breaking the liquid surface. The water was also aerated through a diffuser block for 15 minutes.

(vi) the sensor was then immersed in the fully aerated water in the tank, making sure that the stainless steel portion containing the temperature associated elements was covered;

(vii) few minutes were allowed for the sensor to stabilise, and then the temperature of the solution was read;

(viii) using a screwdriver, the CALIBRATE control on the front panel was adjusted to read:

(viii.1) oxygen concentration corresponding to the solubility value for the temperature of the air-saturated water used. We referred to the Standard Methods (1985), table 421:I, which uses the values determined by Benson and Krause(1980), to correct for the variation of oxygen solubility with temperature and barometric pressure;

(viii.2) % saturation concentration to the barometric pressure;

the display was set to read the figure calculated by the procedure described in Appendix II of the manufacturer's manual;

(ix) replicate samples of the fully aerated water were collected using the procedure already described and were analysed by the Winkler technique to check the concentration saturation values;

Following the procedure described above, it was found that the percentage difference between the observed and tabled DO concentration values was generally less than 5%. This difference was thought to be due to the inherent errors in analysing a sample by the Winkler technique and considered irrelevant in these studies.

Comparison studies between Winkler and membrane electrode methods have generally indicated that the membrane oxygen method is at least as reliable as the chemical method (see McKeown et al.,1967, Reynolds,1969, Avery,1976 and Wilcock et al.,1981) with the advantage that the time spent in chemical analysis is considerably reduced and that it is easier and less tedious to use.

Although sufficient evidence exists concerning the reliability of the membrane electrode method compared with that of the Winkler technique, it was decided to carry out a comparison study between the two methods in order to select the most appropriate and accurate for the computation of the reaeration rate coefficient.

A typical comparison of indicated and chemically analysed DO levels is shown in Figure 15. It is clearly indicated that the equipment performed accurately over its entire scale range. A straight line with r^2=97.8% was obtained for the forty

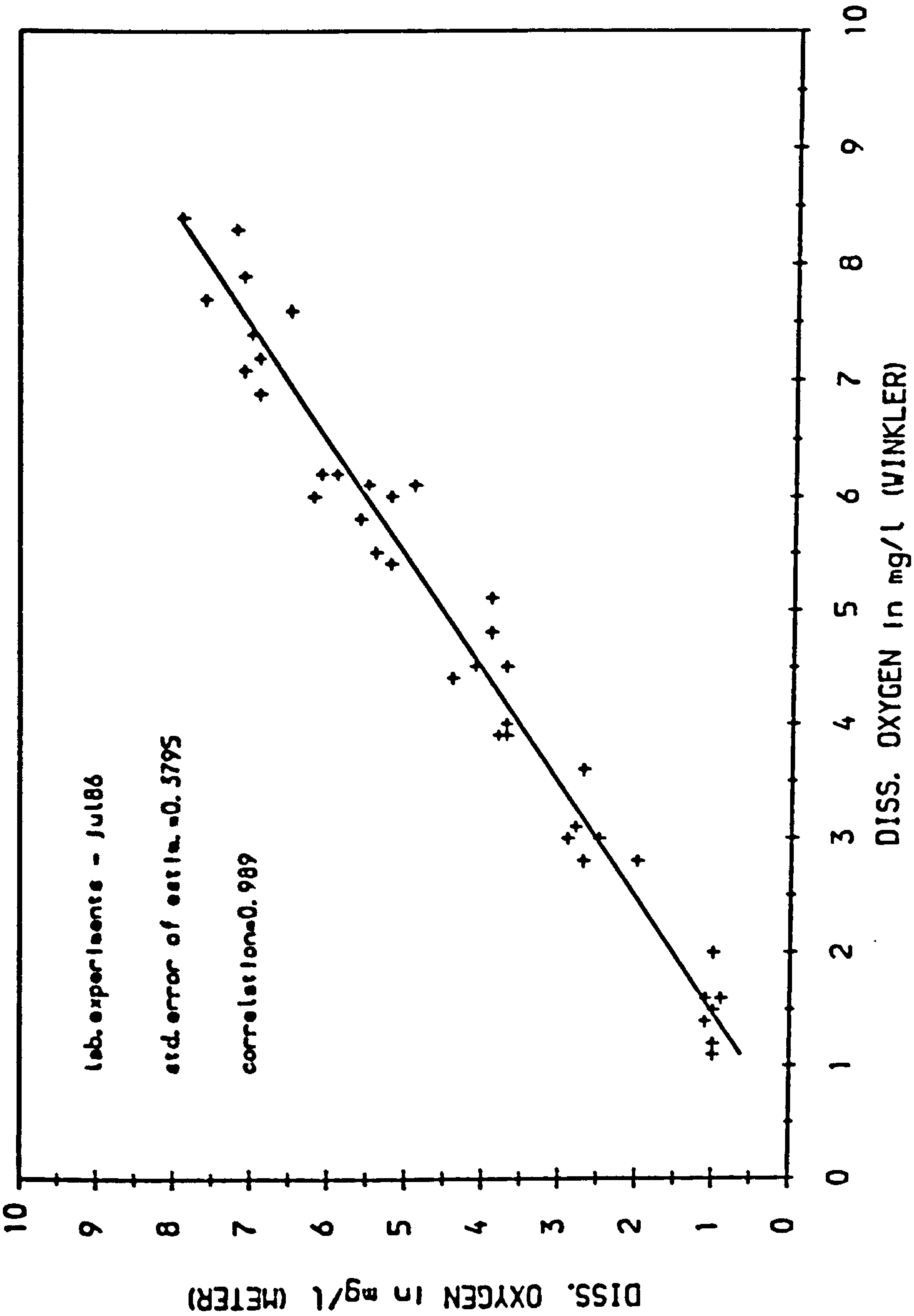


Figure 15: Dissolved oxygen concentration values
DO meter vs. Winkler method

analysed values and there was no evidence against the hypothesis that the straight line coefficient is equal to 1.00 (refer to Appendices A.1 and A.2 for details). It has been also found that the standard deviation between the observed and estimated initial DO concentration measured with the membrane electrode method is almost two times smaller than that measured by the Winkler technique. Another comparison has been made between the estimated reaeration coefficient computed from DO concentrations measured by the DO meter and that computed from DO concentrations determined by the Winkler technique. The standard deviation of the reaeration coefficient measured with the DO meter is about three times smaller than the one obtained from Winkler determinations. It thus appears that the readings given by the DO meter are subjected to less variability than those given by chemical titration. Once the meter has been calibrated, the deviation of the DO levels readings are maintained constant throughout the experiment. In the other hand, the DO concentration values determined by the Winkler technique are subjected to errors in the sampling and titration procedures for each of the samples collected.

Based on the above results, and taking into account the accuracy obtained in each method for the computation of K_2, we chose to express the DO measurements throughout all the experiments using the values given by the membrane electrode method.

4.1.4 The Floating Soluble Solid:

A series of tests have been previously carried out to determine the type of solid to be used and its configuration. Four different chemicals were tested in the annular channel: menthol, salicylic acid, benzoic acid and sodium chloride monocrystals.

The first two, menthol and salicylic acid, have a very low rate of dissolution and were rapidly discarded. Sodium chloride monocrystals had already been used in previous investigations (Shulz,1985 and Giorgetti and Shulz,1986), but their dissolution process was found to be mainly caused by natural convection, which, in this case, proved to be a predominant process at either low or high turbulent conditions (Giorgetti et al.,1986). It has been therefore suggested that a less soluble solid would be more appropriate for future research (Giorgetti,1987;personal communication).

Benzoic acid proved to be a reasonable soluble solid at a temperature range between 5 and 25°C (the most common temperature range found in natural streams), with its dissolution rate being dependent on the degree of water agitation. It is a readily available chemical which has been well studied in mass transfer operations. No major pollution problems are associated with benzoic acid, however dust from handling is capable of cause sneezing and coughing. Its physical and thermodynamic properties are summarised in Table 9.

Benzoic acid (GPR) was cast into a circular metal tin with 6.5 cm of diameter and 0.5 cm of height by compression (100 kN for 1 minute), so that a flat and smooth surface could be obtained. The surface of the organic solid was then carefully smoothed to the same level as the metal tin with a sharp spatula or razor blade. Finally the surface was rubbed with fine sand paper, washed and dried. An alternative method for the benzoic acid casting is to slow melt the solid and then shape it as it gradually cools (Johnson and Huang,1956).

Table 9: Physical and thermodynamic properties of benzoic acid (from McKetta and Cunningham,1977)

Property	Value
Molecular weight	122.12
Melting point (^{o}C)	122.4
Boiling point at 1 atm (^{o}C)	250.0
Specific gravity, 28^{o}/4	1.316
Vapour density (air=1.00)	4.21
Dipole moment	1.7
Index of refraction,^{n}d 131.9^{o}C	1.504
Surface tension at 130^{o}C (dyn/cm)	31 ± 1.3
Heat of fusion (cal/g)	33.9
Heat of combustion (kg.cal)	771.2
Heat of formation,solid (kg.cal/mol)	-93.21
Free energy of formation,solid (kg.cal/mol)	-60.10
Specific heat,from 20^{o}C to melting point (cal/g,^{o}C)	0.287+0.00050t
Cubical expansion coefficient/^{o}C (23.3-122.37^{o}C)	0.00040
Heat of solution in water (at infinite dilution and room temperature) (g.cal/g mol solute)	-6501
Critical temperature (K)	751
Critical volume (cm^{3}/g)	341
Critical pressure (atm)	45.1
Flash point (^{o}C)	121-131
Ignition temperature [^{o}C(in air)]	573
Ionization constant (25^{o}C)	6.339×10^{-5}
Solubility in water at 17.5^{o}C	0.21 parts of benzoic acid in 100 parts of solv.
Toxicity	
Slight effect through ingestion and inhalation	
Oral LD for rabbits is 2 g/kg	
Oral mouse LD_{50}, 2370 mg/kg	
Oral rat LD_{50}, 1700 mg/kg	

The floating device was designed to bear the circular metal tin with benzoic acid in its bottom and was made from polystyrene. The floating soluble solids are shown in Plate 2. One of the problems of this kind of floaters is that they can interfere with the turbulence characteristics in the neighbourhood of the solids' extremes (refer to Figure 16 below). The central part of the solids' flat surface however, where most of the dissolution process takes place, does not appear to be affected by a non-characteristic fluid movement. In fact, as it has been later verified, this was a minor problem which did not have much relevance on the problem of solids' dissolution.

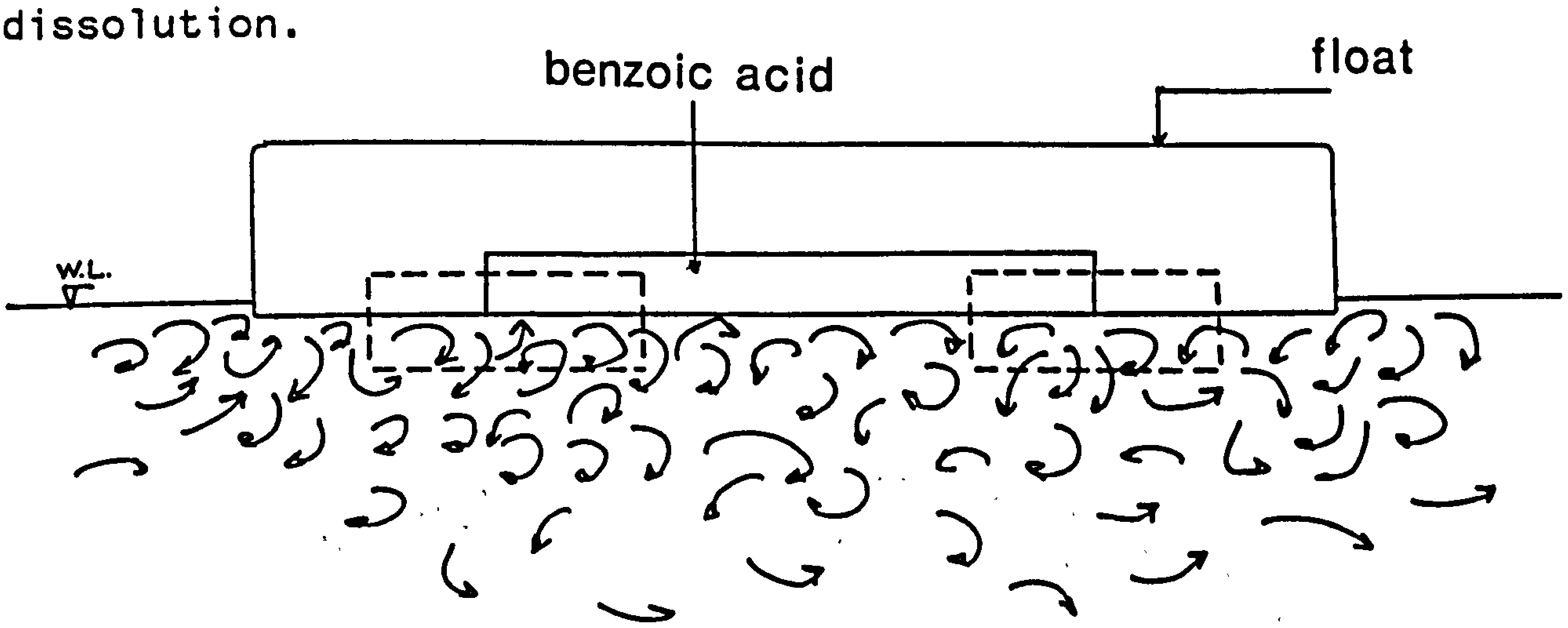


Figure 16: Fluid movement on the surface of the floating soluble solid

Different solids and different floaters have been used in all sort of combinations (randomly chosen), making it possible to observe that the rate of dissolution did not change significantly when replicates of samples and tests were performed. The floaters' shape was therefore considered satisfactory for our purposes.

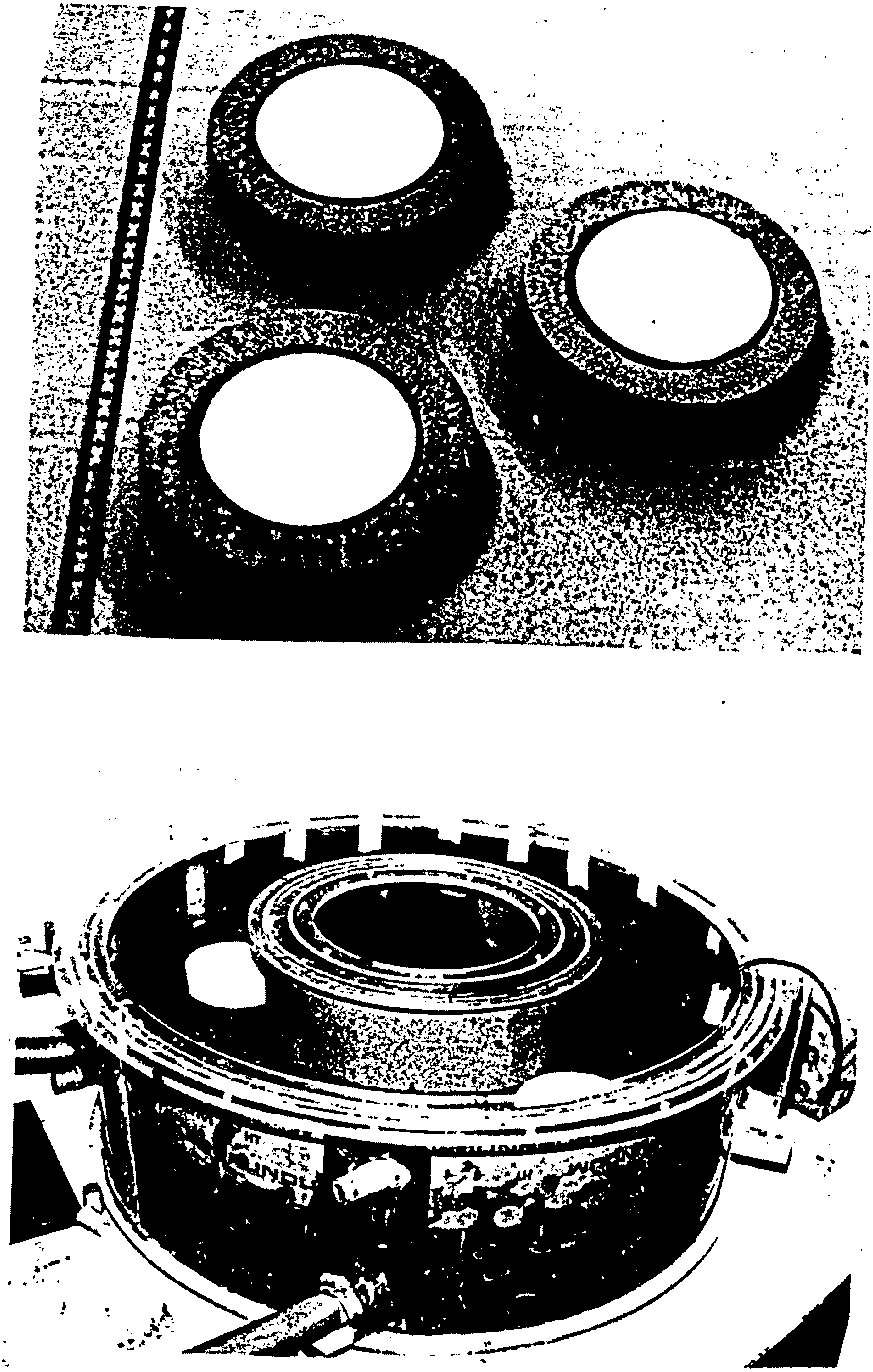


PLATE 2: FLOATING SOLUBLE SOLIDS

4.2 EXPERIMENTAL PROCEDURE:

A total of twelve tests were carried out in order to verify the existence of a relationship between the velocity of benzoic acid dissolution and the rate of oxygen absorption into the water by the simulation of different hydraulic conditions and different scales of turbulence.

The annular channel was used in all experiments, and a set of twelve different hydraulic conditions was established by the combination of four different depth levels (14.0, 12.4, 10.0 and 8.0 cm) with three different velocities of flow (high, medium and low). For each of the 12 tests, the reaeration and velocity of benzoic acid dissolution were measured according to the procedures described below.

4.2.1 General Procedure:

The following general procedure was employed in conducting all 12 tests mentioned above:

(i) the annular channel was filled with tap water to the desired depth (14.0, 12.3, 10.0 and 8.0 cm) and was allowed to stand quiescent overnight;

(ii) the recirculating pump was turned on, the system was brought to the desired velocity level (high, low or medium) and allowed to equilibrate for approximately 10 minutes;

(iii) the depth of the water was measured as already described to check correct the depth;

(iv) the velocity of water was measured as already described;

(v) the flowing water was then stripped with nitrogen gas until a concentration of about 1.0 mg/l was indicated by the DO meter;

(vi) temperature, barometric pressure and DO concentrations were then monitored (by both Winkler and membrane electrode methods) at regular time intervals (10, 30 and 60 minutes) until the system was at or near the DO saturation value;

(vii) previously weighed solids were, simultaneously with the reaeration test, exposed to the flowing water and left circulating for six different lengths of time (15, 30, 45, 60, 75 and 90 minutes);

(viii) the solids were then left drying overnight at constant temperature (20^{o}C) and weighed again (to the nearest 1/1000 g) in the following morning in an analytical balance with 0.0001g of precision;

(ix) reaeration and velocity of solids dissolution could then be computed according to the procedures described in the next two sections;

4.2.2 Reaeration Measurement:

It has been widely recognised that the estimation of oxygen transfer rates is not an easy task, mainly where accuracy is concerned. Although the test is straight forward, the validity of the results is strongly influenced by the experimental procedures and the techniques employed in analysing the test data (Brown and Baillod,1982).

The reaeration coefficient and the equilibrium dissolved oxygen concentration are usually estimated by fitting the concentration versus time data to the following first order reaction model:

$$\frac{dC}{dt} = K_2 (C_s - C) \qquad (110)$$

where C is the DO concentration, C_s is the saturation DO concentration, K_2 is the reaeration rate coefficient and t is the time.

According to Brown and Baillod (1982), there are three immediate areas of concern when one is faced with the problem of fitting a mathematical model to a given set of data. The first is whether the proposed equation correctly model the system under study. The second is how to select the best estimates of the parameters in the proposed model, and the third is to determine the precision of the computed parameter estimates. A discussion of these question in the context of the analysis of unsteady state oxygen transfer data can be found in either Baillod (1979) or Brown (1979).

The parameter estimation problem is solved by choosing values for the unknown parameters in the model so that the values calculated using these parameter values agree as closely as possible with the experimentally observed data. This is usually quantified by the residual sum of squares S, defined as:

$$S = \sum_{i=1}^{n} \frac{1}{\sigma_i^2} (Y_{obs,i} - Y_{calc,i})^2 = \text{minimum} \qquad (111)$$

where $Y_{obs,i}$ is the i-th experimental observation corresponding to the time of observation t_i, $Y_{calc,i}$ is the response value calculated from the model at time t_i using the estimated parameter values, and σ_i^2 is the variance of the i-th observation due to experimental error.

To use the above equation and fit experimental data, the correct model must be specified. Indication of which of the model parameters are to be estimated and the relative precision of the data must also be given. The important characteristic of the model is whether it is linear or non-linear with respect to the parameters to be estimated. The important quality of the data is whether or not the experimental errors are equal or unequal for the observations (Boyle et al.,1974). In other words, the form of the model and the error structure of the data together determine the appropriate method of data analysis.

There are three basic approaches for the estimation of K_2 from the data and equation (110), namely the differential method, the log-deficit method and the exponential method. A general review of these procedures has been published by Brown (1979), Stenstrom et al.(1981) and also by Brown and Baillod (1982). They will be briefly summarised below:

(i) The differential or direct method:

the derivative is directly calculated from the data and equation (110) is rearranged in order to use simple linear regression to estimate K_2 and C_s.

(ii) The log-deficit method:

Equation (110) is integrated and rearranged in the following logarithmic form:

$$\ln(C_s - C) = -K_2t + \ln(C_s - C_0) \qquad (112)$$

in which C_0 is the DO concentration when t=0. The reaeration rate coefficient is then estimated using simple linear regression analysis if C_s is known. Estimates of C_s are found in a standard table as given by the Standard Methods (1985). Several variations of the log-deficit or log-transformation method have been described by Brown and Baillod (1982) and they are generally related to the selection of C_s values and to the degree of data truncation practiced.

(iii) The exponential method:

Equation (110) is integrated and rearranged in the following exponential form:

$$C = C_s - (C_s - C_0) \exp(-K_2 t) \qquad (113)$$

the reaeration rate coefficient is estimated by a non-linear least squares procedure. The search is done numerically and efficient algorithms have been developed to bring the computations within the capabilities of everyone (Press et al., 1986).

Table 10 summarises the data analysis techniques for non-steady state oxygen transfer tests, while Table 11 gives the precision of parameter estimates between exponential, log-deficit and direct methods. Figure 17 shows the residuals for parameter estimation using a typical untruncated data set.

The advantages and disadvantages of each method have been described by Boyle et al.(1974), Brown (1979), Stenstrom et al.(1981) and Brown and Baillod (1982). The consensus of most investigators is that the non-linear least squares regression method using equation (113) is the most desirable of all methods with the best fit log-deficit method coming next.

Table 10: Summary of data analysis techniques
Non-steady state oxygen transfer tests (from Brown,1979)

Method	Equation	C_s	Truncation	Error Structure	Remarks
Surface Saturation	112	surface saturation	usually	biased	K_2 sensitive to assumed C_s
Corrected Saturation	112	mid-depth effective depth	usually	OK except as $C \longrightarrow C_s$	K_2 sensitive to assumed C_s
Measured Saturation	112	from data	only if data are noisy	OK except as $C \longrightarrow C_s$	C_s and K_2 det. from data
Trial and Error	112	trial and error	usually	OK except as $C \longrightarrow C_s$	C_s and K_2 det. from data
Direct Method	110	estimated in analysis	usually	errors increase as $C/\Delta t$ increases	magnifies noise in data
Exponential Method	113	estimated in analysis	no	errors decrease as C increases	C_0, C_s and K_2 det. from data
Time Constant	113	from data	yes	?	limited use,data sensitive to C_0

Table 11: Precision of parameter estimates between exponential, log-deficit and direct methods (Brown,1979)

Method	K_2 (per hour)	Std.error (%)	C_s (mg/l)	Std.error (%)	Dependent Variable
exponential	12.05	0.9	10.39	0.1	C
exp.(weighted)	11.99	0.8	10.39	0.1	C^2
log-deficit	12.11	2.1	10.39	0.0	$\ln(C_s - C)$
direct	12.50	4.0	10.35	0.9	C/ t
direct(weighted)	10.55	9.0	10.32	0.4	ln(C/ t)
TRUNCATED DATA (96% of C_s)					
exponential	12.13	1.9	10.37	0.5	C
exp.(weighted)	12.02	1.7	10.38	0.3	C^2
log-deficit	12.13	0.4	10.39	0.0	$\ln(C_s - C)$
direct	12.67	6.6	10.29	2.0	C/ t
direct(weighted)	11.98	5.3	10.38	0.5	ln(C/ t)

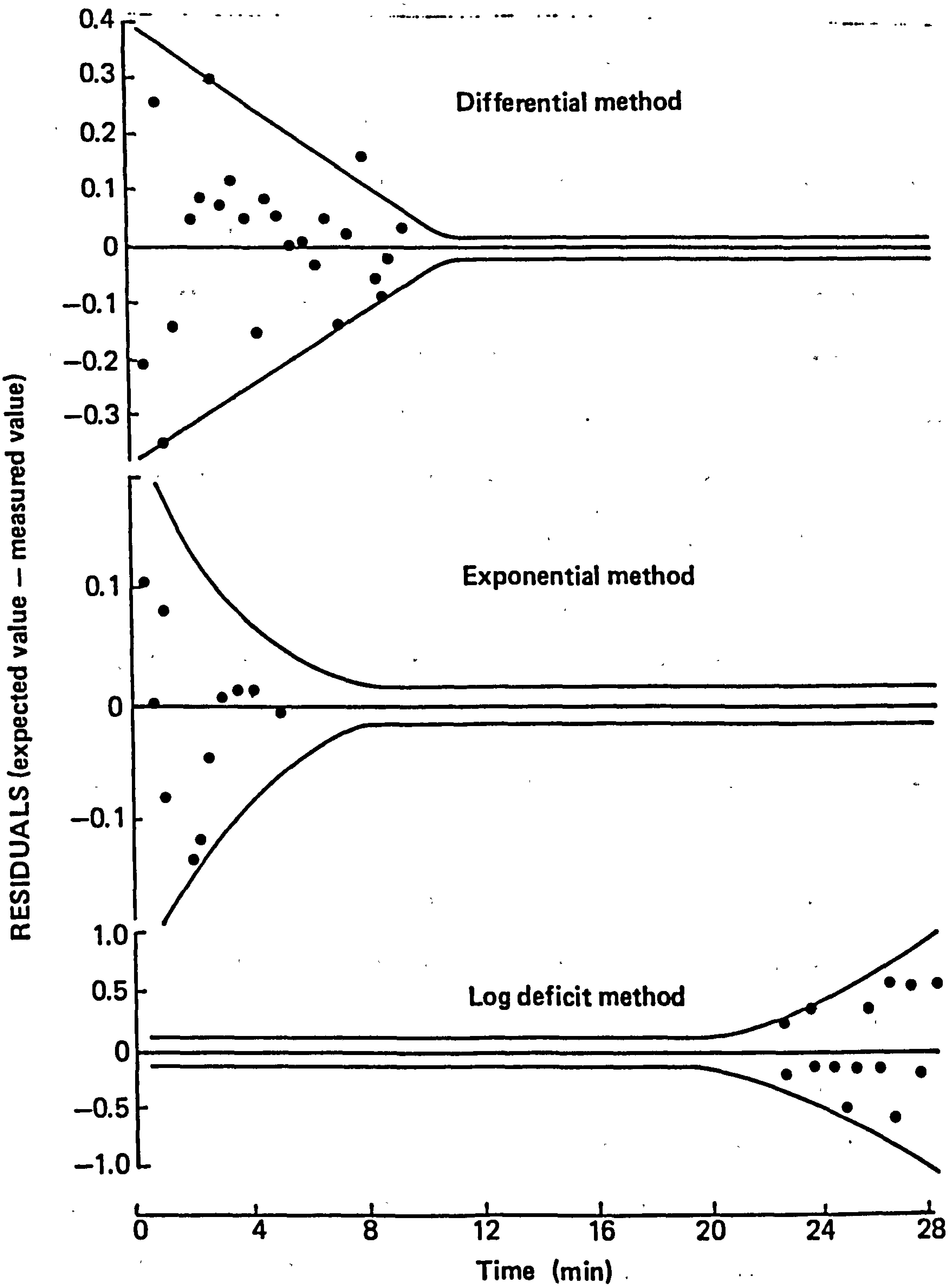


Figure 17: Residuals for parameter estimation using a typical untruncated data set (from Stenstrom,1984)

It has been also recommended that unsteady state oxygen transfer tests be conducted for as long a period of time as practible. A minimum period of time approximately corresponding to a dissolved oxygen concentration of 98% of C_s is suggested. Regression analysis should be based on a minimum of 10 to 15 data values, with approximately 2/3 of these values evenly distributed over the period of time covered by zero to $2/K_2$. The remaining 1/3 of the values should be evenly distributed over the period of time covered by $2/K_2$ to $4/K_2$. Temperature and barometric pressure should be measured at the beginning and end of each test, as a minimum (Brown and Baillod,1982).

Although equation (113) was found to adequately describe unsteady state oxygen transfer data from a great variety of aeration devices, model inadequacy can be manifested during the early portion of the test. In this case, the precision of the least squares estimate of C_0 and a plot of the residuals versus time can give useful information about model adequacy. The problem can be overcome by choosing the best possible estimate for the parameters in the non-linear least squares algorithm in order to assure convergence. If the same estimates for several different sets of initial values of the parameters estimates are obtained, it can be generally assumed that the global optimum has been obtained (see Stenstrom et al.,1981 for more details).

In the event that both residual and error analysis indicate that the model is clearly inadequate, a more refined mechanistic model may be investigated (e.g. Brown,1970 and Giorgetti and Shulz,1986) and/or a more severe data truncation may be applied in order to produce a better fit of the model to the data in the region of greatest interest.

Although it has been generally agreed that the non-linear least squares (NLLS) method applied to equation (113) gives the most accurate parameter estimation, it has not yet been agreed that C_s should be actually used as a variable in this procedure (Rathbun,1981). It was claimed by Rathbun et al.(1980) that the procedure which makes use of a table value for C_s is much more scientific than the procedure of arbitrarily adjust the saturation concentration to give the best straight line on a $\ln(C_s-C)$ versus time plot, as it has been generally proposed (Tsivoglou,1979, Baillod,1979, Brown,1979, Brown and Stenstrom,1980 and Brown and Baillod,1982 among others). Rathbun's et al.(1980) arguments are based on the fact that there has been a number of very careful determinations of C_s in both fresh and sea waters which have been originally summarised by Montgomery (1969). The additional studies of Murray and Riley (1969), Weiss (1970) and more recently, Benson and Krause (1980) and Mortimer (1981), show that the saturation concentration of oxygen in distilled and fresh waters has been accurately determined and that there is no reason for it to vary.

It has been therefore decided to first identify the model which would best describe the process of reaeration and then find the best method to compute K_2.

For this purpose, a set of three experiments have been carried out in order to verify if there was any oxygen losses in the system. The experimental procedure was as follows:

(i) the annular channel was completely filled with distilled water;

(ii) the water was saturated with air:

(iii) the water surface was then totally covered with cling film and care was taken to avoid the formation of bubbles in the system;

(iv) the channel was then covered with its original perspex cover to assure complete closeness of the system;

(v) the pump was switched on so that a velocity of about 0.2 m/s was maintained within the channel:

(vi) the DO concentration values, temperature and barometric pressure were monitored at regular intervals;

If no oxygen losses were verified within the system, as it was the case, a first order reaction model would be sufficient to explain the process of reaeration (equation 110). In fact, as it is shown in Figure 18, the first order reaction model appears to accurately represent the phenomenon. Results of the three deaeration tests (Appendices A.3) show that there is no significant loss of oxygen within the experimental system and that the percentage variation of the DO concentration values, for all three tests, is about 2% and due to the increase in the water temperature observed during the tests.

For the second part, it was decided to carry out a similar comparison to that made by Rathbun et al.(1978) between three commonly used methods for the reaeration rate parameter estimation, namely:

(i) the log-deficit or logarithmic transformation method (LT)

(ii) two-parameter non-linear least squares method (NLLS2),

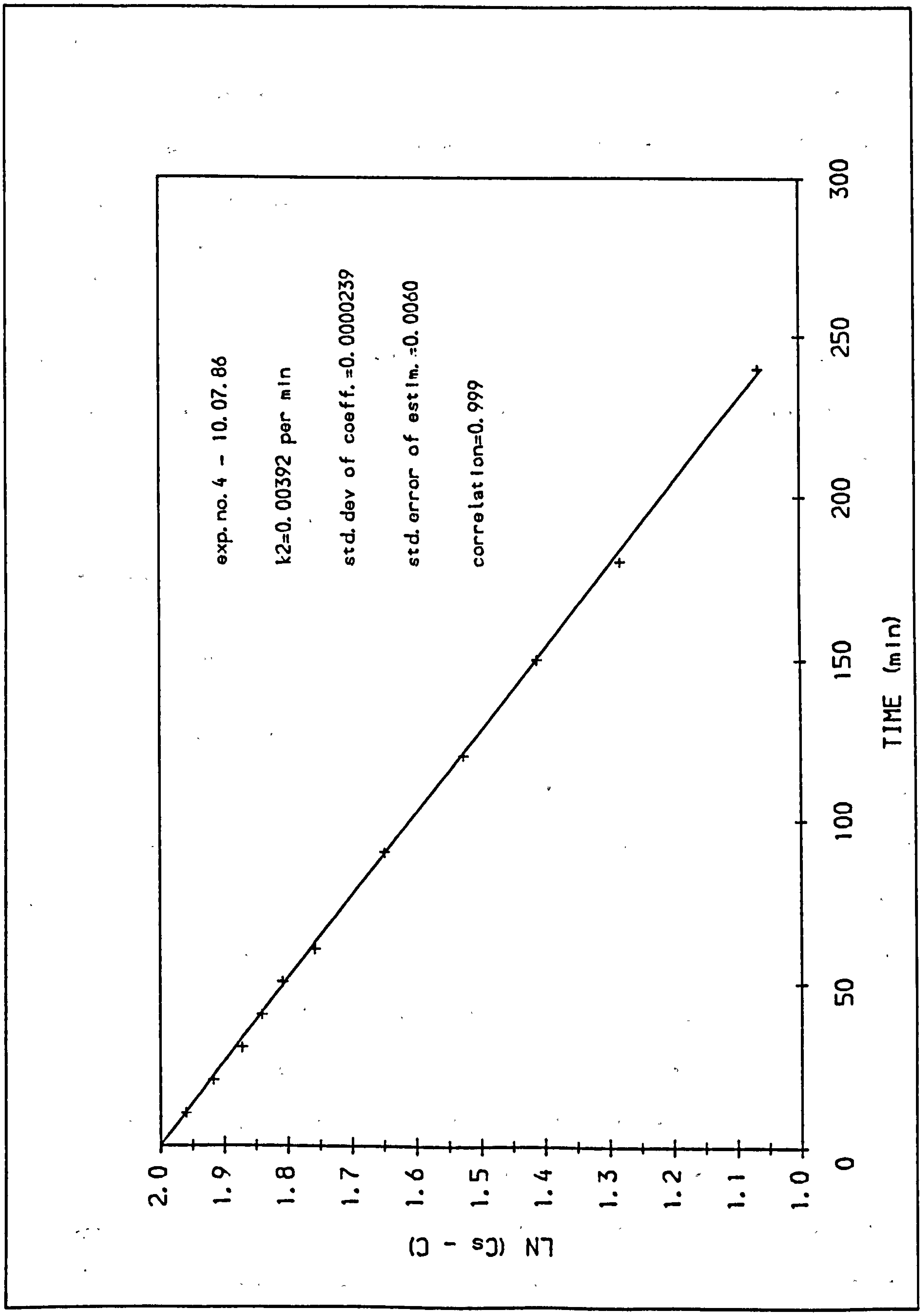


Figure 18: Typical reaeration experiment
(C and C_s are in mg/l)

in which C_s is determined from Table 421:I (Standard Methods, 1985);

(iii) three-parameter non-linear least squares method (NLLS3)

The three procedures were compared in terms of a root mean square error defined as:

$$\text{error} = \frac{[\Sigma(C_e - C_o)^2]^{1/2}}{n} \qquad (114)$$

where C_e is the estimated value of the DO concentration, C_o is the experimentally observed value of the DO concentration and n is the number of observations. The percentage differences between the LT and NLLS methods were also computed for K_2, C_s, C_0 and the error, defined by Rathbun et al.(1978) as:

$$\%\ \text{difference} = \frac{\text{NLLS} - \text{LT}}{\text{LT}} \times 100 \qquad (115)$$

The range of the percentage differences for the two comparisons (LT vs. NLLS2 and LT vs. NLLS3) for the above mentioned parameters and the average error in the DO concentration values are presented in Table 12. Consideration of the results shows that there is a considerable difference between the reaeration coefficient estimated by the LT method and the one estimated by the NLLS procedure, either two or three parameter estimation. A great difference is also verified for the initial concentration estimated by the LT and NLLS2. The percentage difference of the errors is always negative for the twelve runs considered, demonstrating a tendency for the LT procedure to over predict the estimated values at about 50% in relation to the NLLS2 procedure and about 70% in relation to the

NLLS3 procedure. Therefore, in going from the LT to the NLLS3 procedure, the average error is a lot more reduced than going from the LT procedure to the NLLS2 procedure. As it has been pointed out by Rathbun (1981), the best statistical fit of the data is obtained considering C_s as a variable, but this occurs only because there are three fitting parameters rather than two. However, as it has been observed in these experiments and on those reported by Rathbun et al.(1978), the NLLS3 estimates for the oxygen saturation concentration varied from 6.9 to 9.8 mg/l, being many of the values completely unrealistic for the specific conditions of the experiments.

Table 12: Log transformation versus non-linear least squares procedures for parameter estimation

Parameter	Range of percentage differences	
	LT vs. NLLS2	LT vs. NLLS3
K_2	from -27.07 to 20.0	from -26.19 to 88.72
C_0	from -8.56 to 56.33	from -6.00 to 12.42
C_s	——	from -13.73 to 14.69
Error	from -73.9 to -23.4 with average=-51.27	from -89.7 to -34.29 with average=-68.46

Root mean square error		
LT	NLLS2	NLLS3
0.069	0.027	0.013

Based on 41 unsteady-state oxygen transfer experiments, Rathbun et al.(1978) concluded that although the NLLS3 procedure qave the best fit to the data in terms of the root mean square error defined by equation (114), it was in essence a curve fitting process with little consideration of the physical process involved.

The above statement appears to be confirmed by the analysis of the twelve oxygen transfer experiments now carried out. The two-parameter NLLS procedure, with fixed C_s value given by the Standard Methods (1985), has then been chosen for the computation of the reaeration rate coefficient in all experiments herein reported.

The following procedure has thus been selected for the measurement and computation of the reaeration rate coefficient:

(i) collection of 12 data points (DO vs. time) as described by the general procedure and in accord to the recommendations made by Brown (1979) and Brown and Baillod (1982);

(ii) selection of a DO saturation concentration value from Table 421:I of Standard Methods (1985);

(iii) use of a non-linear least squares analysis of the exponential form of the reaeration equation using BMDP Statistical Software (Dixon,1983);

The BMDP Statistical Software estimates the parameters by an iterative algorithm and at each iteration it prints the residual sum of squares and the estimates of the parameters. Once parameter estimates are determined, the program prints estimates of the asymptotic standard deviation of the parameter estimates, and of the correlations between them. The residuals, predicted and observed values of all variables are listed. Plots of the residuals and predicted values against relevant variables as well as normal probability plots of residuals are also printed.

4.2.3 Velocity of Solids Dissolution Measurement:

When studying a solid-liquid system, in particular the rate at which a solid dissolves and is distributed in a liquid under agitation, one has to consider the following factors, as they were originally described by Hixson and Crowell (1931):

(i) Factors concerning the solid, i.e. the rate at which a given mass of a solid dissolves in a liquid depends on:

(i.1) specific surface of the particles of the solid or their average surface per unit weight;

(i.2) uniformity of distribution in size throughout the particles;

(i.3) solubility of the solid for a given liquid;

(i.4) shape and homogeneity characteristics of the particles;

(i.5) diffusion coefficient of the solid for a given liquid;

(i.6) incipient fractures, dust, gas films, agglomerates, density currents and convection streams;

(ii) Factors concerning the liquid:

(ii.1) the agitation of the liquid in contact with the surface of the solid; regardless of whether or not there is a skin layer of slow-moving or stationary liquid immediately adjacent to the solid surface, the agitation of the liquid which is next to this layer or to the surface is the most important factor in the rate of solution of the solid;

(ii.2) temperature; it changes the solubility and increases the actual velocity of reaction through its kinetic influence; it is also important to consider the temperature gradient in relation to the solids solubility (see Table 13)

Table 13: Solubilities of benzoic acid in water at various temperatures (Kirk and Othmer,1978)

Temperature (°C)	Solubility (g/100g water)	Temperature (°C)	Solubility (g/100g water)
0	0.17	50	0.85
10	0.21	60	1.20
20	0.29	70	1.77
25	0.34	80	2.75
30	0.42	90	4.55
40	0.60	95	6.80

(ii.3) the concentration of the dissolved solid already in solution;

(ii.4) the viscosity of the liquid;

(iii) Factors concerning both the solid and the liquid:

(iii.1) the chemical nature of the two;

(iii.2) the relative density relationships;

(iii.3) the proportion of solid and solvent;

(iv) Factors concerning the distribution of the solid in the bulk of the liquid:

(iv.1) the average intensity of agitation of the liquid bulk may be high or low compared to that of the liquid in immediate contact with the surface of the solid;

(iv.2) the uniformity of agitation throughout the liquid also affects the rate at which the thoroughness of distribution is obtained;

(v) Specific factors affecting agitation itself:

(v.1) type of generating motion;

(v.2) shape of container;

(v.3) total volume of the system;

(v.4) generating forces;

(v.5) regimes under different intensities;

(v.6) dynamical similarity;

The well known law concerning the rate at which a dissolved substance diffuses in solution was enunciated by Fick in 1855, and is given by:

$$\frac{\partial c}{\partial t} = -D_m A \frac{\partial c}{\partial y} \tag{116}$$

It states that the coefficient of diffusion D_m is the amount of solute which will cross one square centimetre of cross section A in one unit of time if the change in concentration per centimetre in a direction perpendicular to this cross section is unity. All other motions except that of molecular agitation itself are excluded, and the system is kept at constant temperature and absolutely still.

Noyes and Whitney (cited by Hixson and Crowell,1931) derived a law concerning the rate at which solids dissolve in their own solutions. The rate of concentration change is at any instant directly proportional to the difference between the concentration of a saturated solution, C_s, and the concentration C, existing in the solution at this instant, or in other terms:

$$\frac{dC}{dt} = K_s\ (C_s - C) \tag{117}$$

The action was explained on the assumption that a very thin layer of saturated solution was formed at the surface of the solid, and that the rate at which the solid dissolved was governed by the rate of diffusion from this saturated layer into the main body of the solution. This law, without any assumptions regarding the mechanism by which the process takes place has been quite generally substantiated by experiments.

The Nernst-Brunner theory, subsequently developed, concerning the rate of solution of solids in agitated liquids, assumed the existence of a stagnant film at the interface between the two phases, across which material was transported by molecular diffusion only. It was postulated that at the boundary surface of the different phases the equilibrium is set up at a practically instantaneous velocity compared with the rate of diffusion, so that the velocity of a heterogeneous reaction was determined by the velocities of the diffusion processes that accompanied it.

However, the theory as outlined by Nernst has been criticised and is recognised as an over simplification of the mechanism of mass transfer process at the solid-liquid interface. It has since been demonstrated that the entire resistance to mass transfer does not necessarily lie within this laminar layer in streamline motion. A large part of the resistance may be in the eddy zone of the turbulent stream.

Whether the velocity of the chemical reaction or the rate of diffusion determines the rate of the combined processes of transformation of the solid into its dissolved and distributed products, the three outstanding factors are concentration, surface area and agitation. It was based on these ideas that Hixson and Crowell (1931) developed a quantitative method for the evaluation of the mass transfer coefficient on the assumption that the surface area of the solid particles was proportional to the two-thirds power of the volume or the weight of dissolving solids.

In an extension of Hixson and Crowell studies, Hixson and Baum (1941) proposed an approximate equation for the mass transfer coefficient with the simplified assumption that the total area of the surfaces of the suspended solids was constant and that the change in concentration as the dissolution proceeded was small. The average concentration driving force can then be expressed by logarithmic means as follows:

$$W_0 - W = K_s A_m (C_s - C)_m t \tag{118}$$

where W_0 is the initial weight of the solid at time t=0, W is the weight of solid after a time t, K_s is the solids dissolution coefficient, A_m is the surface area between the solid and liquid phases and $(C_s-C)_m$ is the log mean of the concentration change. The experimental results obtained employing the above model were correlated by a similar equation to that used by Gilliland and Sherwood (1934):

$$\left[\frac{kl}{D_m}\right] = K \left[\frac{\mu}{\rho D_m}\right]^a \left[\frac{Rd^2 \rho}{\mu}\right]^b \tag{119}$$

where k is the mass transfer coefficient, l is the diameter of the mixing tank, D_m is the molecular diffusivity, μ is the liquid's viscosity, ρ is the liquid's density, d is the diameter of the impeller, R is the stirring speed, K is a proportionality constant, a is the exponent of the Schmidt number and b is the exponent of the Reynolds number.

Gilliland and Sherwood (1934) found a and b to be 0.44 and 0.83 respectively. Hixson and Baum (1941) found these exponents to be 0.50 and $0.62 < b < 1.40$, while Johnson and Huang (1956) gave $0.422 < a < 0.526$ and $0.596 < b < 0.948$, leading to the conclusion that the Danckwerts' surface renewal theory, developed for a gas-liquid system, can also be extended to a solid-liquid system (the mass transfer coefficient is proportional to the square root of D_m). The surface renewal theory may be pictured as applying to a solid-liquid interface by the following postulation (Johnson and Huang,1956):

> "A thin layer of saturated concentration is assumed to exist at the interface. The controlling mass transfer process between solid and liquid is pictured as that between the saturated liquid layer and liquid phase, where turbulence is assumed to reach the surface of the saturated layer."

It was based on the above theories and on the development of the floating soluble solid technique reported by Shulz (1985), Giansanti and Giorgetti (1986), Giorgetti and Shulz(1986) and Giorgetti et al.(1986), that a dissolution model has been derived under the following assumptions:

(i) the process of dissolution takes place normal to the surface and the effect of agitation of liquid against all parts of the surface is essentially the same;

(ii) the solid shape is predominantly cylindrical with the ratio between the height and base area being approximately equal to 0.004, i.e. the surface area of the solid can be approximated by the base area for calculation effects;

(iii) the change in concentration is so small that the average concentration driving force can be expressed by the difference between the solid weights;

(iv) the velocity of solids dissolution is constant throughout the surface area of the solid;

Therefore, if we consider a linear dimension x of the solid being dissolved along a time t, then:

$$x = x(t) \longrightarrow dx = V_s.dt \quad (120)$$

$$dW = \rho.A_s.dx = \rho.A_s.V_s.dt \quad (121)$$

$$W_0 - W = \int_0^t dW = \int_0^t \rho.A_s.V_s.dt \quad (122)$$

Integration of equation (122) leads to the final form of the dissolution model which is given by:

$$W_0 - W = \rho.A_s.V_s.t \quad (123)$$

where W_0 is the initial weight of the solid at time t=0, W is the weight of the solid after a time of exposure t, ρ is the specific weight of the solid, A_s is the surface area of the solid given by πr^2, V_s is the velocity of solids dissolution and t is the time of exposure.

The velocity of solids dissolution can be viewed as a coefficient which is the resultant rate of the combined processes of transformation of the solid into its dissolved and distributed products, without any assumptions regarding the mechanism by which the process takes place.

Benzoic acid dissolves into the water and simultaneously react with it (ionic dissociation) according to the following chemical reactions:

$$C_6H_5COOH \text{ (solid)} \longrightarrow C_6H_5COOH \text{ (in solution)} \quad (124)$$

$$C_6H_5COOH \text{ (in solution)} \longrightarrow C_6H_5COO^- + H^+ \quad (125)$$

The equilibrium constants are given as follows:

$$K_{a1} = \frac{[BzOH]_l}{[BzOH]_s} \quad \text{and} \quad K_{a2} = \frac{[BzO^-]\,[H^+]}{[BzOH]_l} \qquad (126)$$

The dissociation of benzoic acid into water is a very slow reaction ($K_{a2}=4\times10^{-5}$) and the dissolution process appears to be ruled by equation (124). It is well known that the mass transport can be increased if the substance transported into another phase reacts there chemically, but a chemical reaction can be slowed down by a mass transfer resistance with the transport rate being lower than the conversion rate.

Of the many theories proposed to study the effect of a simultaneous reaction on the rate of absorption of a solute into a chemically reactive liquid, the most cited ones are: Lewis and Whitman's film theory, Higbie's penetration theory and Danckwerts' surface renewal theory. It has been shown by Levenspiel (1972) that in many cases the two-film, penetration and surface renewal models, although very different in the physical point of view, lead to almost the same quantitative predictions. The choice of a model on which to base the predictions is therefore mainly a matter of convenience, and for that reason the film theory is preferred.

During homogeneous reactions the chemical conversion occurs at all places where the reactants are present. The reaction rate term has to be included and the process is mathematically represented by:

$$D_m \left(\frac{d^2c}{dy^2}\right) + R' = 0 \qquad (127)$$

where R' is the reaction rate term defined as (for a n-th order reaction):

$$R' = -k_r\ C^n \tag{128}$$

Since the transported substance is converted at all places, the concentration gradient is increased and a sufficiently fast reaction will therefore increase mass transfer.

During heterogeneous reactions, diffusion and reaction are separated. The reaction occurs at a reaction interface only and the mass transfer coefficient is not influenced by the chemical reaction. We will restrict ourselves to the case of irreversible first order heterogeneous reaction and assume that the bulk of the liquid is well mixed and that all mass transfer resistance is localised in a thin boundary layer of thickness δ_c (i.e. assume a two-film model). Two parameters can then be defined as follows:

(i) the Hatta number, which is given by:

$$Ha = \sqrt{(D_m . k_r / k_L^2)} \tag{129}$$

It represents the ratio between the mass transfer coefficients with and without chemical reaction and also the ratio between the thickness of the boundary layer and the penetration layer δ_r of the concentration distribution with chemical reaction.

(i.1) if Ha >> 1, we have a very fast reaction occurring within the boundary layer;

(i.2) if Ha << 1, the reaction is very slow and only a negligible part of the reaction occurs in the boundary layer;

The Hatta number is therefore the criterion for whether the reaction occurs completely in the bulk of the liquid (Ha < 0.3, for practical purposes) or completely in the boundary layer

(Ha > 0.3, for practical purposes).

(ii) the rate of physical absorption is increased by a factor

$$F_c = \sqrt{(1 + Ha^2)} \qquad (130)$$

which is universally applicable, i.e. valid under all flow conditions;

In the case of mass transfer with heterogeneous chemical reaction, the chemical enhancement factor F_c is unity, and the rate of conversion (mass flux) is in all cases given by:

$$\varnothing_a'' = k_a\,(C_{a\infty} - C_{ai}) = k_a C_{a\infty}\,[1 - (C_{ai}/C_{a\infty})] \qquad (131)$$

Considering the case of a first order reaction, the above equation can be rewritten as:

$$\varnothing_a'' = k_a\,(C_{a\infty} - C_{ai}) = -R_a = k_r' C_{ai} \qquad (132)$$

where the reaction rate constant k_r' is related to the outer size of the interface (macroscopic reaction rate constant) with dimension [L/T]. It is related to the chemical reaction rate constant k_r $[T^{-1}]$ by the specific interface area a $[L^2/L^3]$ as follows:

$$k_r = a.k_r' \qquad (133)$$

Substituting the above equation into equation (132), the ratio $C_{ai}/C_{a\infty}$ can be calculated as:

$$\frac{C_{ai}}{C_{a\infty}} = \frac{k_a}{k_r' + k_a} = \frac{1}{1 + \dfrac{k_r'}{k_a}} \qquad (134)$$

and the overall conversion rate is therefore given by:

$$\varnothing_a'' = k_a C_{a\infty}\left(\frac{1}{1 + \dfrac{k_a}{k_r'}}\right) \qquad (135)$$

Three principal situations can then be distinguished as follows:

(i) $k_r' \ll k_a$, $C_{ai} = C_{a\infty}$, $\o_a'' = k_r' C_{a\infty}$ (136)

the reaction is so slow compared with the mass transfer process that mass transfer does not decrease the reaction rate and the concentration of A is uniform and equals to $C_{a\infty}$;

(ii) $k_r' \gg k_a$, $C_{ai} = 0$, $\o_a'' = k_a C_{a\infty}$ (137)

the reaction is so fast that the concentration of A at the interface is practically zero and physical mass transport determines the overall reaction rate;

(iii) $k_r' = k_a$, $0 < C_{ai} < C_{a\infty}$, $\o_a''$ given by (135) (138)

both chemical reaction and mass transfer determine the overall conversion rate;

From previous studies of the dissolution of solids into the water surface (refer to Giorgetti and collaborators), and also from preliminary tests carried out with benzoic acid floating on the water surface, it has been concluded that the resultant overall velocity of solids dissolution increases as agitation increases.

It then appears reasonable to conclude that if the chemical reaction is fast compared to the rate of diffusion (refer to case (ii) above), the resultant overall velocity of solids dissolution will be ruled by the diffusion rate, in which event, increasing the agitation will have a considerable effect on solids dissolution.

Since benzoic acid is a slightly soluble solid (at a temperature range of 5 to 25^{o}C) in the water, its rate of dissolution is considerably increased by agitation (Hixson and

Baum,1941, and Johnson and Huang,1956), and also taking into account equation (137) it is possible to conclude that most of the resistance to mass transfer due to the liquid phase controls the process of dissolution. At the boundary layer of the different phases (solid/liquid) the equilibrium is set up very quickly (refer to equation 126a) and the velocity of the heterogeneous reaction is determined by the velocities of the diffusion process that accompanies it. With agitation (rapid water movement = larger volume of water) the ratio between mass and volume increases so that the equilibrium is set up in the direction of solids dissolution, thus increasing the rate of dissolution at higher rates of agitation.

As previously recognised, the process of oxygen absorption into the water is: (1) greatly increased by the rate of agitation or turbulence of the water, (2) ruled by diffusion processes ($K_L(O_2) = f(Sc)^{-1/2}$), and (3) mainly hindered by the resistance of the liquid phase as suggested by the two-film model. It appears that these factors similarly affect the benzoic acid dissolution rate at the water surface.

The contact area between the gas and the liquid phases is greatly increased by the rate of turbulence in the water, whereas the contact area between the solid and liquid is practically the same when the rate of turbulence is increased. As it has been stated by McCready and Hanratty (1984), the rate of mass transfer at a gas-liquid interface is almost an order of magnitude larger than would be predicted for a solid-liquid boundary. One reason for this is that for a clean interface the liquid is mobile and there is not as much damping of high frequency velocity components as at a fixed boundary. Another reason is that there are a number of possible sources for velocity fluctuations in the liquid close to a gas-liquid interface. It is then expected that the rate of solids dissolution can be greatly increased by the rate of liquid agitation, but in a lower rate than the gas absorption into the water at higher levels of turbulence.

The velocity of solids dissolution was measured according to the method described in section 4.2.1. It was computed by plotting the difference in weights against time according to the dissolution model (equation 123) and applying least squares analysis using Minitab (Ryan et al.,1980).

A typical plot of a floating soluble solid test is shown in Figure 19. As it can be observed, replicate samples were used for the measurement of the velocity of solids dissolution to provide an accurate measure of the errors involved in any individual experiment and also to provide an accurate measure of the model fitness. The following statistical analysis has been therefore carried out for all dissolution tests:

(i) a regression analysis on all twelve points obtained (6x2 replicates) according to the linear model below:

$$Y_{ij} = \beta_0 + \beta_1 x_i + E_{ij} \qquad (139)$$

where $i = 1,2,\ldots,6$

and $j = 1,2$

E_{ij} is the error, approximately estimated by a normal distribution of zero mean and σ_e^2 variance.

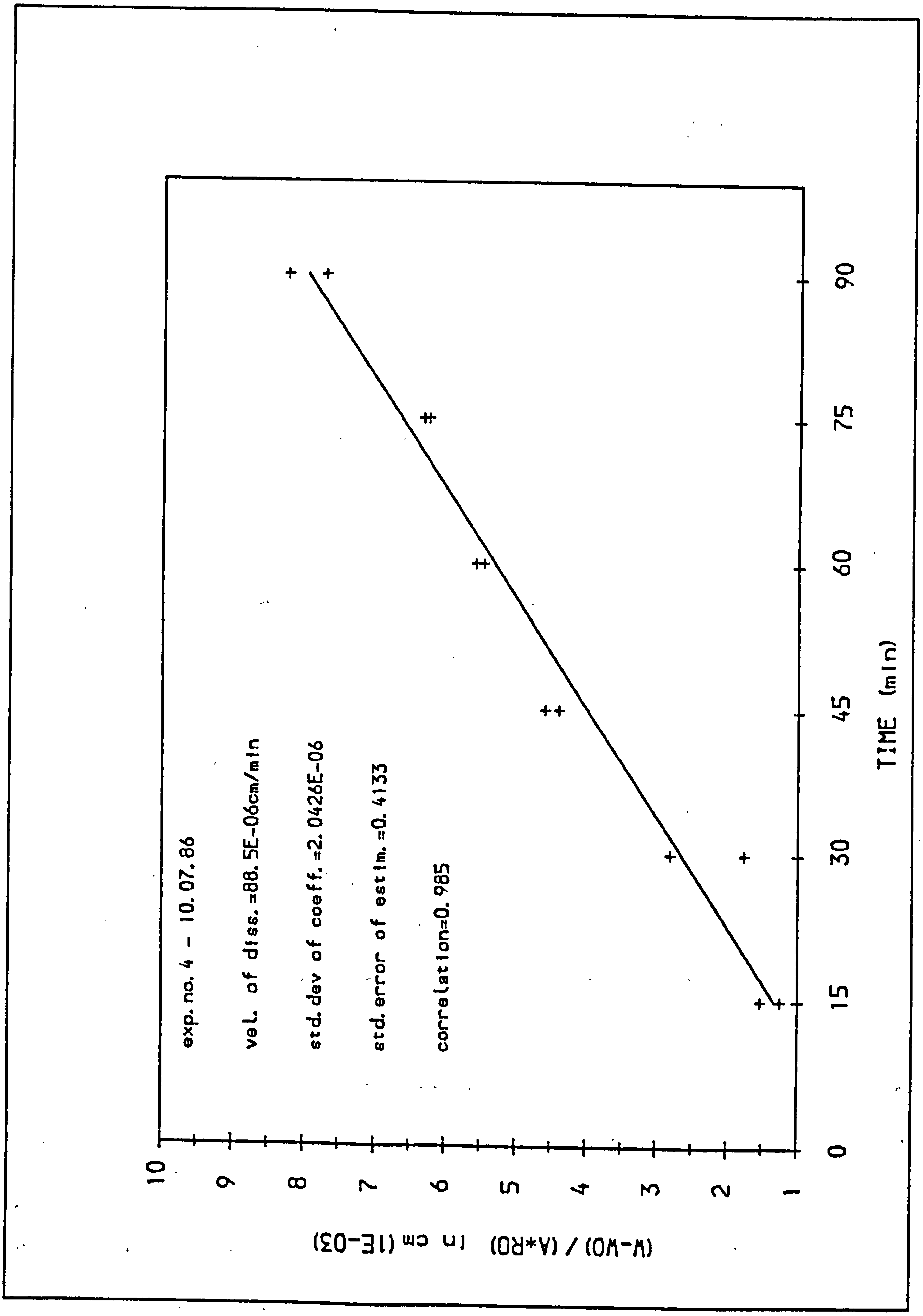


Figure 19: Typical floating soluble solid test

(ii) σ_e^2 is estimated by:

$$\hat{\sigma}_e^2 = [\sum_i^6 \frac{(y_{i1} - \bar{y}_{i.})^2 + (y_{i2} - \bar{y}_{i.})^2}{(2 - 1)}]/6 \qquad (140)$$

which is independent of the validity of the linear model because we have replicate samples;

(iii) now consider a regression of the 6 means according to the linear model below:

$$\bar{Y}_{i.} = \beta_0 + \beta_1 x_i + F_i \qquad (141)$$

where F_i is the error approximately estimated by a normal distribution with zero mean and $\sigma_e^2/2$ variance;

(iv) if the linear model is valid, the mean square of the regression of equation (141), on 4 degrees of freedom, estimates $\sigma_e^2/2$ and thus σ_e^2 is estimated by 2x(Error MS);

(v) a hypothesis test is then set up as follows:

H_0:linear model is valid;

H_1:linear model is not valid;

and $$F_{4,6} = \frac{2\text{x(Error MS)}}{\sigma_e^2} \qquad (142)$$

(vi) the model is rejected if the calculated value of F is greater than the table value at the 10% level of significance;

(vii) a dot diagram of the residuals was also obtained by Minitab to check the assumption that the residuals follow a normal distribution;

(viii) residuals were plotted against predicted values and also against time of exposure; if the mathematical model is appropriate, the residuals should be unrelated to the levels of any known variable, in particular to the levels of response itself (random distribution of points should be obtained);

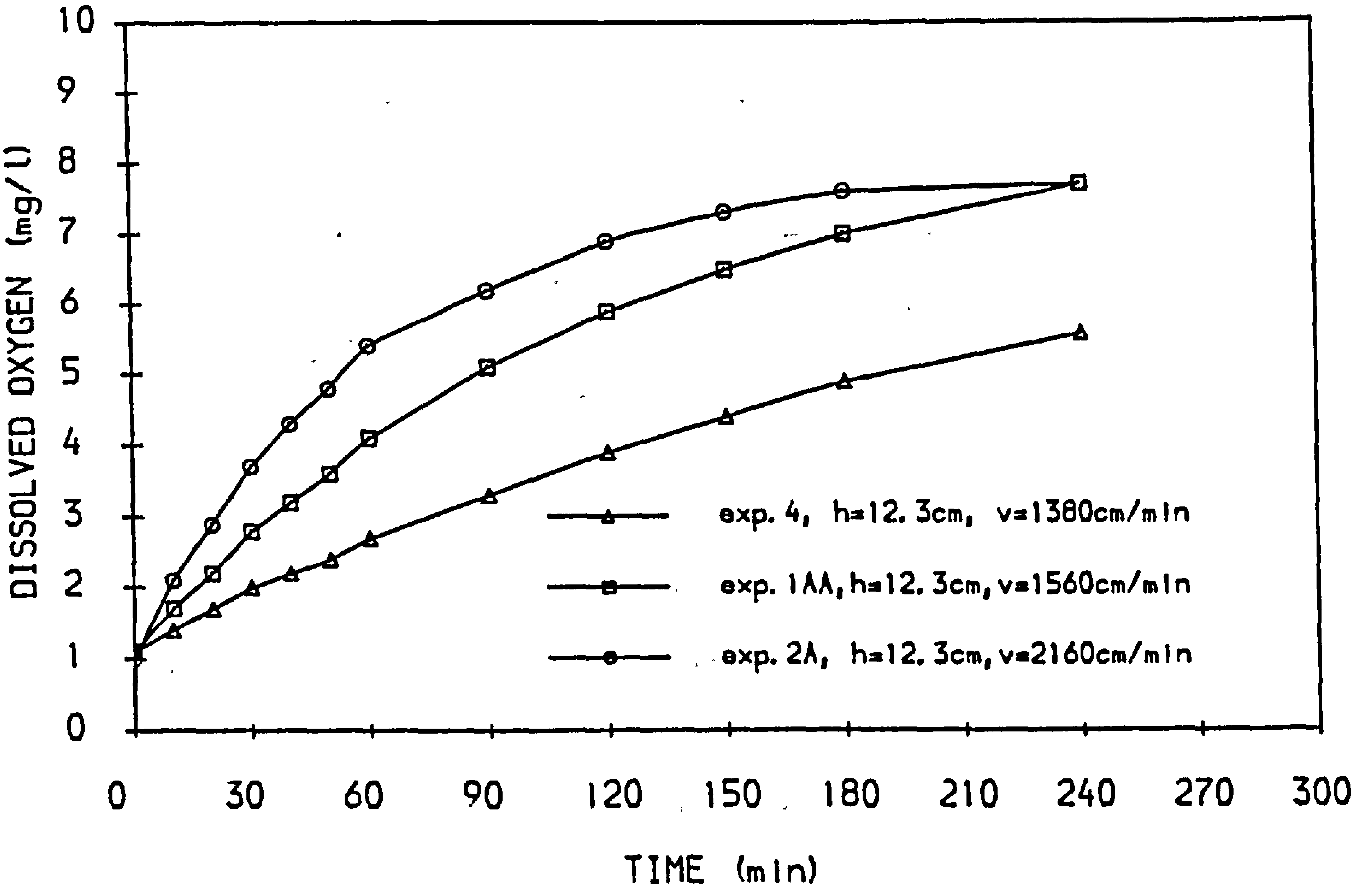
The overall result of the above statistical analysis revealed that the dissolution model (equation 123) developed herein was appropriate for the computation of the velocity of solids dissolution. In all experiments the calculated value of $F_{4,6}$ was smaller than the table value at the 10% level, and the calculated residuals varied randomly, as expected, in almost all experiments.

4.3 RESULTS AND DISCUSSION:

The twelve reaeration tests are presented in Figures 20A and 20B. For each different depth, three reaeration curves were obtained, each with a different velocity of flow (high, medium or low). These plots clearly indicate a direct correlation between K_2 and velocity of flow, and an inverse correlation between K_2 and depth, as it was expected and reported in previous studies (see Bennett and Rathbun,1972 or Wilson and MacLeod,1974).

The overall results obtained in these preliminary experiments are summarised in Table 14.

Although no attempt has been made to quantify the relationship between the velocity of solids dissolution, V, and the oxygen mass transfer coefficient, K_L, as it is shown in Figure 21, it is clear that a good and definite correlation exists between the two processes. This is statistically confirmed by a correlation coefficient r = 0.957. The above



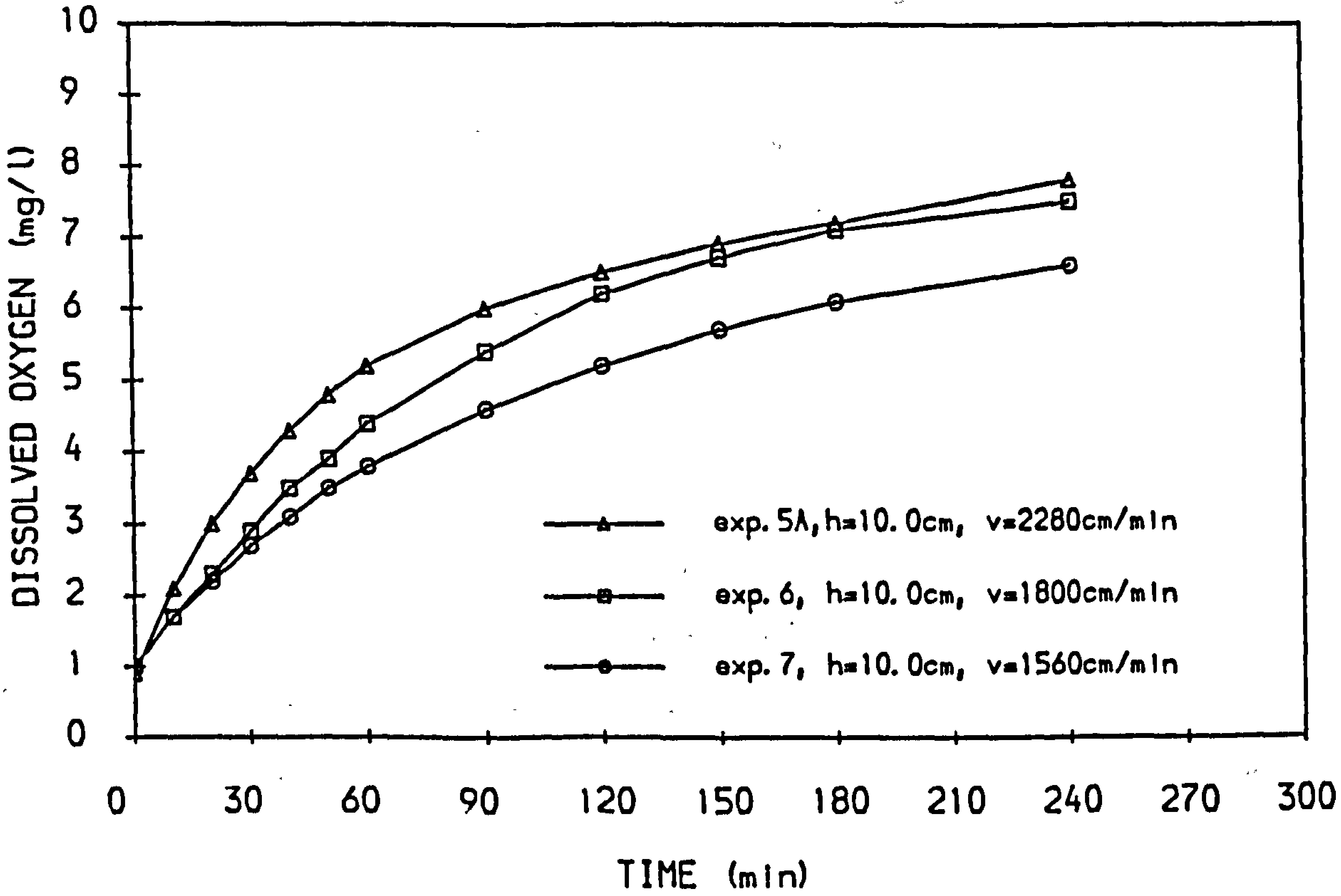
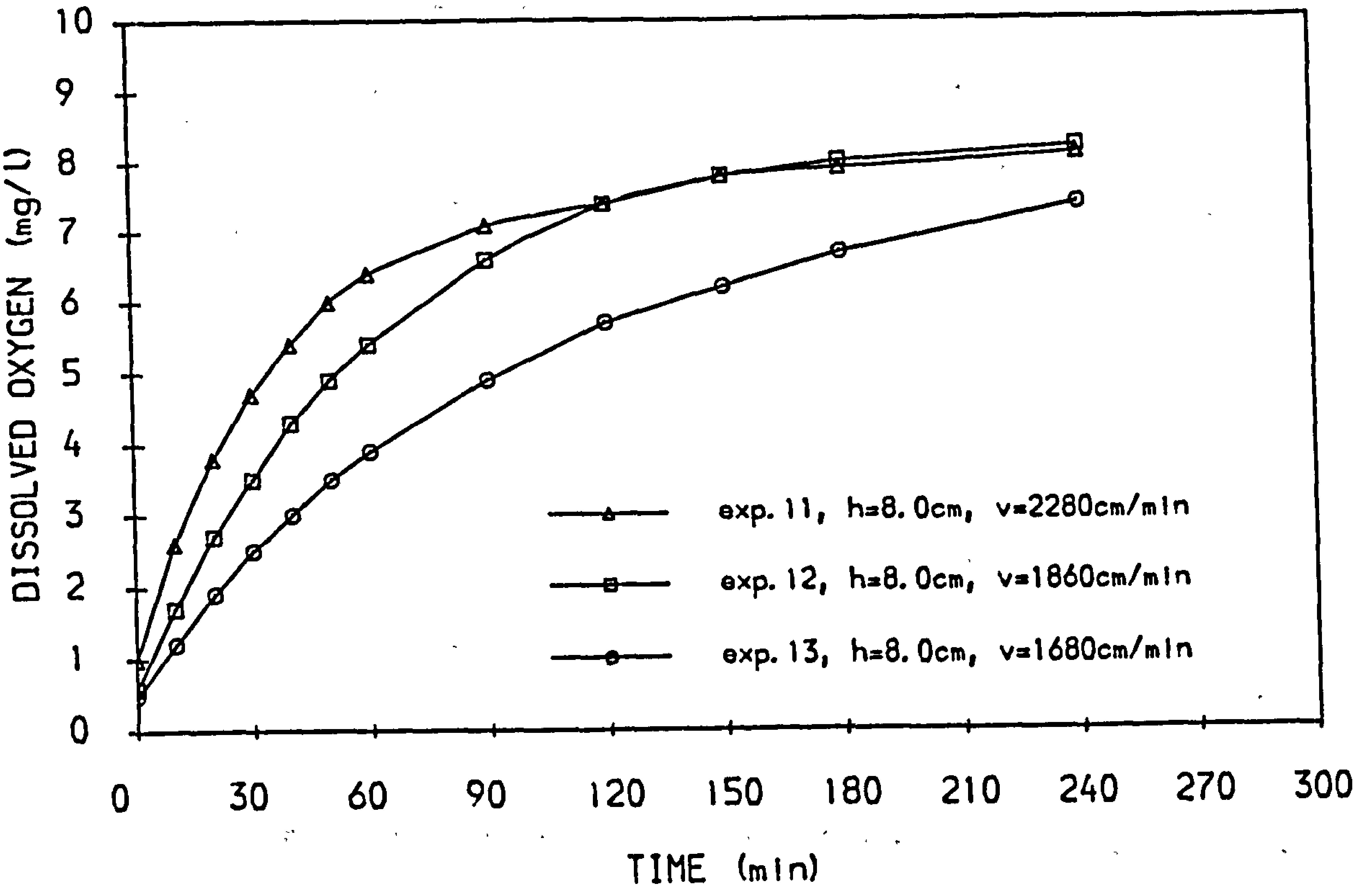


Figure 20A: Reaeration experiments (preliminary tests)



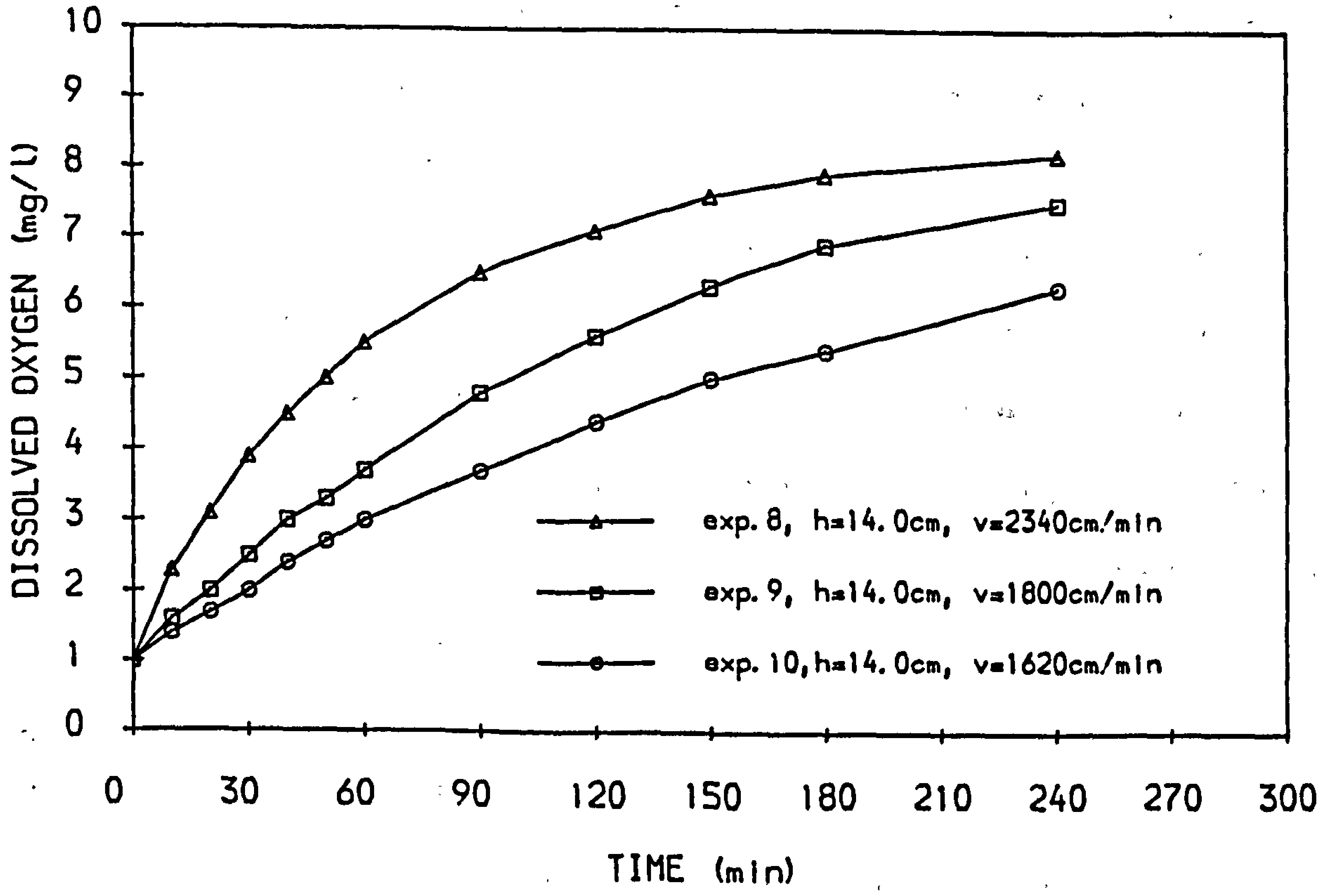


Figure 20B: Reaeration experiments (preliminary studies)

Table 14: Overall laboratory experimental results comparing reaeration and dissolution processes at different hydraulic conditions

Test number	Average velocity (m/s)	Average depth (cm)	Reaeration rate coeff. K_2 (per min)	Oxygen transf.coeff. K_L (cm/min)	Velocity of solids dissol. (cm/min)
1	0.38	8.0	0.02310	0.184	0.000177
2	0.31	8.0	0.01692	0.135	0.000142
3	0.28	8.0	0.00868	0.069	0.000095
4	0.38	10.0	0.01195	0.119	0.000144
5	0.30	10.0	0.01105	0.111	0.000135
6	0.26	10.0	0.00752	0.075	0.000103
7	0.36	12.3	0.01677	0.206	0.000209
8	0.26	12.3	0.00856	0.105	0.000117
9	0.23	12.3	0.00394	0.048	0.000088
10	0.39	14.0	0.01472	0.206	0.000167
11	0.30	14.0	0.00801	0.112	0.000118
12	0.27	14.0	0.00486	0.068	0.000089

results also confirm the observation from previous studies that an increase in the rate of agitation or turbulence (here expressed as a combination of velocity and depth levels) considerably increases the velocity of solids dissolution.

Considerable accuracy has been achieved in the measurement of the two mass transfer coefficients. An average asymptotic standard deviation of about 0.0026 min^{-1} has been obtained for the K_2 values, computed by the NLLS2 procedure, and an average standard deviation of 4.0×10^{-6} has been obtained for the velocity of solids dissolution, computed by least squares analysis (see Appendices A.4).

4.4 SUMMARY AND CONCLUSIONS:

A total of twelve tests have been carried out in a preliminary basis to investigate the following:

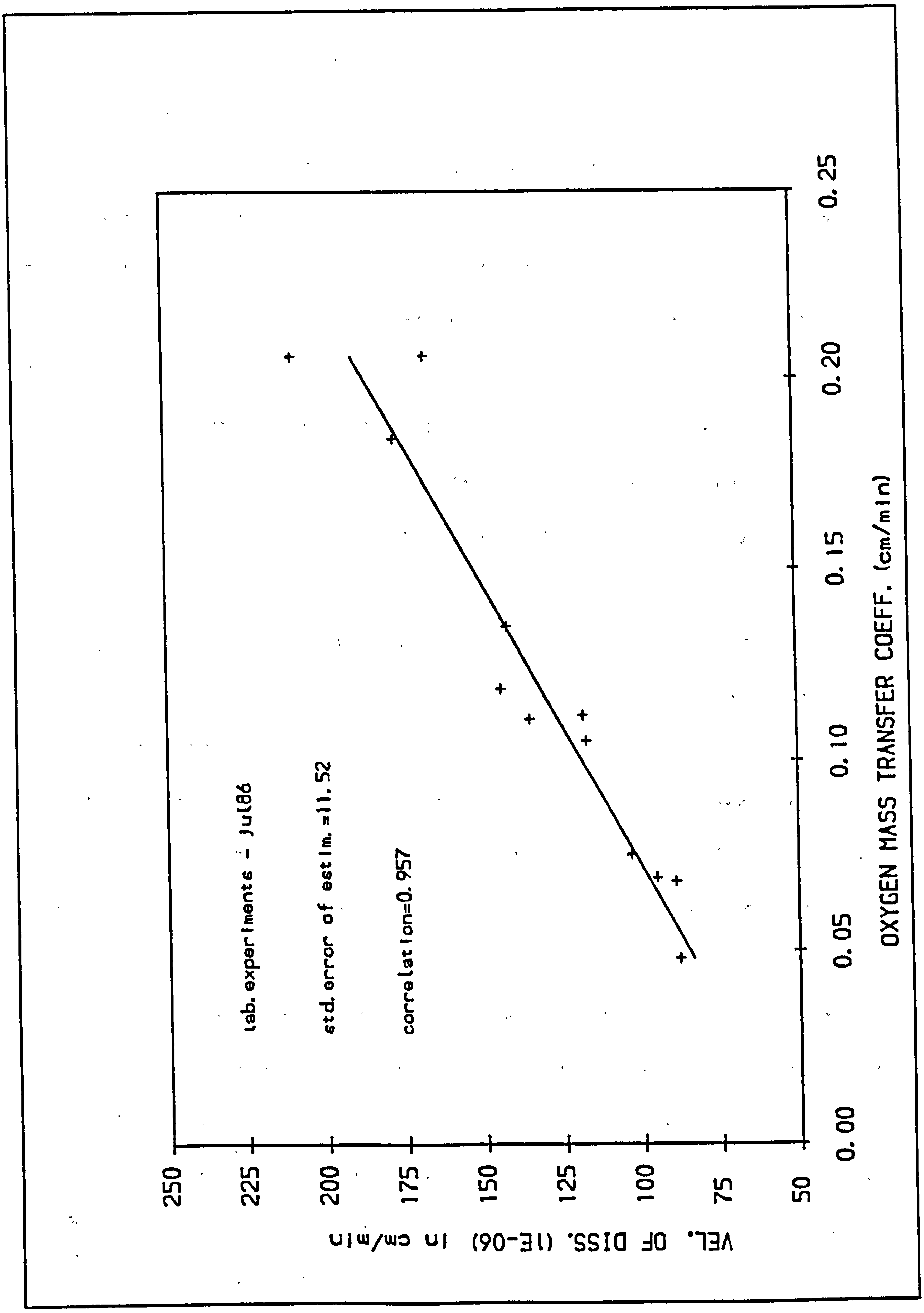


Figure 21: Relationship between the oxygen transfer coefficient and the velocity of solids dissolution

(i) an accurate method for the measurement of the reaeration rate coefficient and the velocity of solids dissolution;
(ii) the best method for the computation of the reaeration and velocity of solids dissolution coefficient;
(iii) verify the possible existence of a relationship between reaeration and solids dissolution processes;

And the conclusions derived from these experiments are as follows:

(i) the membrane electrode method has been selected as the most accurate method for the measurement of DO concentration changes;
(ii) a first order reaction model was shown to best describe the reaeration process;
(iii) the two-parameter non-linear least squares procedure has been considered the most accurate method for the computation of the reaeration rate coefficient;
(iv) the benzoic acid dissolution model herein developed, regardless the mechanism by which the dissolution process takes place, was shown to accurately describe the process of solids dissolution;
(v) it has been shown that where a chemical reaction is taking place simultaneously with the dissolution process, and specially when its velocity is slow compared to the rate of diffusion, the resultant overall velocity is supposed to be ruled by the rate at which the chemical change takes place. In this case increased agitation has little effect. On the other hand, if the chemical reaction is fast compared to the rate of diffusion, the resultant overall velocity will be ruled by the

diffusion rate, in which event, increasing the agitation will have a considerable effect upon solids dissolution (Hixson and Crowell,1931);

(vi) the relationship between the reaeration coefficient and the two hydraulic parameters, velocity and depth, is in good agreement with previously reported models given in the literature;

(vii) the relationship between the oxygen transfer coefficient and the velocity of benzoic acid dissolution was preliminary found to be linear and highly correlated;

(viii) further investigation, both in the laboratory and field, of the demonstrated potentiality of the floating soluble solids method for the measurement of reaeration in small streams, is needed;

CHAPTER 5

Subsequent Tests

The second part of the laboratory studies was planned in order to investigate the individual and combined effects of three different hydraulic factors - velocity, depth and roughness - upon three different processes - atmospheric reaeration, propane gas desorption and benzoic acid dissolution at the water surface.

Qualitative and quantitative evaluation of the behaviour of such processes at the various hydraulic conditions was made possible by the employment of statistical techniques for experimental design and analysis.

5.1 THE EXPERIMENTAL DESIGN:

By the statistical design of experiments we refer to the process of planning the experiment so that appropriate data will be collected, which may be analysed by statistical methods resulting in valid and objective conclusions. When the problem involves data that are subjected to experimental errors, statistical methodology is the only objective approach to analysis (Montgomery,1984).

The first step in planning an experiment is to formulate clear statements of the objectives of the test program, as above.

The second step is to select independent variables or factors to be investigated in the experiment, which in this case are velocity, depth and roughness.

Third, a response or dependent variable must be chosen (reaeration rate coefficient, propane gas desorption rate coefficient and velocity of benzoic acid dissolution). Thought must also be given to how the response will be measured and to the probable accuracy of such measurements.

In selecting an experimental design, which is of primary importance in the experimental process, the experimenter must determine the difference in true response he wishes to detect and the magnitude of risks he is willing to tolerate so that an appropriate sample size may be chosen. It must also be determined the order in which the data will be collected and the method of randomisation to be employed. A mathematical model for the experiment must also be proposed, so that a statistical analysis of the data may be performed.

It has been shown that factorial designs are most efficient when two or more factors are to be studied. By a factorial design we mean that in each complete trial or replication of the experiment all possible combinations of the levels of the factors are investigated. They are more efficient than one-factor-at-a-time experiments and necessary when interactions may be present to avoid misleading conclusions. Factorial designs allow effects of a factor to be estimated at several levels of the other factors (although linearity between e.g. 2 levels may be assumed), yielding conclusions that are valid over a range of experimental conditions.

A 2^3 factorial design has been chosen for these laboratory studies, where there are two quantitative factors - velocity and depth - and a single qualitative factor - roughness - which will be investigated at two levels, as follows:

Table 15: The chosen factors and levels

Factor	Level (-)	Level (+)
Velocity (m/s)	0.25	0.50
Depth (cm)	10.0	16.0
Roughness	smooth	coarse

The complete arrangement requires ($2^3 = 8$) runs. In a comparative experiment, the number of observations on each treatment is called the number of replhBations. A fundamental principle of such experiments is that it is essential to carry out more than one test on each treatment in order to estimate the size of the experimental error and the precision of the estimates of the treatment effects. In the present study, a series of three replicates for each of the different hydraulic conditions were run, totalizing 24 tests for each of the response variables (K_2, K_p and V_s), making up to 72 runs altogether.

A display of the levels to be run in a design such as the 2^3 factorial design is called a design matrix. The three common notations for the design matrix of a two-level factorial is given in Table 16, and the eight treatment combinations are graphically displayed as a cube, as shown in Figure 22.

Statistical methods require that errors are independently distributed random variables. An essential technique which usually makes this assumption reasonable is called randomisation, as mentioned before. By randomisation we mean that both the allocation of the experimental material and the

Table 16: Design matrix notation for the 2^3 factorial design

Run	V	D	R		V	D	R
1	-	-	-	1	0	0	0
2	+	-	-	V	1	0	0
3	-	+	-	D	0	1	0
4	+	+	-	VD	1	1	0
5	-	-	+	R	0	0	1
6	+	-	+	VR	1	0	1
7	-	+	+	DR	0	1	1
8	+	+	+	VDR	1	1	1

order at which the individual runs or trials of the experiment are to be performed are randomly determined. If the tests are performed sequentially in time, then the order of the tests should be randomised. If a different experimental unit is used in each test, then the unit should be selected randomly. Both these operations can be done by using a table of random numbers.

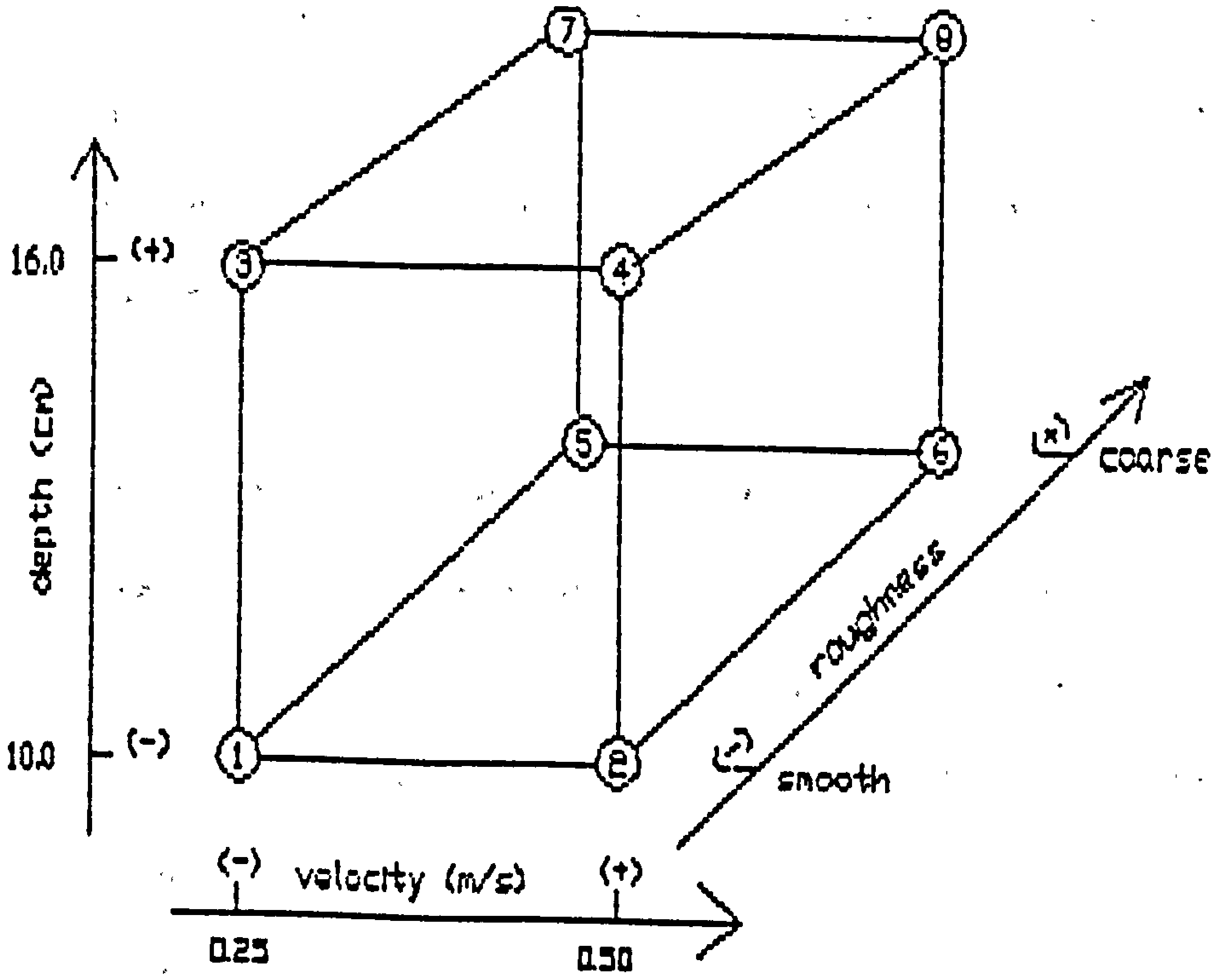


Figure 22: The 2^3 factorial design

Since only one experimental unit (the annular channel) was available, it was practically impossible to change the roughness element from one experiment to another. It has thus been decided to run half of the tests with a coarse sand paper, and the other half with a smooth sand paper. Randomisation of the experiments was provided by assigning a different number to each of the 24 tests (8 runs times 3 replicates) initially planned for each of the response variables, and then, from a table of random numbers, the final sequence of the tests could be determined.

The three response coefficients (K_2, K_p and V_s) could be simultaneously measured at each of the eight different hydraulic conditions so that, in fact, 24 tests have been run instead of the 72 initially thought.

During the actual data collection process, a careful monitoring of the progress of the experiment has to be carried out in order to ensure that it is proceeding according to the plan. Particular attention must be paid to randomisation, measurement accuracy, and maintenance of the experimental environment as uniform as possible.

5.2 EQUIPMENT AND PROCEDURE MODIFICATIONS:

All tests have been carried out in a room at constant temperature to better control its effects upon the response variables. The temperature was set at 15^oC. The room temperature could be set at any desired level between 5 and 30^oC, and was found to fluctuate approximately ± 0.3^o from the set value. Air circulation was provided by a bank of three fans mounted just under the ceiling at the rear of the room.

The same annular channel described in section 4.1.1 was used in these subsequent experiments. A roughness element was introduced by applying sand paper to its bed and walls. Two kinds of sand paper were chosen to simulate different roughnesses. The first one was a coarse waterproof sand paper made from zirconia material CX-95 with particle size of 0.410 mm from Duraco. The other paper was also waterproof, with particle size of 0.0197 mm from Carborundum. Because of the small width to depth ratio, it was decided to cover not only the bed of the channel, but also the circular walls, otherwise a possible significant effect of roughness upon the response variables could be misled.

Velocity of flow within the channel was monitored by a floating method. By knowing the average length of the recirculating course and the average time of travel that a standardised float (about 80% submersed) takes to cover this length, it is possible to compute the average velocity of flow within the channel. A comparison study between the current meter and floating methods revealed that there was no significant evidence that the mean velocity values obtained at various hydraulic conditions by different methods were different at the 10% level of significance. Based on the above analysis and on the fact that the current meter method was time consuming and subjected to frequent drifts of the meter, it has been decided to compute the average velocity of flow within the annular channel using the standard floating device.

The method selected is also subjected to errors and can sometimes be less accurate than the current meter method. But because the main interest was to verify the effect of extreme velocities (low or high) combined with the two other factors on the response coefficients, it was thought that the float method could give average velocity values within the range of accuracy required, as verified by statistical analysis.

Velocity of the jet entering the channel has also been monitored by means of an L-shaped Pitot tube held against the flow at the exit of the orifice (and entrance of the channel). Average jet velocities were computed by the observation that the height of the water column reached within the tube is proportional to velocity, as below:

$$V_j = \sqrt{(2.g.h)} \qquad (143)$$

The reaeration rate coefficient and velocity of solids dissolution have been measured and computed as described in sections 4.2.2 and 4.2.3, respectively. The propane gas desorption rate coefficient was measured by the employment of a rather sophisticated technique originally described by Swinnerton and Linnenbom (1967), later modified by Shultz et al.(1976). The measurement technique and the computation of the propane desorption rate coefficient is as follows:

5.2.1 Propane Gas Desorption Measurement:

The modified gas tracer technique is dependent on the assumption that the ratio between the reaeration rate coefficient and the desorption rate coefficient of the tracer gas is independent of temperature and turbulence intensity. The ratio for propane gas has been previously determined in the laboratory and was found to be between 1.36 (Rainwater and Holley,1984) and 1.39 (Rathbun et al.,1978), with the difference between these two values probably due to the experimental errors involved in its measurement. To further investigate the exact behaviour of the desorption rate coefficient at different hydraulic conditions, similar studies to those of Rainwater and Holley (1984) and Bales and Holley (1986) were conducted in the annular recirculating channel according to the planned experimental design.

The theories of absorption in which a chemical moves from air to liquid can be used equally well for desorption in which a chemical moves from liquid to air (Danckwerts,1970). Volatilisation of organic compounds from water is usually described by the two-film model of Lewis and Whitman (1924). The film coefficients of the model are estimated by summing up the liquid phase resistance and the air-phase resistance in series, so that:

$$\frac{1}{k_{oL}} = \frac{1}{k_L} + \frac{R\,T}{Hk_G} \qquad (144)$$

where k_l and k_G are the liquid and gas film mass transfer coefficients, respectively, H is the Henry's law constant, R is the ideal gas constant, T is the absolute temperature and k_{oL} is the overall mass transfer coefficient.

It has been shown by Rathbun and Tai (1981,1982) that, for average conditions, more than 90% of the resistance to mass transfer for propane gas volatilisation is in the liquid phase ($H > 10^{-3}$ atm.m^3/mol). According to the above equation, as the

Henry's law constant increases, the air-phase resistance for desorption decreases, and if the background atmospheric level of propane is negligible and it is promptly dispersing as it is desorbing, then the concentration of propane in the atmosphere is insignificant, and the overall mass balance equation is reduced to a first order reaction model of the type:

$$\frac{dC}{dt} = - K_p\, C \tag{145}$$

where C is the dissolved gas concentration, t is time, and K_p is the desorption rate coefficient expressed by:

$$K = \frac{k_p}{h} \tag{146}$$

in which k_p is the surface film coefficient and h is the water depth (Yotsukura et al.,1983). It is worth noting that the above model has been quite generally substantiated by experiment (e.g. Tsivoglou et al.,1965, Tsivoglou,1967, Rathbun et al.,1978 and Rainwater and Holley,1984).

The actual measurement of the propane gas desorption rate coefficient involves the employment of a very sophisticated chromatographic technique. Hydrocarbon concentrations contained in water samples are determined using the so called purge and trap method, which has been carefully described by Rainwater and Holley (1984). Gas chromatographic equipment (see Figure 23) and procedures (propane gas solution preparation, sample collection and hydrocarbon analysis) used for the present tests are similar to those reported by Rainwater and Holley (1984). A few modifications, however, have to be introduced for a better adjustment of the equipment (e.g. carrier gas flow rate of 30-40

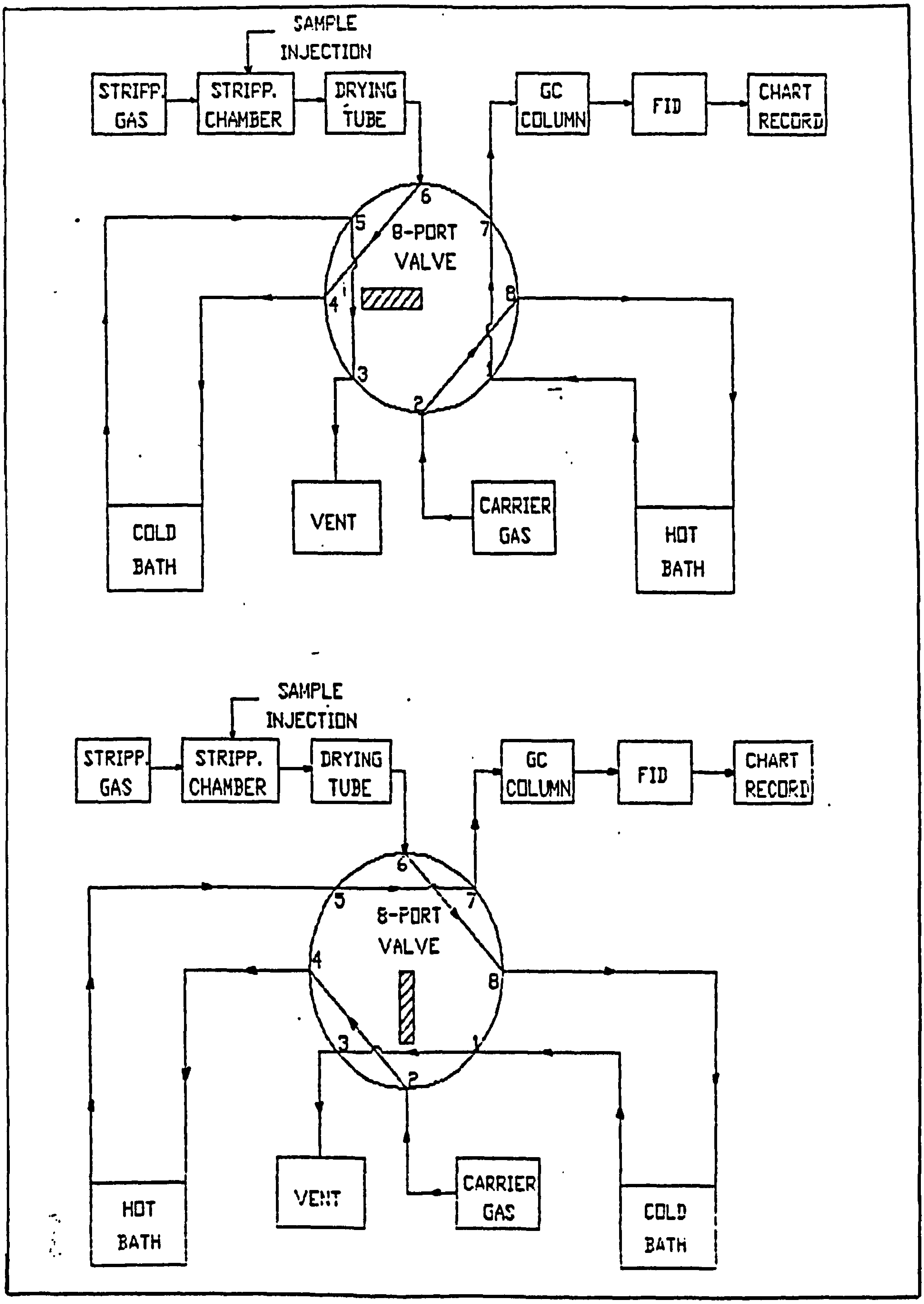


Figure 23: Hydrocarbon gas analysis equipment

ml/min at 40 psi and hot oil bath temperature at 120^{o}C).

The GC used in these experiments was a Becker Gas Chromatograph Packard Model 417 with a flame ionisation detector. The detector flame burned a mixture of air and hydrogen flowing at 250 ml/min (30 psi) and at 30 ml/min (20 psi), respectively. Both the detector and injection port temperatures were set at 150^{C} and the oven temperature was set at 120^{o}C. The above gas flow rates and temperatures were found to give the best response of the GC for the propane gas analysis. For the usual hydrocarbon concentrations of the order of 30 µg/l in the water samples, the analysis of 10ml of sample required the GC detector response to be set at 16 attenuation and range 100. A typical chart output is shown in Figure 24 below:

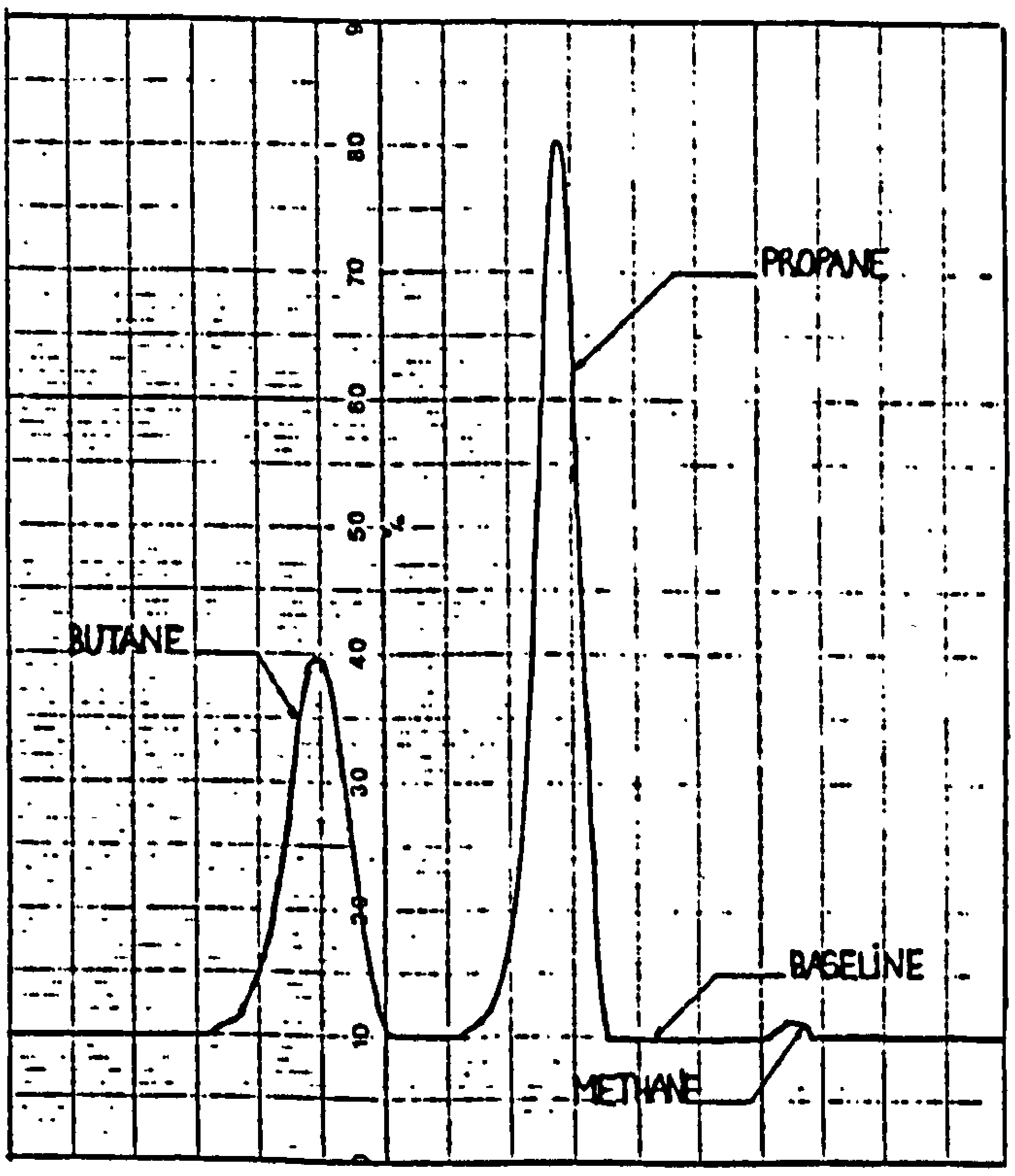


Figure 24: Typical GC output

The purge and trap apparatus was mounted on a vertical board which could be moved either upwards or downwards in order to make the change of the baths (refer to Rainwater and Holley,1984 for a detailed description of the routine procedure for the hydrocarbon analysis) easier when operating the system. The baths themselves were mounted on a track which could be moved from left to right and vice-versa (see Plate 3).

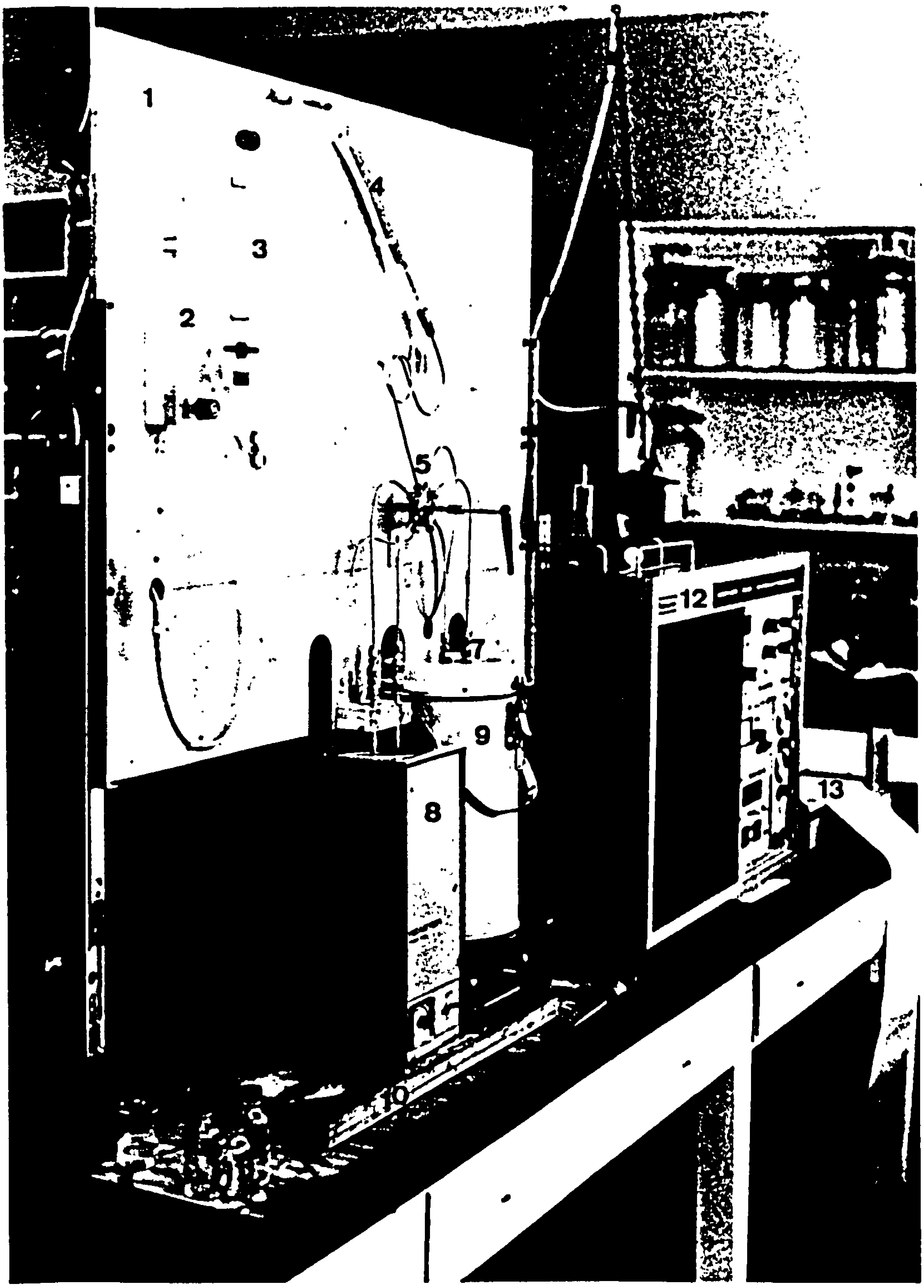
The GC response had to be constantly calibrated and checked for linearity. This was done following recent suggestions from Holley (1986, written communic.), where it is no longer necessary to know the absolute concentration of propane in a sample. Only the concentration of propane relative to other samples is needed. The linearity testing procedure was therefore as follows:

(i) a water solution of propane (commercially available propane, BS 4250) is prepared according to the procedure outlined by Rainwater and Holley (1984); this solution is arbitrarily assigned a concentration of 30 µg/l;

(ii) twenty millilitres of this solution are diluted to make 2000 ml of a stock solution called A-1;

(iii) solution A-1 is diluted according to Table 17 to obtain the standards which are used to check the linearity of the machine response;

(iv) samples of the standards are siphoned into 60 ml sample bottles using 1/8 inches diameter Teflon tubing; it is important that care be exercised in order to minimise agitation and exposure to the atmosphere during the dilution



1. VERTICAL BOARD
2. STRIPPING GAS FLOW METER
3. STRIPPING CHAMBER
4. DRYING TUBE
5. EIGHT PORT VALVE
6. HOT TRAP
7. COLD TRAP
8. HOT OIL BATH
9. LIQUID NITROGEN BATH
10. HORIZONTAL TRACK
11. SAMPLE BOTTLES
12. GC MACHINE
13. STRIP CHART RECORDER

PLATE 3: HYDROCARBON GAS ANALYSIS EQUIPMENT

Table 17: Water solution standards

Standard No.	Vol. of A-1 added (ml)	Solution Vol.(ml)	Propane (μg/l)
A-2	100	1000	30.0
A-3	75	1000	22.5
A-4	50	1000	15.0
A-5	25	1000	7.5
A-6	10	1000	3.0

and transfer of the standards;

(v) one ml of formalin is added to each sample bottle to prevent biodegradation of propane;

(vi) the bottles are capped with Teflon lined septa and stored in a dark room at 4°C;

(vii) the linearity of the machine response is checked using these standards; the machine response (integrated area) is plotted against assigned concentration, as shown in Figure 25; if the system is operating properly, a straight line results;

(viii) machine response is checked with the standards before, during and after each batch of unknown samples are analysed;

Different sampling schedules were used depending on the hydraulic conditions within the annular channel, with either 15 or 30 minutes sampling intervals. A total of 5 samples were taken during each test at 0, 15, 30, 45 and 60 minutes at rapid flow conditions, or at 0, 30, 60, 90 and 120 minutes at slow moving flows.

The propane gas desorption coefficient was computed from equation (145), by a NLLS estimation procedure using BMDP Statistical Software (Dixon,1983). A typical plot of a propane

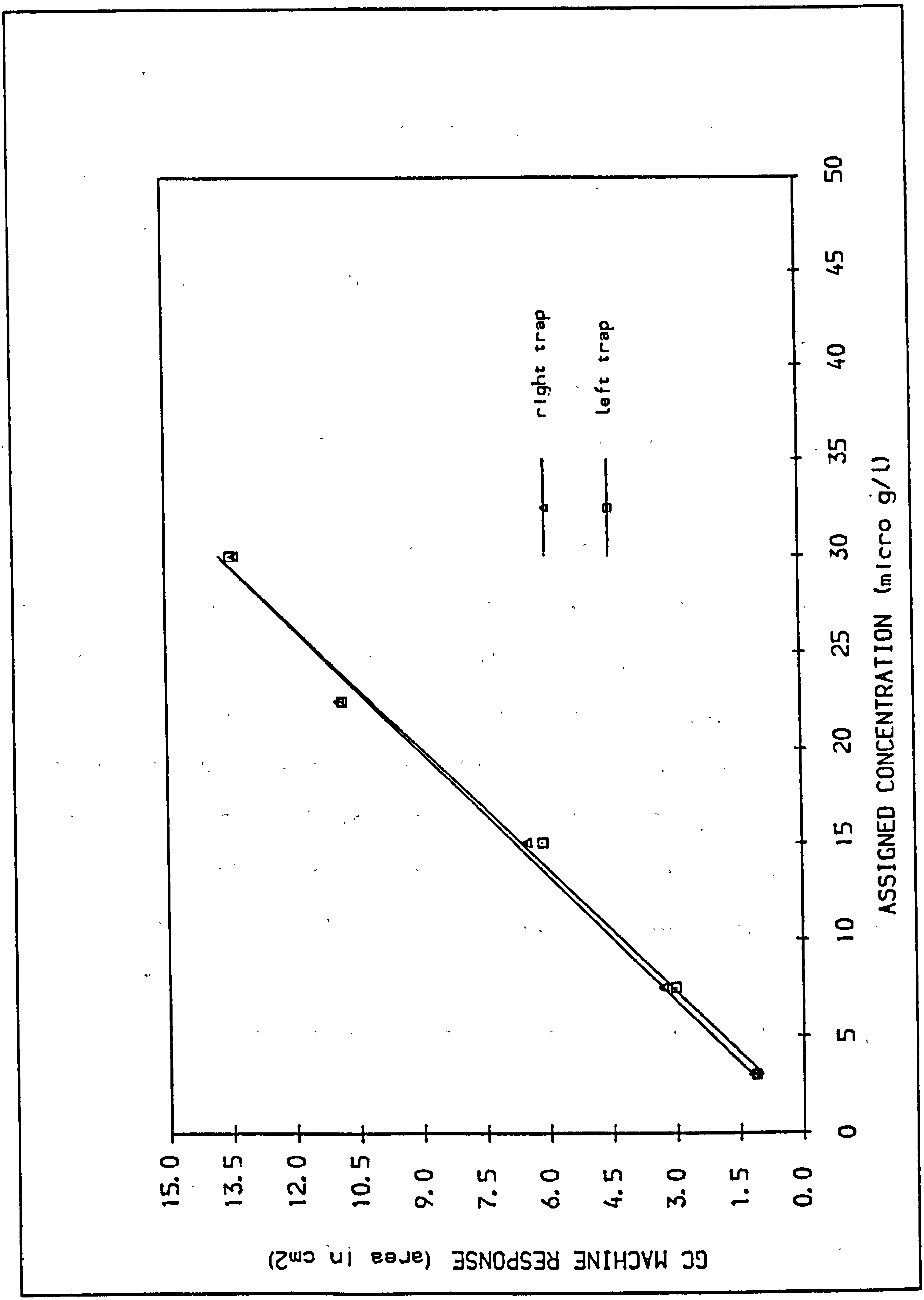


Figure 25: Typical linearity test of GC machine response

gas desorption test is shown in Figure 26, where it can be clearly observed that the propane desorption process is accurately represented by the first order reaction model. The accuracy of the propane gas desorption coefficient obtained was quantified in terms of the asymptotic standard deviation given by the BMDP program.

The accuracy of the GC analysis was evaluated using data from 10 different sets of linearity tests carried out in each trap (right and left), as shown in Appendices B.1. Statistical analysis performed with these data revealed the following:

(i) the precision of the procedure can be estimated to be equal to 0.090 in terms of the coefficient of variation defined by the ratio between the standard deviation and the mean for the measured concentration values;

(ii) the precision of the procedure decreases with decreasing propane concentration; the coefficient of variance increased from about 0.040 for 30 µg/l to 0.150 for 3 µg/l, which was expected due to the rather poor sensibility of the GC machine to detect very low hydrocarbon concentrations;

(iii) there is no significant evidence that the propane concentration values obtained from the right trap are statistically different from those obtained from the left trap at the 10% level of significance;

(iv) the slopes of the best fit lines through the water solution linearity test data were estimated to be 3.14 for the right trap and 3.15 for the left trap, thus confirming statement (iii);

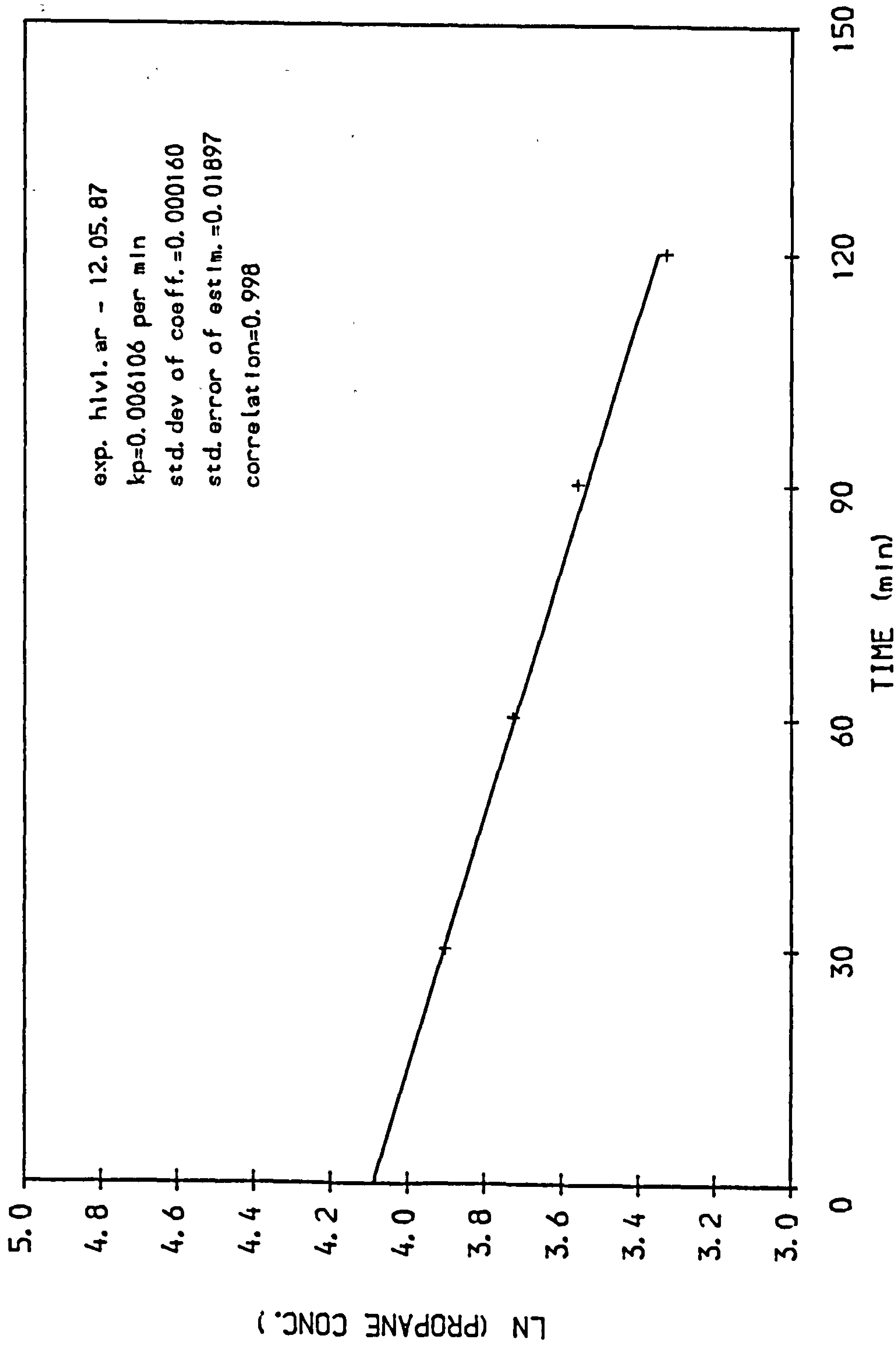


Figure 26:Typical propane gas desorption experiment
(propane gas concentration in mg/l)

Based on the above analysis, it was decided to work with propane concentrations ranging from 10 to 100 µg/l to avoid inaccurate GC response at propane gas concentrations lower than 10 µg/l.

The average level of accuracy for the hydrocarbon analysis (c.v.=9%) has been therefore considered an acceptable level for the above range of measured propane concentrations, where the GC machine can properly respond (see linearity tests).

5.3 THE FACTORIAL DESIGN EXPERIMENTAL RESULTS:

The obtained results, 24 data points for each of the response variables, were analysed according to the following three-factor analysis of variance model:

$$Y_{ijkl} = \mu + \alpha_i + \beta_j + \Gamma_j + (\alpha\beta)_{ij} + (\alpha\Gamma)_{ik} + (\beta\Gamma)_{jk} + \\ + (\alpha\beta\Gamma)_{ijk} + E_{ijkl} \qquad (147)$$

with

$$\Sigma(\alpha_i) = 0 \qquad \Sigma(\alpha\beta)_{ij} = 0$$

$$\Sigma(\beta_i) = 0 \qquad \Sigma(\alpha\Gamma)_{ik} = 0$$

$$\Sigma(\Gamma_i) = 0 \qquad \Sigma(\beta\Gamma)_{jk} = 0$$

$$\Sigma(\alpha\beta\Gamma)_{ijk} = 0$$

where $i = 1,2,...,a$ levels

$j = 1,2,...,b$ levels

$k = 1,2,...,c$ levels

$l = 1,2,...,n$ replicates

Assuming that the velocity, depth and roughness factors (α, β and Γ) are fixed, the analysis of variance table 18 can be constructed. A computer program has then been developed for a three-factor fixed effects analysis of variance model, which gives the F-ratios of main and interaction effects, the estimates of such effects, and also computes the residuals estimated from the difference between observed and predicted values according to equation (147). Details are given in Table 18 below and also in Appendices C.1 to C.5.

Table 18: The analysis of variance table for the three factor fixed effects model (Montgomery, 1984).

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Expected Mean Squares	F_0
A	SS_A	$a-1$	MS_A	$\sigma^2 + \frac{bcn\sum \tau_i^2}{a-1}$	$F_0 = \frac{MS_A}{MS_E}$
B	SS_B	$b-1$	MS_B	$\sigma^2 + \frac{acn\sum \beta_j^2}{b-1}$	$F_0 = \frac{MS_B}{MS_E}$
C	SS_C	$c-1$	MS_C	$\sigma^2 + \frac{abn\sum \gamma_k^2}{c-1}$	$F_0 = \frac{MS_C}{MS_E}$
AB	SS_{AB}	$(a-1)(b-1)$	MS_{AB}	$\sigma^2 + \frac{cn\sum\sum (\tau\beta)_{ij}^2}{(a-1)(b-1)}$	$F_0 = \frac{MS_{AB}}{MS_E}$
AC	SS_{AC}	$(a-1)(c-1)$	MS_{AC}	$\sigma^2 + \frac{bn\sum\sum (\tau\gamma)_{ik}^2}{(a-1)(c-1)}$	$F_0 = \frac{MS_{AC}}{MS_E}$
BC	SS_{BC}	$(b-1)(c-1)$	MS_{BC}	$\sigma^2 + \frac{an\sum\sum (\beta\gamma)_{jk}^2}{(b-1)(c-1)}$	$F_0 = \frac{MS_{BC}}{MS_E}$
ABC	SS_{ABC}	$(a-1)(b-1)(c-1)$	MS_{ABC}	$\sigma^2 + \frac{n\sum\sum\sum (\tau\beta\gamma)_{ijk}^2}{(a-1)(b-1)(c-1)}$	$F_0 = \frac{MS_{ABC}}{MS_E}$
Error	SS_E	$abc(n-1)$	MS_E	σ^2	
Total	SS_T	$abcn-1$			

The usual diagnostic checks have been applied to the residuals of the 2^3 design for each of the response variables considered. Examination of the residuals suggested that their variance increased as the predicted value increased for the K_2, K_L and K_p rate coefficients (refer to Appendices C.6). Regression analysis between the log of standard deviation of the three replicates for each of the eight different runs and the log of the mean of these replicates provided a better evidence of this effect (refer to Appendices C.7). A log transformation of the original data (Appendices C.8 to C.10), as suggested by regression analysis, resulted in residuals with an approximately constant variance. The residuals from the log-transformed data are more nearly normally distributed as well (Appendices C.11).

However, as one can observe from the computer outputs given in the Appendices, there is no practical change in the statistical significance of the results, and for ease of physical interpretation the results of the analysis using the original data are discussed in the following.

The calculated effects, standard errors and F-ratios for the 2^3 factorial design, for each of the response variables herein studied are summarised in Tables 19 to 22. Comparison of the effects estimates with their standard errors and respective F-ratios suggests that the bold items require interpretation, while the apparent effects remaining could be generated by noise.

It is clear from the results that the effect of velocity alone upon all the response variables studied (K_2, K_L, K_p, V_s), is the most important effect to be considered. In general it represents an increase of about 20% (% about the mean) on the K_2 and K_p rate coefficients, and an increase of about 40 to 60% (% about the mean) on K_L and V_s when velocity changes from 0.25 to 0.50 m/s. The smaller velocity effect on K_2 and K_p is due to an also important effect of depth upon these two coefficients. The depth effect is to reduce both reaeration and propane gas desorption by about 10% (% about the mean) when depth changes ble 19: Calculated effects, standard errors and F-ratios for 2^3 factorial design; reaeration rate coefficient, K_2

Effect	Estimate ± std.error ($\times 10^{-2}$)	F-ratio
in effects		
oughness (R)	0.193±0.065	8.917
depth (D)	-0.740±0.065	131.682
velocity (V)	1.490±0.065	536.775
wo-factor interaction		
R x D	-0.124±0.065	3.684
R x V	0.095±0.065	2.157
D x V	-0.600±0.065	86.420
Three-factor interaction		
R x D x V	-0.098±0.065	2.293

Table 20: Calculated effects, standard errors and F-ratios for 2^3 factorial design; propane desorption coefficient, K_p

Effect	Estimate ± std.error ($\times 10^{-2}$)	F-ratio
Main effects		
roughness (R)	0.220±0.070	9.987
depth (D)	-0.609±0.070	76.577
velocity (V)	1.210±0.070	304.551
Two-factor interaction		
R x D	-0.162±0.070	5.397
R x V	0.169±0.070	5.929
D x V	-0.493±0.070	50.154
Three-factor interaction		
R x D x V	-0.153±0.070	4.854

Table 21: Calculated effects, standard errors and F-ratios for 2^3 factorial design; oxygen transfer coefficient, K_L

Effect	Estimate ± std.error ($\times 10^{-1}$)	F-ratio
ain effects		
roughness (R)	0.213±0.073	8.651
depth (D)	-0.045±0.073	0.381
velocity (V)	1.760±0.073	590.875
o-factor interaction		
x D	-0.103±0.073	2.023
x V	0.094±0.073	1.675
x V	-0.331±0.073	20.855
ee-factor interaction		
x D x V	-0.099±0.073	1.844

Table 22: Calculated effects, standard errors and F-ratios for 2^3 factorial design; velocity of solids dissolution, V_s

Effect	Estimate ± std.error ($\times 10^{-5}$)	F-ratio
Main effects		
roughness (R)	-0.575±0.300	3.321
depth (D)	0.075±0.300	0.053
velocity (V)	5.080±0.300	259.218
Two-factor interaction		
R x D	-0.825±0.300	6.853
R x V	-1.790±0.300	32.312
D x V	-0.842±0.300	7.126
Three-factor interaction		
R x D x V	-0.842±0.300	7.131

Obs: Percentage points of F-distribution are as follows:
10% level - F-ratio = 3.048
5% level - F-ratio = 4.494
1% level - F-ratio = 8.531

from 10.0 to 16.0 cm. There is no significant effect of depth upon either K_L and V_s, as expected.

The effect of roughness alone upon the response variables considered revealed to be significant only at both 1 or 5% level of significance. Previous analysis of variance (one-way analysis of variance, Appendices C.12), indicated that the effect of roughness can be more significant at shallow and rapid flows than in any other conditions, as it would be expected.

The only interaction effects which must be considered are the velocity x depth and the velocity x roughness combinations. The velocity x depth interaction is highly significant for K_2, K_L and K_p, but only 5% significant for V_s. Its average effect is to reduce all processes being considered as much as 5% in terms of the percentage about the mean of the response variables, when the hydraulic conditions change from a lower to a higher level, as would be expected.

The high significance of the velocity x roughness interaction effect upon the velocity of benzoic acid dissolution (although small when compared with the main effects) must also be interpreted. Its effect is to reduce the dissolution process by about 10% when the hydraulic conditions change from a lower to a higher level. In other words the benzoic acid dissolution is higher at smooth conditions than at coarse conditions considering a high velocity level. The above experimental observation appears to be more empirical than of practical or physical significance, since one would expect higher dissolution rates at coarse and high velocity conditions. It was therefore concluded that although there is reasonable evidence that the fitted model is a reasonable approximation of the solids dissolution process at the water surface, there is some statistical evidence that a more complex model involving the two and three factor interaction would be an improved fit. However, these additional interactions are of little practical significance and make any physical interpretation of the model difficult.

The above results have been summarised in Figures 27 and 28, which shows a true and real similarity between the responses of K_2 and K_p to the two level change in hydraulic conditions, and also between the responses of K_L and V_s to the same changes. It should be noted, however, that there is no empirical evidence for the assumption of straight lines, as shown in the plots. These have only been assumed for ease of interpretation. As a matter of fact, previous diagnostic checking of residuals has suggested that quadractic terms involving velocity and depth

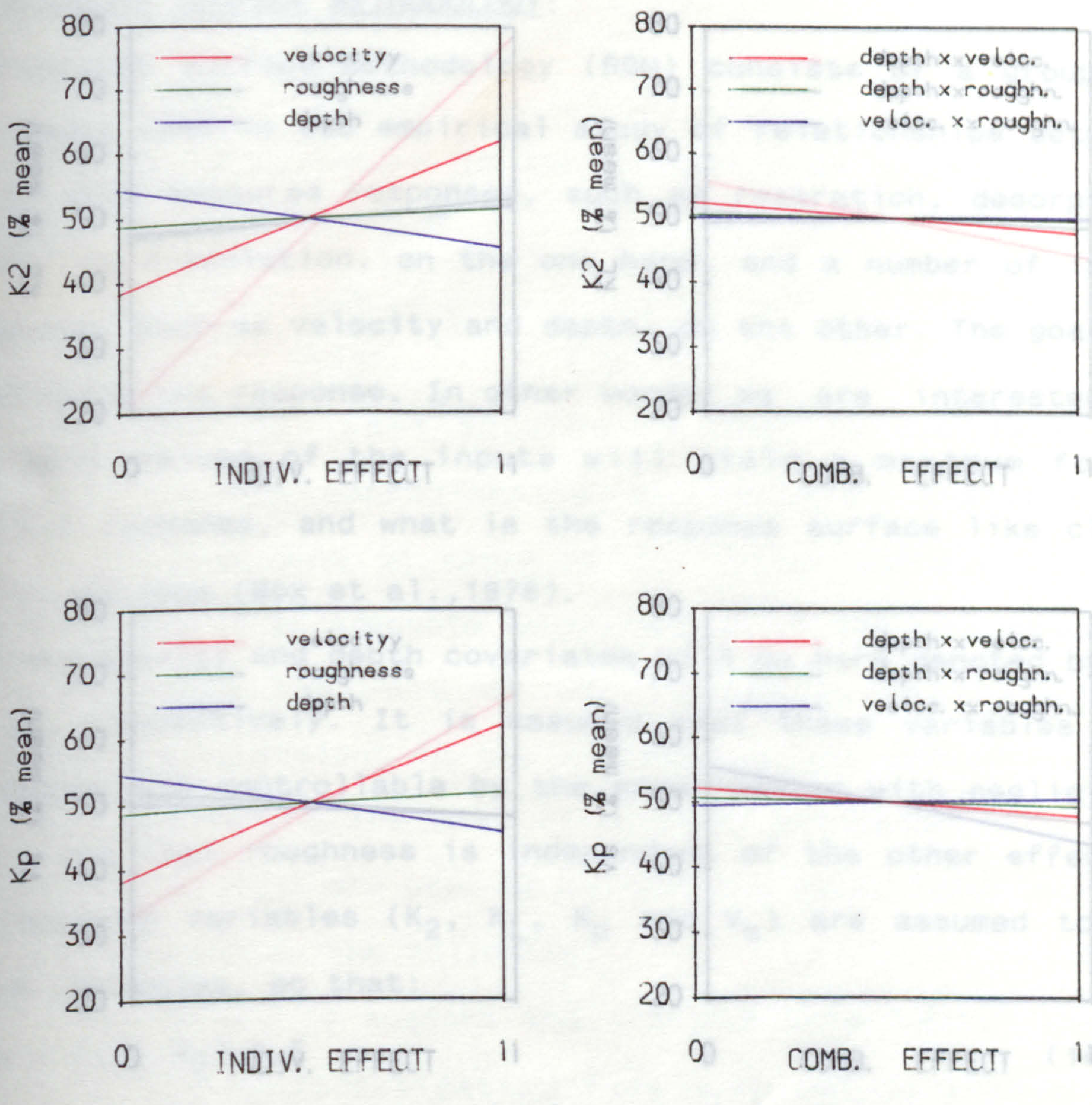


Figure **27** - Estimated individual and combined effects on K2 and Kp

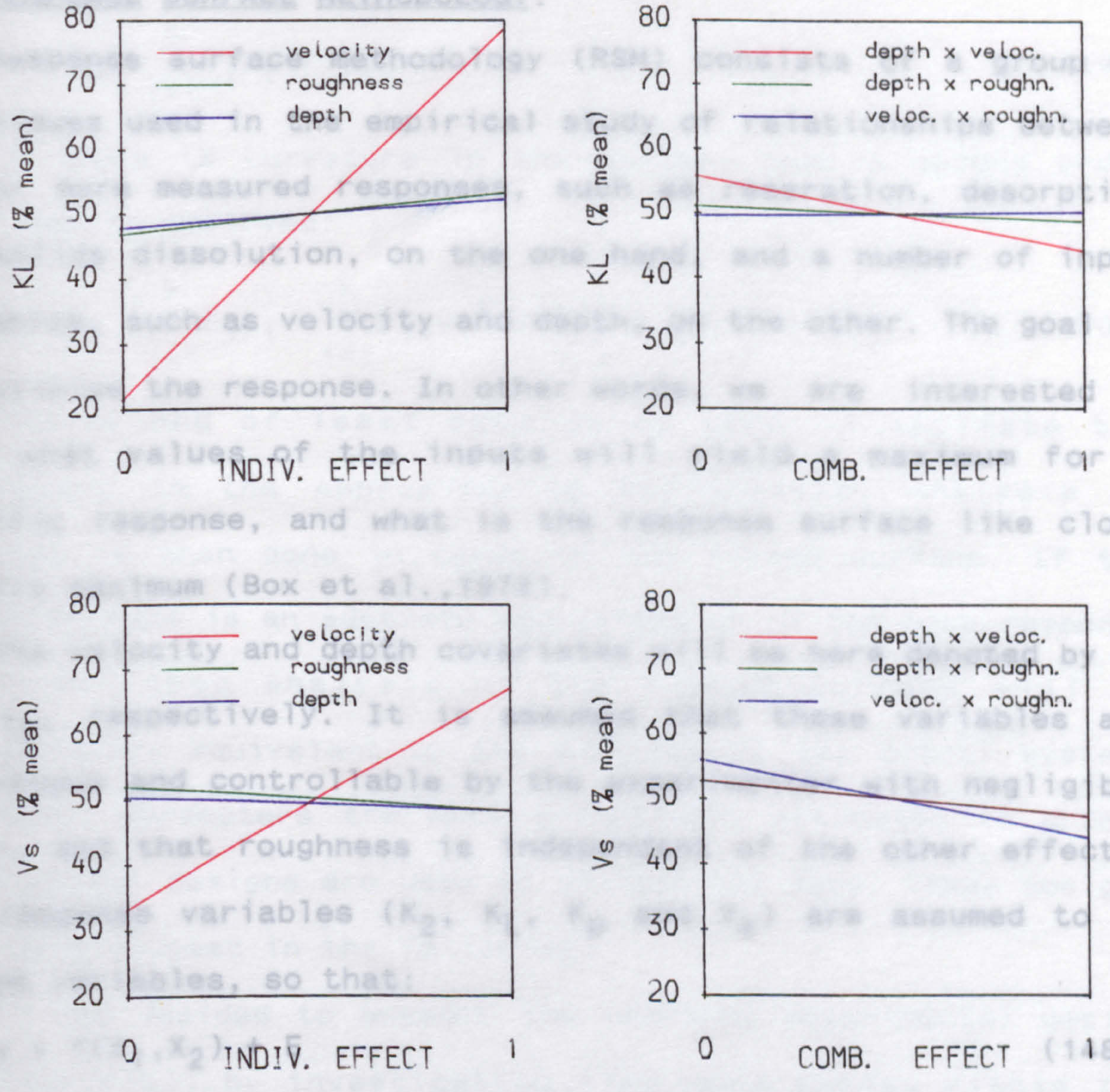


Figure **28** - Estimated individual and combined effects on KL and Vs might be needed in a model which adequately represents the processes at interpolated levels of the variables. The fitting and use of these approximating functions called response surface methodology will be discussed in the following.

5.4 RESPONSE SURFACE METHODOLOGY:

Response surface methodology (RSM) consists of a group of techniques used in the empirical study of relationships between one or more measured responses, such as reaeration, desorption and solids dissolution, on the one hand, and a number of input variables, such as velocity and depth, on the other. The goal is to optimise the response. In other words, we are interested to know what values of the inputs will yield a maximum for a specific response, and what is the response surface like close to this maximum (Box et al.,1978).

The velocity and depth covariates will be here denoted by X_1 and X_2, respectively. It is assumed that these variables are continuous and controllable by the experimenter with negligible error, and that roughness is independent of the other effects. The response variables (K_2, K_L, K_p and V_s) are assumed to be random variables, so that:

$$y = f(X_1,X_2) + E \tag{148}$$

where y is the response variable and E is the random error component. If the expected response is denoted by $E(y)=\Phi$, then the surface represented by $\Phi=f(X_1,X_2)$ is called a response surface.

In most RSM problems the form of the relationship between the response and the independent variables is unknown, so that the first step in RSM is to find a suitable approximation for the true functional relationship between y and the set of independent variables (Montgomery,1984).

Usually a low order polynomial in some region of the independent variables is employed, such as:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + E_i \qquad (149)$$

If there is curvature in the system, then a second order model can be employed:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i} \sum_{j} \beta_{ij} x_i x_j + E_{ij} \qquad (150)$$

The method of least squares is used to estimate the parameters in the approximating polynomials. Analysis of variance is then done in terms of the fitted surface. If the fitted surface is an adequate approximation of the true response function, then analysis of the fitted surface will be approximately equivalent to the analysis of the actual system. The model parameters are most effectively estimated if proper experimental designs are used to collect the data. These designs will be discussed in the following.

It was decided to augment the previous experimental design (2^3 factorial) by investigating five more points within the region of interest. Since the response variables were found not to be significantly affected by the roughness factor, it was assumed that roughness is independent of the other factors, and the previous data obtained could then be partially used at this stage of the experimental design as shown below:

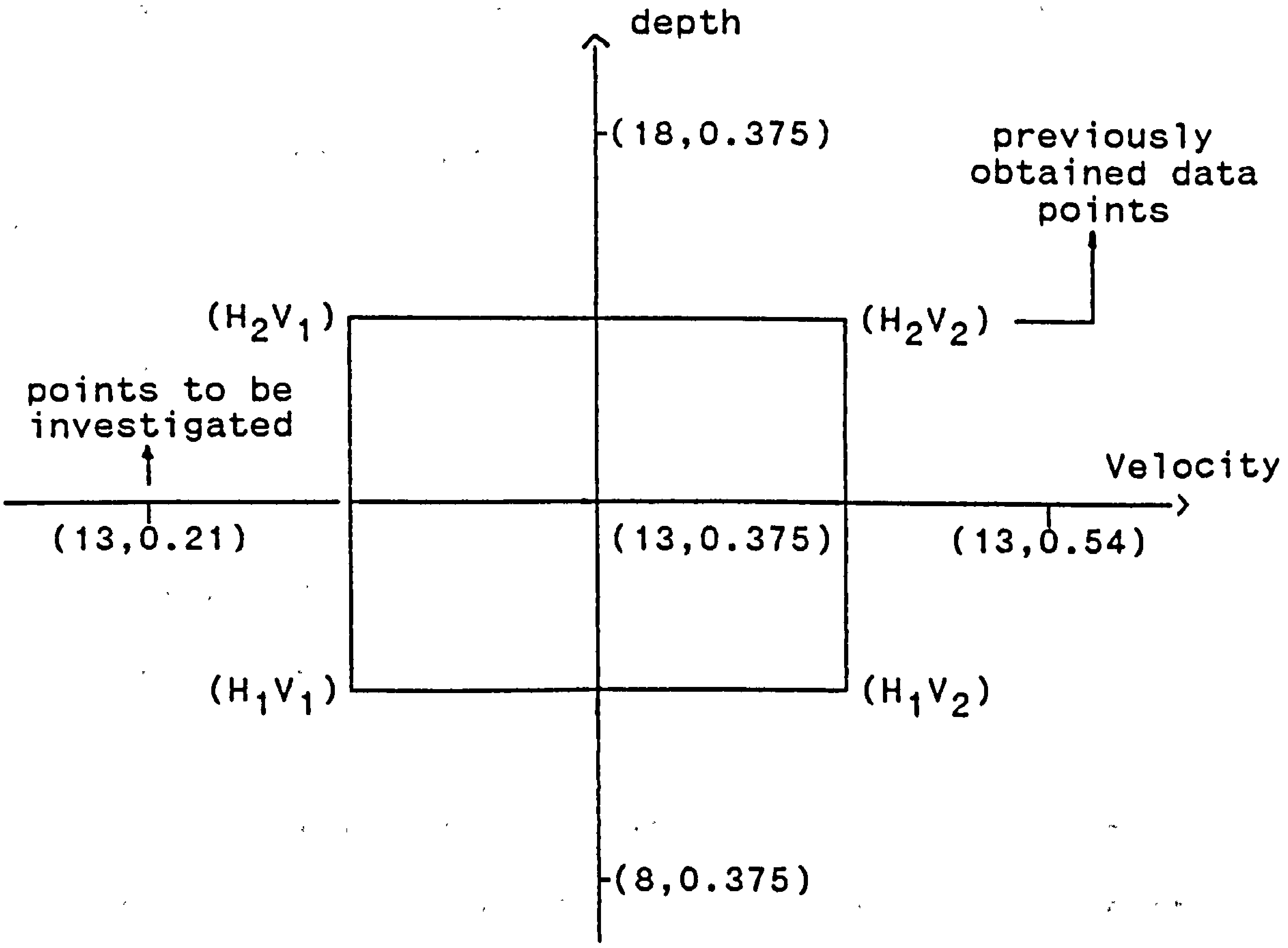


Figure 29: Response surface design

The above design is often called central composite design. It consists of a 2^2 factorial (previously obtained data usually coded in the ±1 notation) augmented by 2k axial points $(\pm\alpha,0)$, $(0,\pm\alpha)$ and n_0 centre points (0,0). The central composite design is made rotatable by the choice of α, and this value depends on the number of points in the factorial portion of the design. In fact, $\alpha=(F)^{1/4}$, which in this case - 2^2 factorial - yields $\alpha=1.414$.

We have therefore chosen to perform 12 more experimental runs for each of the response variables, as follows:

(i) four replicates for the centre point (13,0.375) to allow a preliminary first-order model fitting and estimation of the experimental error involved;

(ii) two replicates for each of the four axial points to allow a second-order model fitting;

(iii) the order of experiments has been randomised as previously described in section 5.1;

First-order response surfaces have been preliminary fitted to the data. Analysis of variance of the fitted surfaces indicated that interaction and quadractic effects were highly significant for the K_2, K_L and K_p coefficients, but not significant for the velocity of solids dissolution V_s, as it has been previously found in the 2^3 factorial design residuals analysis.

Second-order response surfaces were then fitted to the data (for K_2, K_L and K_p only). The analysis of the fitted second-order response surface is often called canonical analysis, description of which can be found in statistical text books (e.g. Box et al.,1978 and Montgomery,1984). The actual data and a summarised statistical analysis of the first and second-order models have been included in Appendices (D.1 to D.7).

The practical results of the response surface analysis have been plotted in the form of two and three-dimensional surfaces, as shown in Figures 30 to 37. The analysis and discussion of such results are described in the next section.

5.5 DISCUSSION:

The discussion of the experimental design results will be separated in two parts. The first part will be concerned with the two depth-averaged rate coefficients, K_2 and K_p, and their

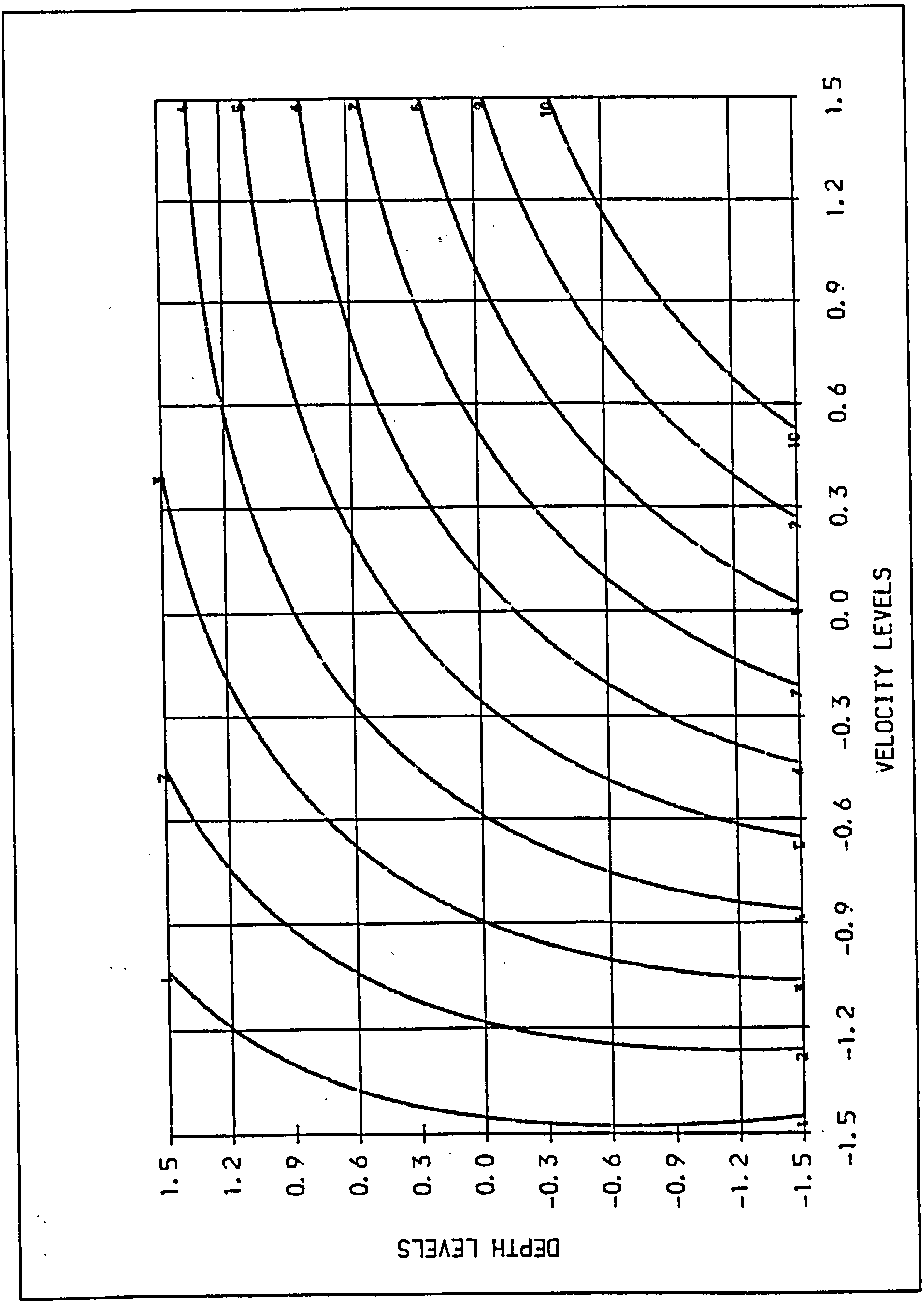
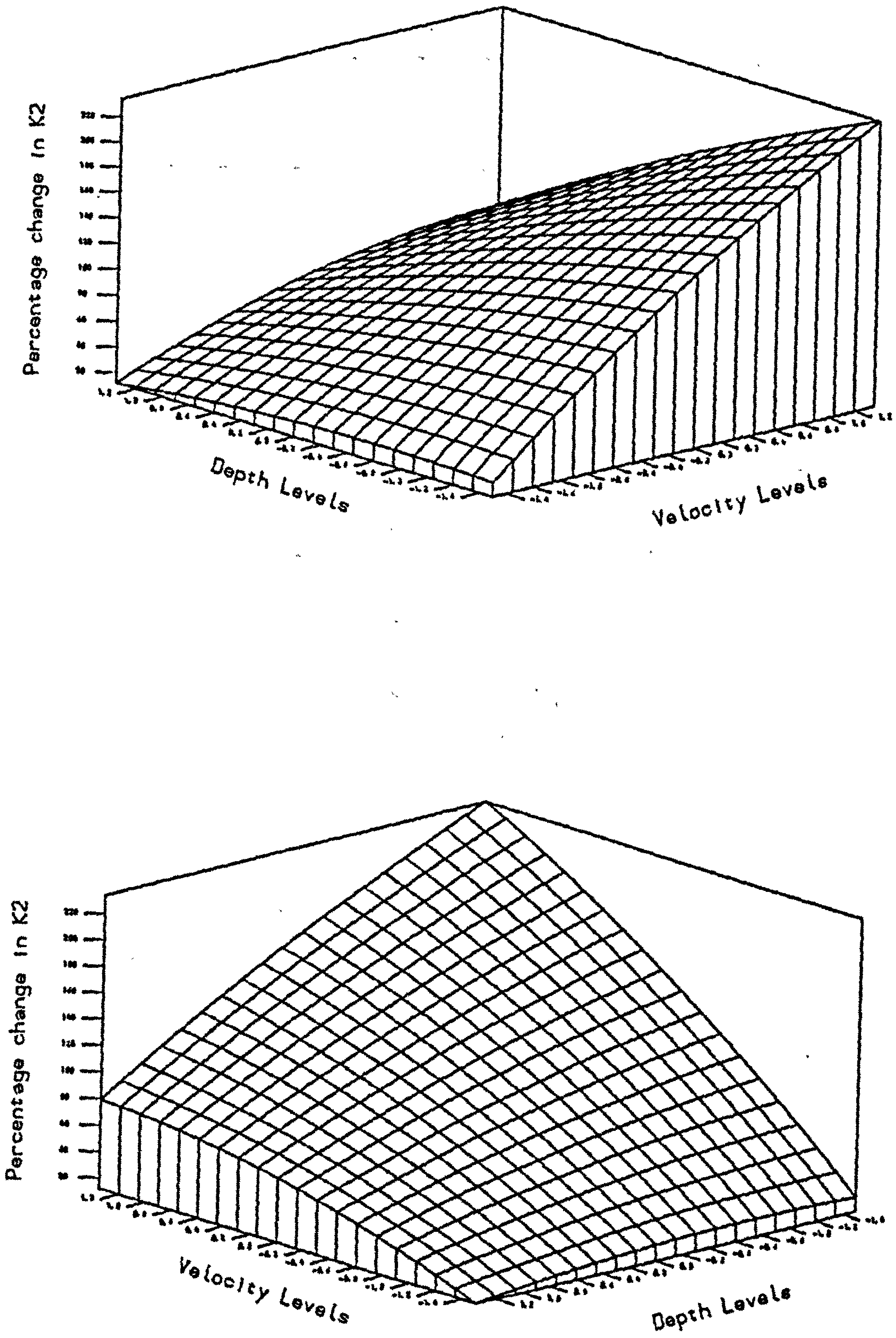


Figure 30: Surface contours for the reaeration coefficient K_2



e 31: Three dimensional response surface for K_2

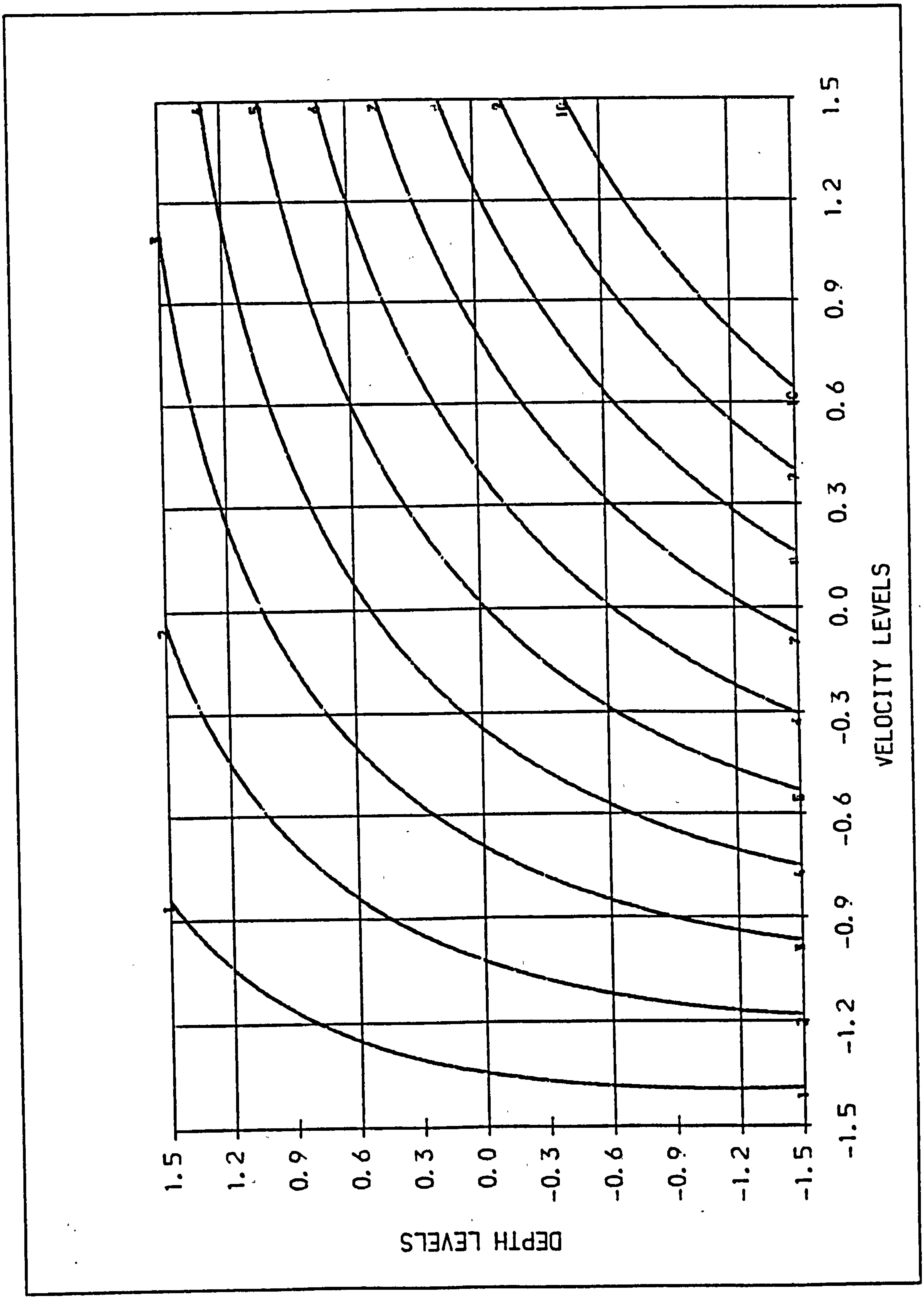


Figure 32: Surface contours for the propane gas desorption coefficient, K_p

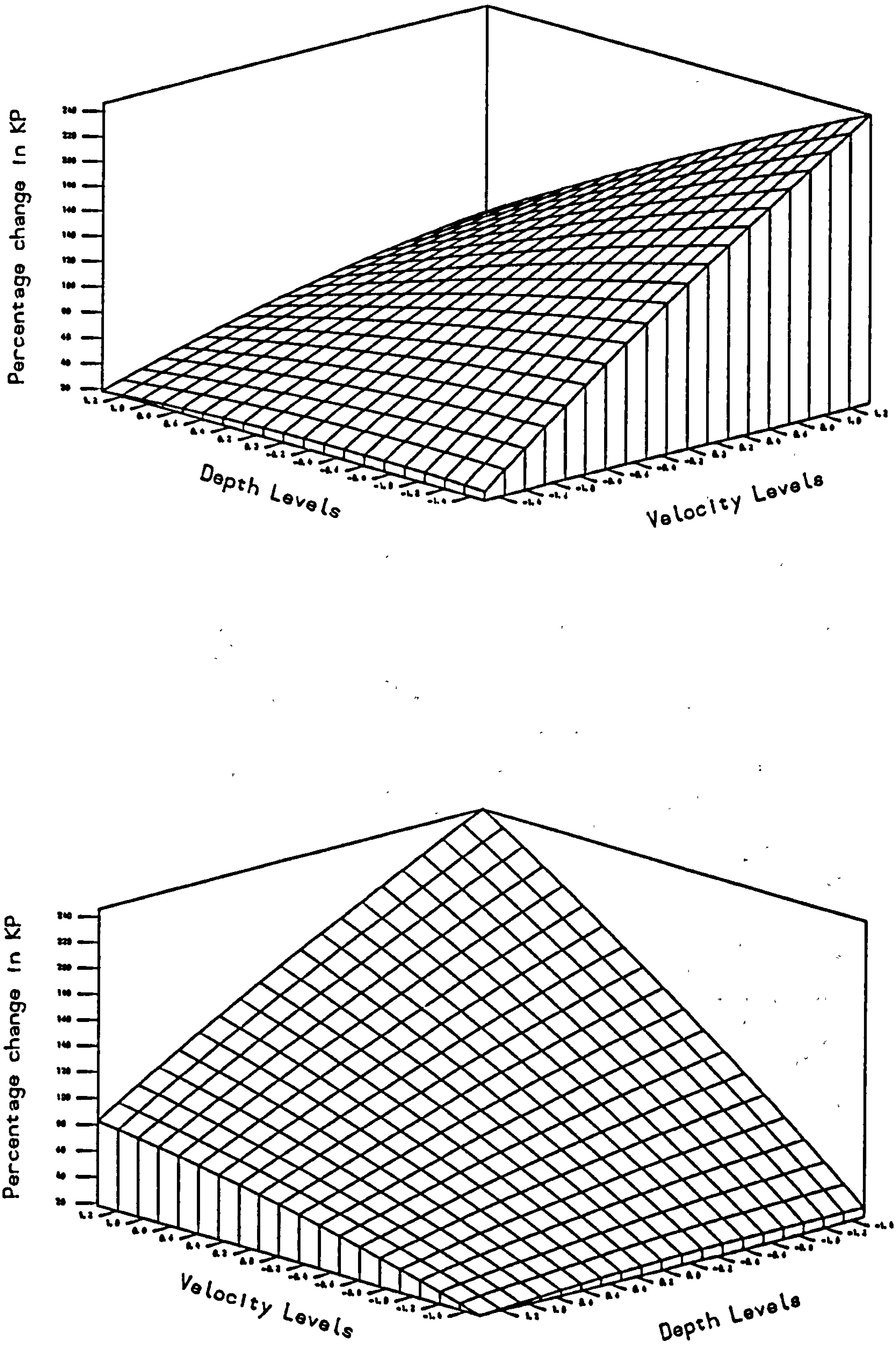


Figure 33: Three dimensional response surface for K_p

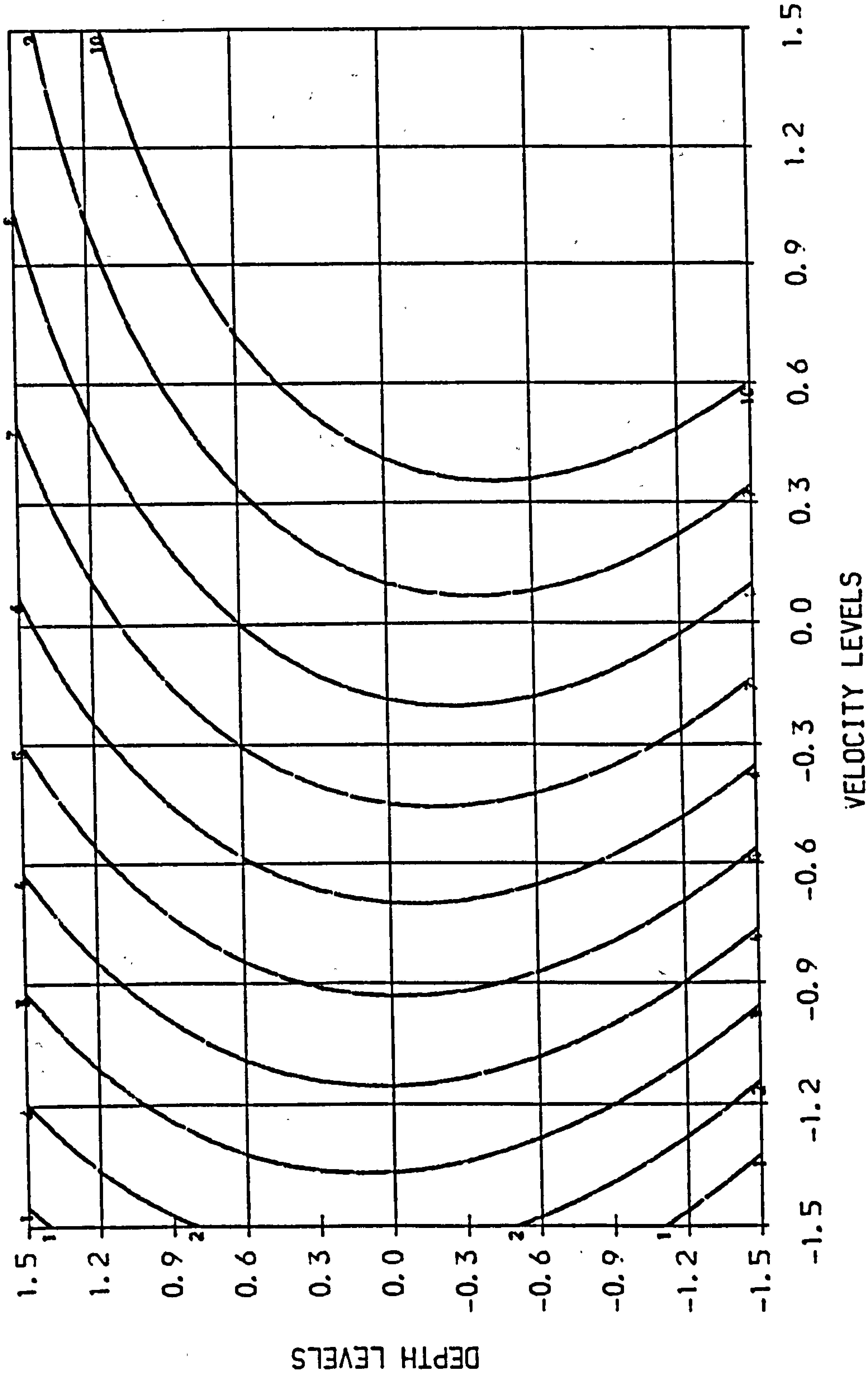


Figure 34: Surface contours for the oxygen transfer coefficient K_L

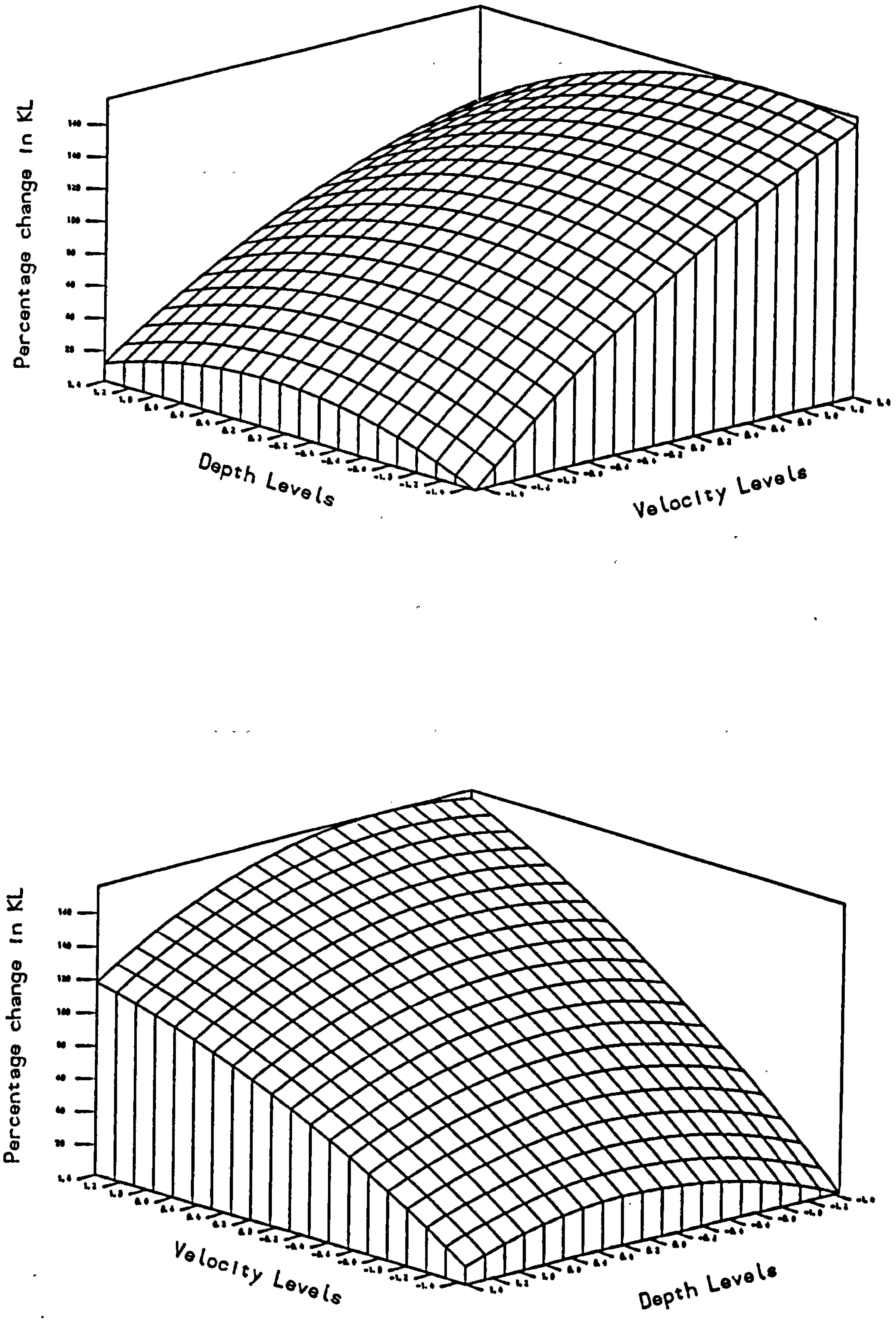


Figure 35: Three dimensional response surface for K_L

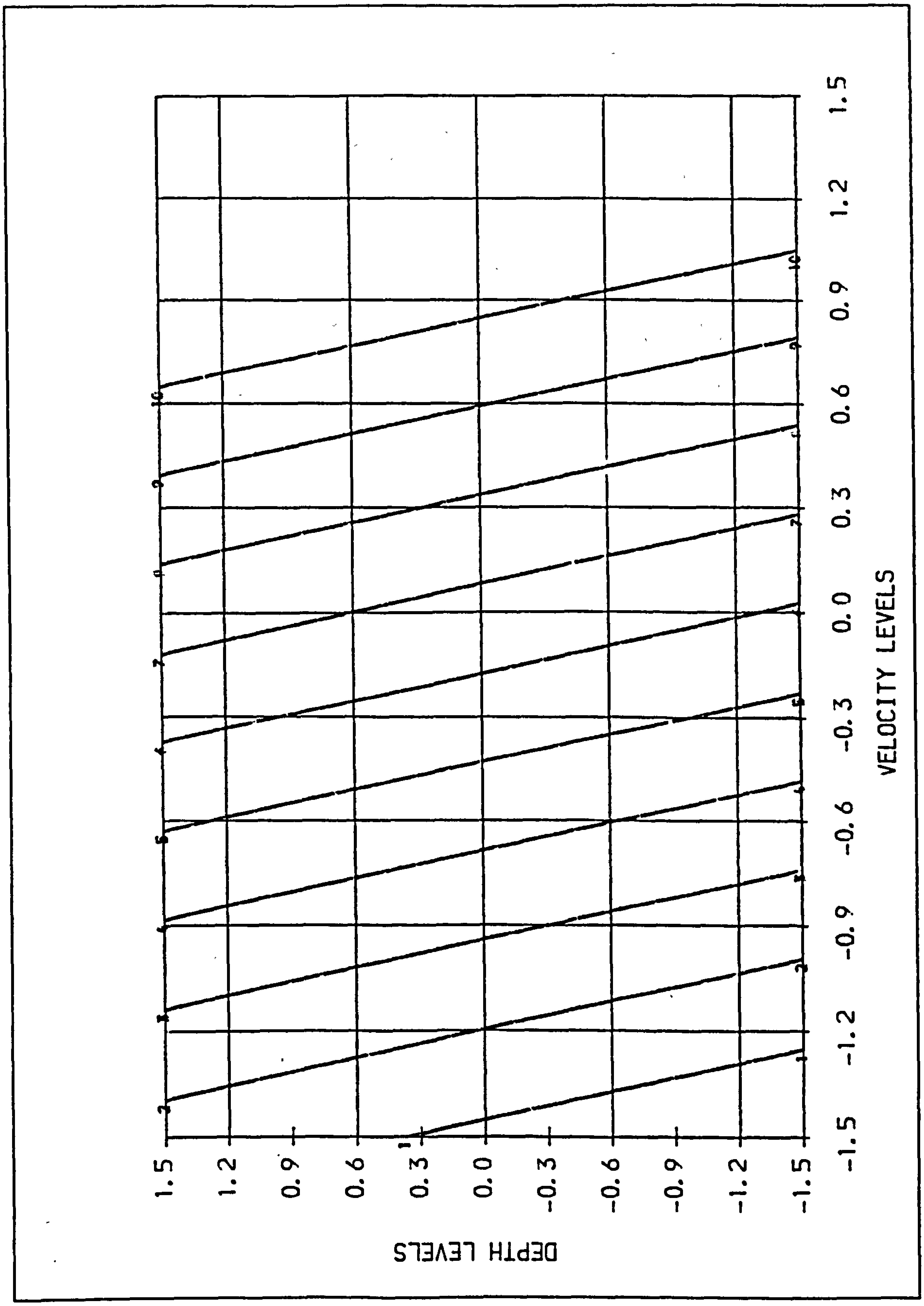


Figure 36: Surface contours for the velocity of solids dissolution V_s

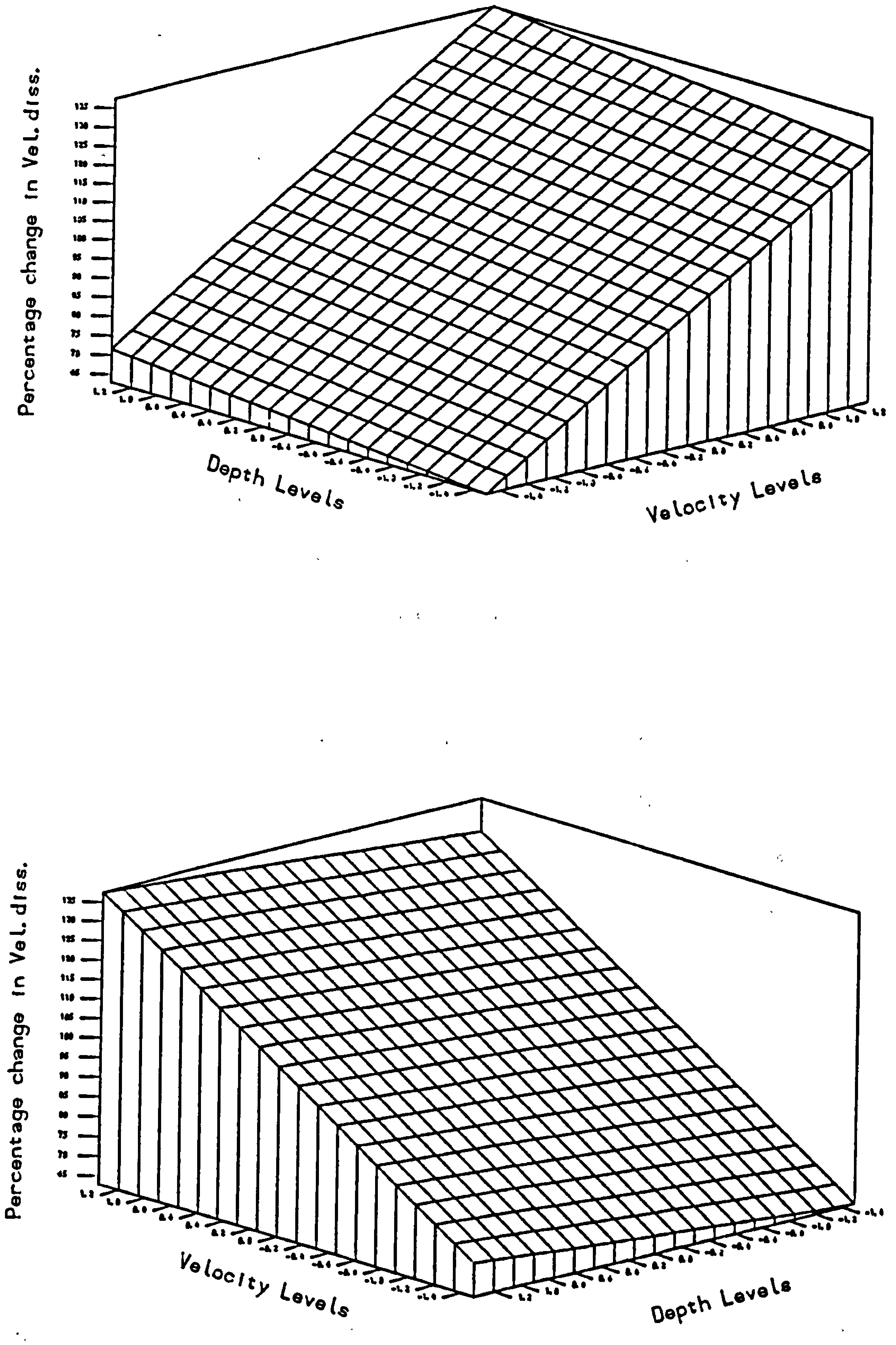


Figure 37: Three dimensional response surface for V_S

variation and behaviour in relation to the velocity x depth interaction effects. The second part is concerned with the variation of the two mass transfer coefficients, K_L and V_s, in relation to the same velocity x depth interaction effects.

As it is clearly shown in the first four figures (30 to 33), the reaeration and propane gas desorption processes appear to be very similar between each other. The maximum response for the two rate coefficients occurs at a region where velocity is maximum and depth is minimum, while the minimum response occurs when velocity is minimum and depth is maximum, as it would be expected according to most of the conceptual and empirical models relating the rate coefficients to relevant hydraulic variables.

The similar behaviour of the propane gas desorption process in relation to the reaeration process at the various simulated hydraulic conditions, seems to confirm the most important assumption of the modified gas tracer technique, that the K_2/K_p ratio is constant and independent of temperature and turbulent intensity. This ratio has been presently estimated to be 1.365 ± 0.030 (at the 10% level of significance), which is in perfect agreement with previous reported values (Rathbun et al.,1978, Rainwater and Holley,1984 and Bales and Holley,1986).

Furthermore, as it is suggested by the plotted response surfaces, the effect of depth upon the two rate coefficients appears to be significant only at higher velocities. In other words, a 60% change in depth (10.0 to 16.0 cm) at rapid flows can produce as much as 200% change in both K_2 and K_p, while the same 60% change in depth at slow moving conditions produces only an 80% change on the rate coefficients.

In reviewing the experimental results showing the relationship between the reaeration rate coefficient and depth of flow, Shulz (1985) and Shulz and Giorgetti (1986), demonstrated that most of the values of the power of depth in relation to K_2 are in the range -0.8 to -1.2, with mean -1.05, and also indicated that -1.0 is an average value which should not be carelessly used because of the following:

(i) the possible existence of a non-uniform DO concentration in the bulk of the liquid;

(ii) the presence of surface disruption, which increases the air-water contact area and consequently decreases the depth in the volume/area ratio;

(iii) the existence of greater scales of motion, such as secondary currents which also participate in the process of surface renewal;

It has been recommended that a thorough study be carried out in order to better understand the variations of the power of depth in relation to K_2 (Shulz and Giorgetti,1986).

The results herein obtained show that the power of depth in relation to K_2 can be as high as -1.26 at higher velocities (0.50 m/s) and that it can be as low as -0.40 at lower velocities (0.25 m/s). The same appears to apply to the propane gas desorption coefficient, with the power of depth being equal to -1.33 at higher velocity levels and equal to -0.47 at lower velocity levels. It is seen that no significant difference exists between the relationships of both K_2 and K_p with depth at either low or high velocity levels, thus confirming the use of hydrocarbon tracers for the determination of reaeration in streams.

The above findings have been substantiated by the compilation of 90 reaeration rate coefficients measured at various hydraulic conditions at several places in England and the U.S.A. (Zizon et al.,1978). The reaeration response to the velocity x depth interaction appears to produce the same sort of depth dependence. In another words, a weaker depth-dependence of the reaeration rate coefficient at slow moving flows which seems to become stronger as velocity increases (Appendices E.1 and E.2).

It has been also possible to show that the rate of energy dissipated, estimated from velocity of jet measurements (Appendices F.1), follows the above verified pattern with most of the energy being dissipated at low depth and high velocity conditions (Appendices F.2 and F.3). As it has been described before (Chapter 1), it is generally accepted that the rate of energy dissipation per volume of liquid aerated has a direct effect on the mass transfer rate, and is mathematically expressed by:

$$K_2 \alpha \epsilon^n \qquad (151)$$

where the exponent n of the rate of energy dissipated is usually between 0.0 and 0.5 (Shulz and Giorgetti,1986).

To expand the range of energy dissipation rates for the stream reaeration correlation, Roberts (1984) combined the data of Parkhurst and Pomeroy (1972) with the data compiled by

Bennett and Rathbun (1972). The combined data base consisted of 281 observations of oxygen transfer in streams and laboratory flumes over four orders of magnitude of specific power dissipation, $0.1 < (P/V) < 2300\ W/m^3$, where (P/V) was calculated from:

$$(P/V) = \frac{US}{\rho g} \tag{152}$$

His results indicate a reaeration coefficient proportional to $(P/V)^{0.808}$, with the 95% confidence limits for the power of (P/V) being between 0.776 and 0.840.

Based on 566 oxygen transfer rate observations in 24 streams in the U.S.A., Tsivoglou and Neal (1976) used an energy dissipation model to correlate their data, which has been later modified by Roberts (1984), who chose to express it as follows:

$$K_2 = 1.83\text{x}10^{-5}(P/V) \tag{153}$$

where the exponent of (P/V) is equal to unity.

In summarising the results obtained in an assessment of the steady-state propane gas tracer method for determining K_2, at two different locations in New York, U.S.A., Yotsukura et al.(1984) showed that the propane gas transfer coefficient was proportional to 0.50 power of the energy dissipated. It was stated, however, that this result was not intended for a generalised correlation, since it was based on three data points only.

One is therefore left with a controversial subject where a common relationship between the reaeration and energy dissipation has not yet been agreed, with the power of energy dissipation actually varying from 0.0 to 1.00.

The power of the energy dissipation rate has been herein estimated to be 0.78 in average, and thus appears to be in some agreement with previous studies. As it has been stated by Roberts (1984), Shulz (1985) and Shulz and Giorgetti (1986), the highest powers of the energy dissipated are explained by a particular case of very turbulent systems (Reynolds number range is between 4×10^4 to 1×10^5 in the present experiments) leading to surface disruption, which appears to be the case. Otherwise, the observed transfer rates agree closely with the surface renewal theory, i.e. situations where the air-water surface is unbroken, the power of the energy dissipation rate should be between 0.20 and 0.50.

The above results thus seem to further substantiate the experimental observation of a weak depth-dependence of both reaeration and propane gas desorption process at slow moving conditions, which becomes stronger as velocity increases, and also appear to be in accord with the existing theories of turbulence.

The second part, concerning the oxygen transfer coefficient and velocity of solids dissolution responses to the velocity x depth interaction are then discussed as follows.

As it is shown in Figures 34 to 37, both the oxygen transfer coefficient and the velocity of solids dissolution responses seem to be independent of depth, as it had been previously demonstrated by the 2^3 factorial design statistical analysis. The slight effect of depth shown in these figures were thought to be generated by noise, since there are neither physical or statistical basis for the consideration of such variations.

The most important effect to be considered is the velocity effect, which in this case appears to be controlling both processes. According to the mass transfer theories, an increase in water agitation can produce a considerable increase in the mass transfer coefficients. It is herein shown that a 100% increase in velocity produces about a 160% increase in the oxygen transfer response and about an 80% increase in the velocity of solids dissolution response.

It has been demonstrated that both the oxygen absorption and the solids dissolution processes have their main resistance to mass transfer in the liquid phase (Chapter 4). It has also been shown that the rate of mass transfer at a gas-liquid interface is almost an order of magnitude larger than would be predicted for a solid-liquid boundary due to the more mobile interface and to the lower damping of high frequency velocity components than at a fixed boundary (McCready and Hanratty,1984).

The results herein obtained have shown that the oxygen is being more effectively absorbed at higher velocities than the solid is being dissolved at the same flow conditions, suggesting, as expected, the existence of a limiting factor between the two processes.

A reasonable explanation for this limitation appears to be connected to the surface area of contact between the two phases, either gas-liquid or solid-liquid, since the physical processes of oxygen absorption and solids dissolution at the water surface seem to be very similar to each other as shown in Figures 35 and

Considering the case of oxygen being absorbed into a turbulent water body, the contact area between the gas and liquid phase is greatly increased by an increase in the level of turbulence of the water, and therefore the rate of oxygen absorption increases as the volume to surface area ratio decreases.

The case of benzoic acid being dissolved at the surface of a turbulent water body appears to be slightly different. It seems that the contact area between the solid and the liquid phases is practically the same both at low or high water turbulence levels, so that the rate of solids dissolution increases with increased water agitation (as shown in Chapter 4 and experimentally observed in the present study), but in a much lower rate than the oxygen is actually being absorbed at higher turbulence levels.

Although the present study confirms the findings of previous works on the development of a floating soluble solids technique for the measurement of reaeration rates in small streams, showing that there exists a definite and clear relationship between the reaeration and solids dissolution processes, care should be taken in understanding the main limitations of the solids dissolution method. In other words, it appears that a simple relationship between the two rate coefficients, as it has been obtained for the modified gas tracer technique, does not apply for the floating soluble solids technique. The ratio between the oxygen transfer coefficient and velocity of solids dissolution is not actually constant nor independent of turbulent and mixing conditions, as the reaeration to propane gas desorption coefficients ratio appears to be. As a matter of fact, the K_L/V_s ratio is rather a strong function of velocity of flow, as it will be discussed in the next chapter.

5.5 SUMMARY:

A total of 144 laboratory tests have been carried out to investigate the following:

(i) the individual and interaction effects of velocity, depth and roughness upon the reaeration rate coefficient, propane gas desorption rate coefficient, and velocity of benzoic acid dissolution at the water surface;

(ii) how the selected response variables are affected by a set of independent variables over some specified region;

(iii) what settings of the variables yields a maximum (or a minimum) response, and what is the response surface like close to this maximum (or minimum);

(iv) indirectly assess the modified gas tracer and floating soluble solids techniques for the determination of reaeration rates in streams;

The main conclusions drawn from the above tests can then be summarised as follows:

(i) the velocity factor is the most important effect to be considered in relation to all response variables studied; a 100% increase in velocity levels yields a 20% increase in both K_2 and K_p, and about 40 to 60% increase in V_s and K_L, respectively;

(ii) the effect of depth alone has been also found to be important; its general effect is to reduce the response variables (K_2 and K_p) as much as 10% in terms of the percentage about the mean;

(iii) the roughness factor was found to be irrelevant for the range of hydraulic conditions studied;

(iv) the interaction effect of velocity and depth has been further studied by response surface methods, which revealed the following:

- (iv.1) a weaker depth-dependence of both K_2 and K_p at low velocity levels ($K_2 \alpha h^{-0.40}$ and $K_p \alpha h^{-0.47}$);
- (iv.2) a stronger depth-dependence of both K_2 and K_p at high velocity levels ($K_2 \alpha h^{-1.26}$ and $K_p \alpha h^{-1.33}$);
- (iv.3) the above conclusions have not only been substantiated by the analysis of natural river data, which confirms the above experimental observations, but also by the analysis of energy dissipation response for the same hydraulic conditions;
    - (iv.3.1) the power of the energy dissipation rate in relation to K_2 has been estimated to be 0.78 in average, and found to be in reasonable agreement with the literature;
- (iv.4) both K_L and V_s have found to be depth-independent, as expected, and strongly affected by the velocity factor;

(v) the assumption that the K_2/K_p ratio is constant and independent of turbulent intensity and mixing conditions has been herein confirmed and estimated to be 1.365 ± 0.030, and also in agreement with previous reported values;

(vi) the physical processes of oxygen absorption and solids dissolution at the water surface seem to be very similar between each other;

(vii) it has been observed that the oxygen absorption at the gas/liquid interface is a more effective process than the solids dissolution at the water surface for the same hydraulic conditions;

(viii) it has been suggested that there exists a limiting factor between the two processes, most probably connected to the surface area of contact between the two phases, either gas-liquid or solid-liquid;

CHAPTER 6

The Mathematical Representation of the Relationship between Reaeration and Solids Dissolution Processes

Although the correlation between the reaeration and dissolution processes has repeatedly been observed (refer to Giorgetti and collaborators), its mathematical representation has proven difficult to obtain, apparently due to the scarcity of related data.

The only available mathematical representation, which express K_2 as a function of V_s, has been presented by Shulz (1985). It is based on the observation of both the reaeration coefficient and velocity of sodium chloride monocrystals dissolution variation within a turbulent agitated tank, and is given by:

$$K_2 = \frac{4.4 \times 10^{-4}}{60} + \frac{5.6 \times 10^{-2}}{Sc^{1/2}} \left[\frac{6000\ V_s - 1.9 \times 10^{-2}}{4.9}\right]^{0.60} \qquad (154)$$

An indirect approach has been employed for the derivation of the above model supported by the correlation verified for both K_2 and V_s against the incoming water flow to the tank. It appears, however, that no attempt has been made to evaluate the application of equation (154) to natural stream situations.

It is therefore the purpose of this chapter to describe the development of a mathematical equation directly relating the reaeration and solids dissolution processes, based on the overall experimental data (preliminary + subsequent tests) herein obtained.

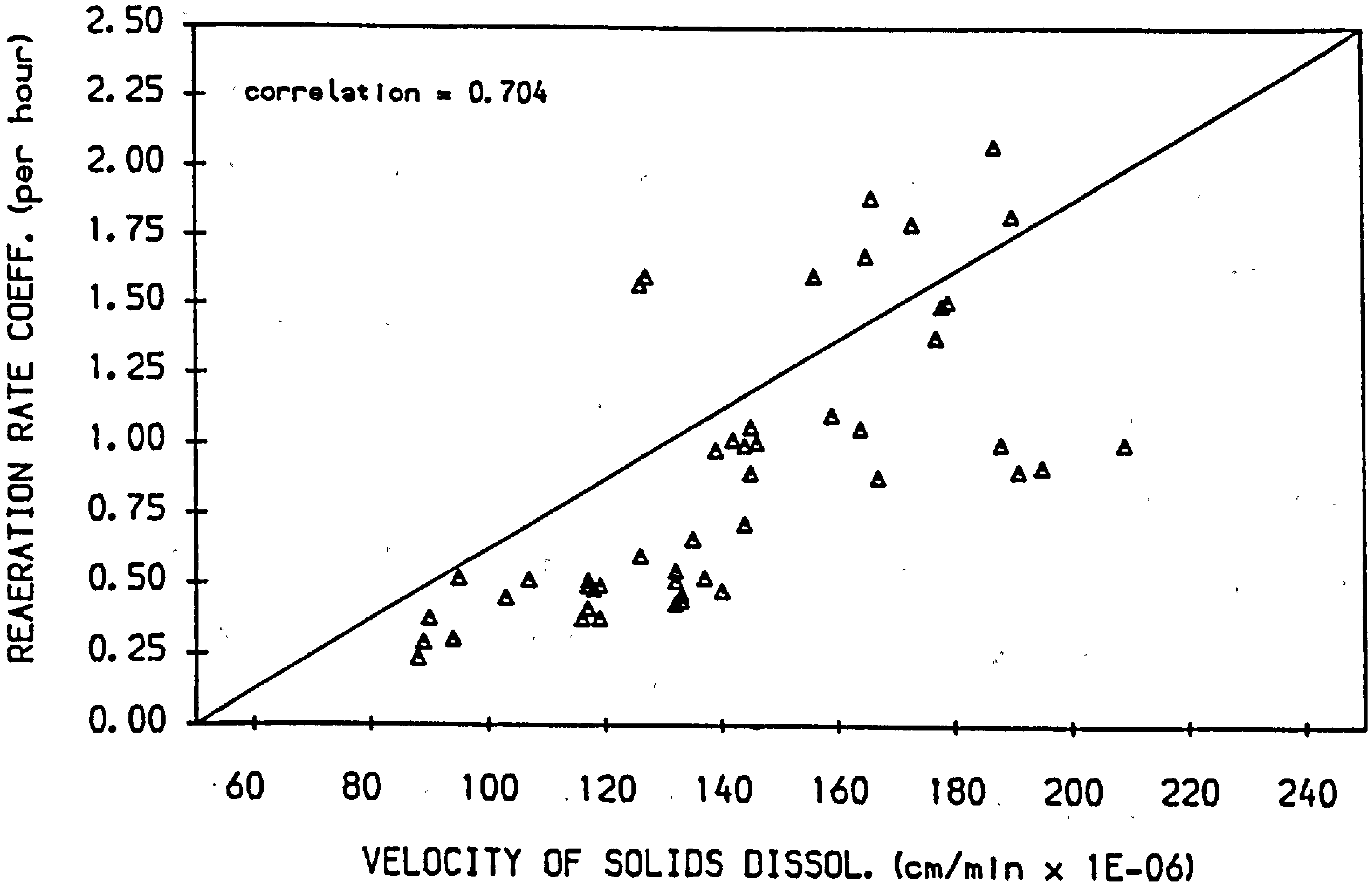
6.1 REAERATION x SOLIDS DISSOLUTION CORRELATION:

As a first step in the model building procedure, the correlation between the reaeration and dissolution processes is examined.

From 48 experimental observations at the various hydraulic conditions herein studied, it has been possible to obtain the two plots shown in Figure 38. The upper plot shows the data distribution and the correlation between K_2 and V_S. Although there is some scatter about the line of perfect correlation at high values of both K_2 and V_S, it is seen that a reasonable correlation exists between the two coefficients, which is statistically confirmed by a correlation coefficient value of 0.704. The bottom plot, between K_L and V_S, shows an even higher correlation ($r = 0.800$) and less data scatter than the previous plot, as would be expected.

Both K_L and V_S are depth independent, dimensionally compatible [L/T], and, as shown in Chapter 5, their response to both velocity and depth changes appear to be very similar. On the other hand, K_2 is a depth dependent coefficient, dimensionally incompatible with V_S, and its response surface is not as similar to that of V_S, as the K_L response surface. A less significant correlation should be thus expected between K_2 and V_S than between K_L and V_S, as indicated in Figure 38.

As previously concluded, there is neither theoretical nor experimental basis for the ratio between the reaeration characteristic coefficient (here expressed by K_L) and V_S to be constant and independent of turbulence and mixing conditions, as



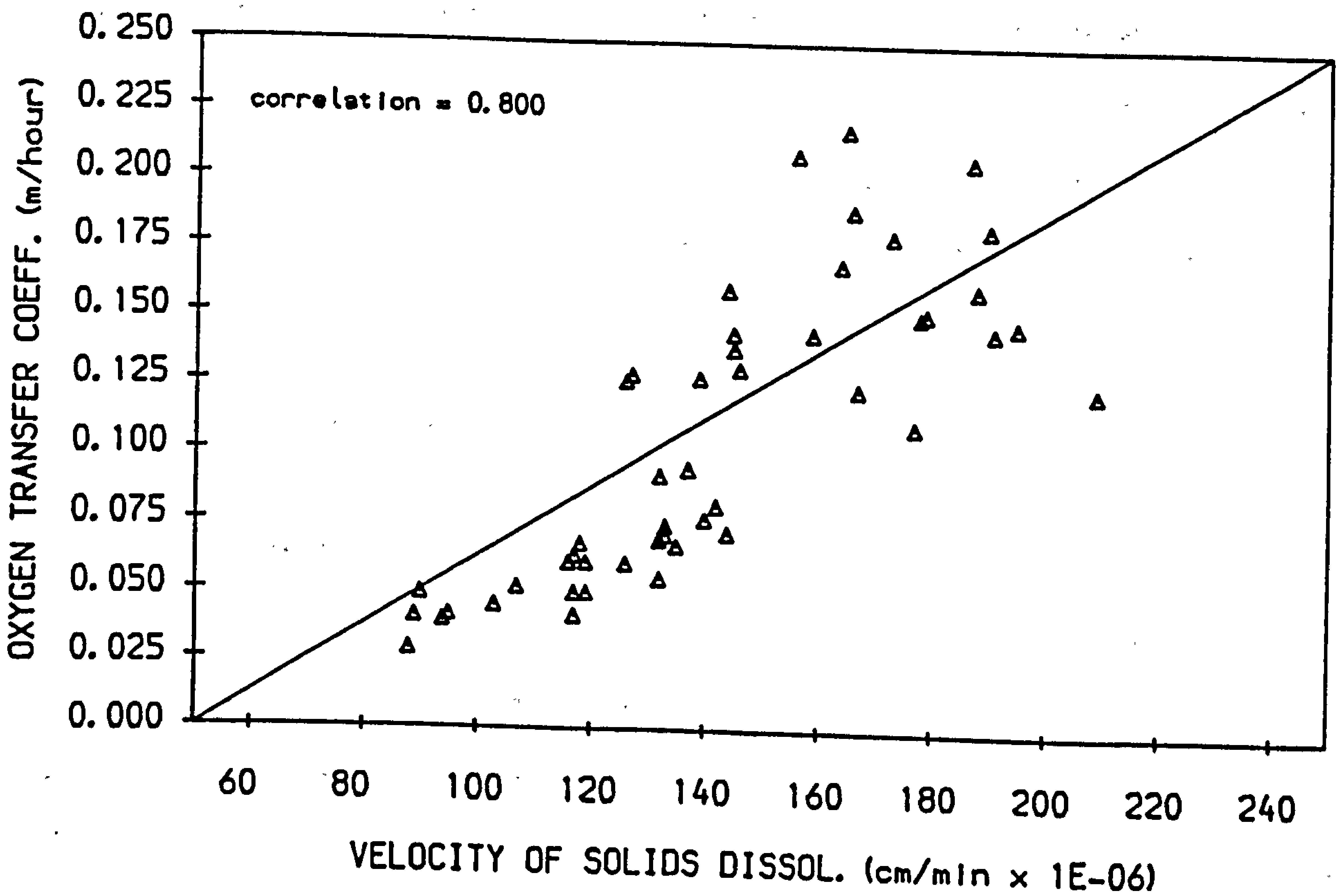


Figure 38: Reaeration x Solids Dissolution Correlation

a direct relationship would indicate. Actually, the two coefficients, K_L and V_s, vary differently with the water velocity (used as a measure of turbulence within the flume), probably due to the limited contact area between the solid and liquid phases when compared to the gas/liquid interfacial area (refer to Chapter 5 for discussion).

It has been therefore decided not to express K_L as a direct function of V_s, but to express the ratio between the two coefficients as a function of the level of turbulence within the system, here expressed by the average water velocity.

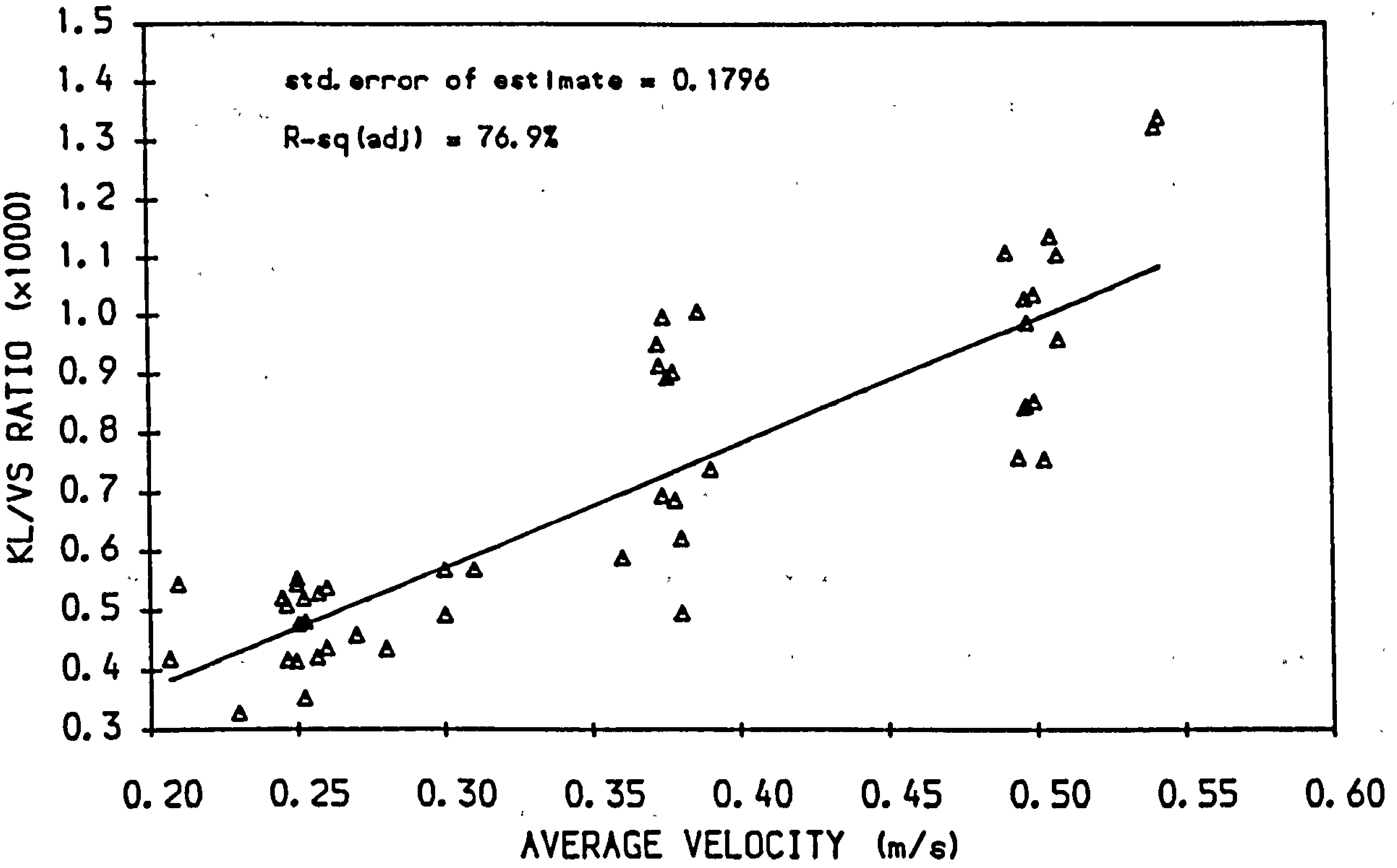
6.2 THE REAERATION/SOLIDS DISSOLUTION RATIO EXPRESSED AS A FUNCTION OF TURBULENCE:

Statistical analysis of the overall experimental data have indicated that a strong correlation is obtained when the ratio between the two mass transfer coefficients is plotted against the average velocity of flow (r = 0.87), as shown in the upper plot of Figure 39. The best curve fitted to the data is given by the following equation:

$$\frac{K_L}{V_s} = 2100.65\ U^{1.08} \qquad (155)$$

where K_L is the oxygen mass transfer coefficient in m/h, V_s is the velocity of benzoic acid dissolution in cm/min, and U is the average velocity of flow in m/s.

It is however observed that the relationship expressed by the above formula is not dimensionally sound. The same ratio K_L/V_s has then been plotted as a function of the Reynolds number in an attempt to overcome this limitation (see bottom plot of



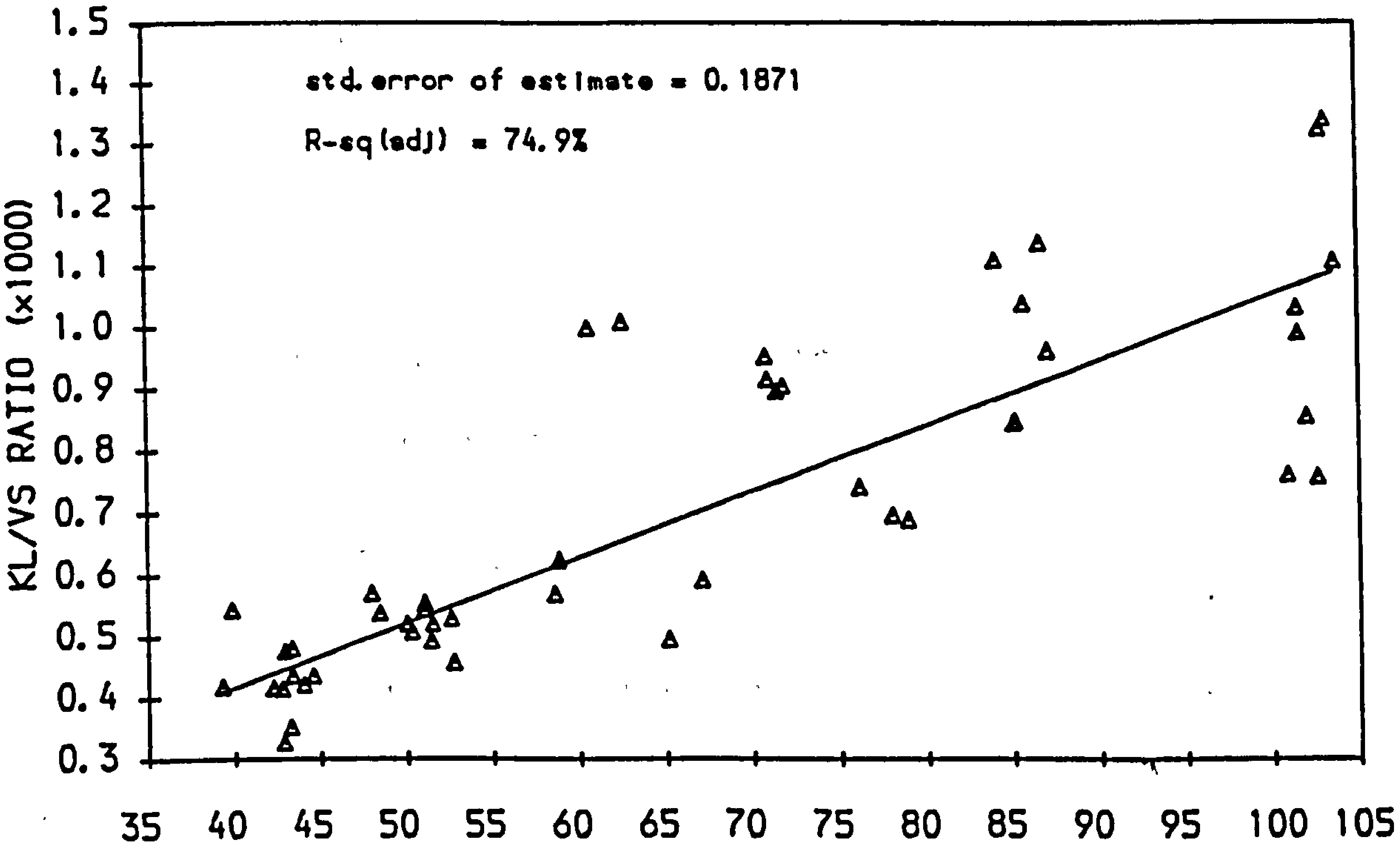


Figure 39: K_L/V_S ratio as a function of turbulence

Figure 39). There is no statistical evidence that the correlation between the two variables has been significantly reduced in this case (r = 0.84). The mathematical expression which relates the K_L/V_s ratio as a function of the Reynolds number is then given by:

$$\frac{K_L}{V_s} = 9.279\times10^{-3}\ Re^{1.01} \qquad (156)$$

where K_L is in m/h and V_s is in cm/min.

The above equation shows that there exists an almost linear relationship between the coefficients' ratio and the level of turbulence within the experimental system, expressed by the unity power of the Reynolds number.

It has been later verified that the above expression could be statistically improved by substituting the oxygen mass transfer coefficient by the actual reaeration rate coefficient, according to the following relationship:

$$K_2 = \frac{K_L}{H} \qquad (157)$$

where H is the average depth of water in the annular channel. Equation (156) then becomes,

$$\frac{K_2}{V_s} = 1.534\times10^{-3}\ \left(\frac{Re}{H}\right)^{1.15} \qquad (158)$$

where K_2 is the reaeration rate coefficient in hours^{-1}, V_s is the velocity of benzoic acid dissolution in cm/min, Re is the non-dimensional Reynolds number, and h is the average depth of flow in m.

The better fitness of this equation to the data has been statistically confirmed by the R^2 statistics, which is

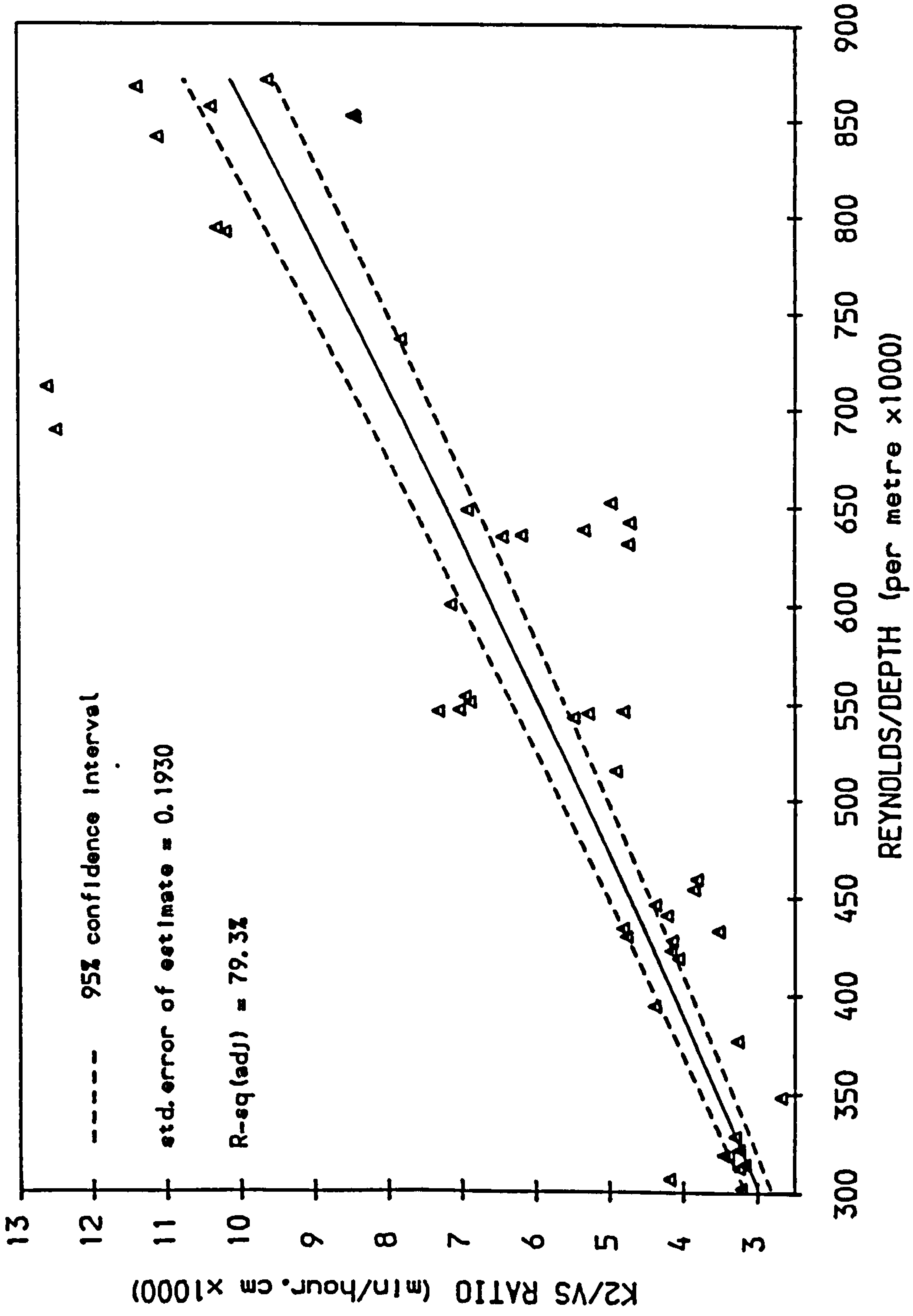


Figure 40: K_2/V_s ratio as a function of turbulence

defined as the proportion of total variation about the mean Y explained by the regression. It has been herein estimated to be 79.3%, as shown in Figure 40. The 95% confidence interval for the above has also been calculated and is shown by the broken lines in Figure 40.

The practical application of such a relationship for the determination of reaeration rates in less artificial conditions (e.g. long concrete lined channel) by the floating soluble solids technique will then be discussed in the next chapter.

CHAPTER 7

Field Measurement of K_2 and V_s

Preliminary Tests

A series of nine floating soluble solids and five disturbed equilibrium tests were carried out during the months of September and October of 1986. These have been conducted in a preliminary basis not only for the testing of the floating soluble solids technique in less artificial conditions than those found in the laboratory, but also for the acquisition of some experience on the measurement of the channel hydraulic characteristics (e.g. velocity of flow, depth and traveltime), and on the measurement of the reaeration rate coefficient by the disturbed equilibrium method.

7.1 THE WHITTLE DENE CHANNEL:

The Newcastle and Gateshead Water Company owns an old aqueduct, not entirely uniform, which carries clean water between several reservoirs, and is part of the Newcastle's main water supply system.

The masonry lined channel made in a rough rock cut, deeply pitted, with the Manning's roughness coefficient estimated to be about 0.025, is approximately 4.2 km long and located near a place called Harlow Hill, 25 km west of Newcastle upon Tyne.

The particular stretch of the channel which has been used for the present studies starts off with a top width of 4.10 m from the River Pont. The cross-section is constant throughout a distance of about 75 m, where a sluice gate is located. The canal downstream of the sluice gate has a top width of 2.70 m, which is maintained throughout a distance of 1.7 km when it narrows down to a width of 2.50 m. The remaining course is of constant trapezoidal cross-section, 2.50 m wide, 1.40 m deep, with side slopes 4:1 and bed slope of 0.0018 m/m. At a distance about 2.7 km of its total length, a Venturi meter is located, but it was not working at the time when measurements were taken.

The first 1.6 km of the channel which goes from the River Pont to Ouston Moor is reasonably uniform but has two main inconveniences which prevented us from using the entire reach in these experiments:

(i) it carries water through three long tunnels;
(ii) at a distance of about 80 m downstream of the second tunnel, a weir is located;

From the remaining 2.6 km, a study reach of about 1000 m was chosen, from the Ouston Moor to Dodley Road. Along this reach, three stations were located as follows (also refer to Figure 41):

(i) injection point, about 1.6 km downstream of the sluice gate;
(ii) upstream sampling point, about 320 m downstream of the injection point;
(iii) downstream sampling point, about 720 m downstream of the first sampling point;

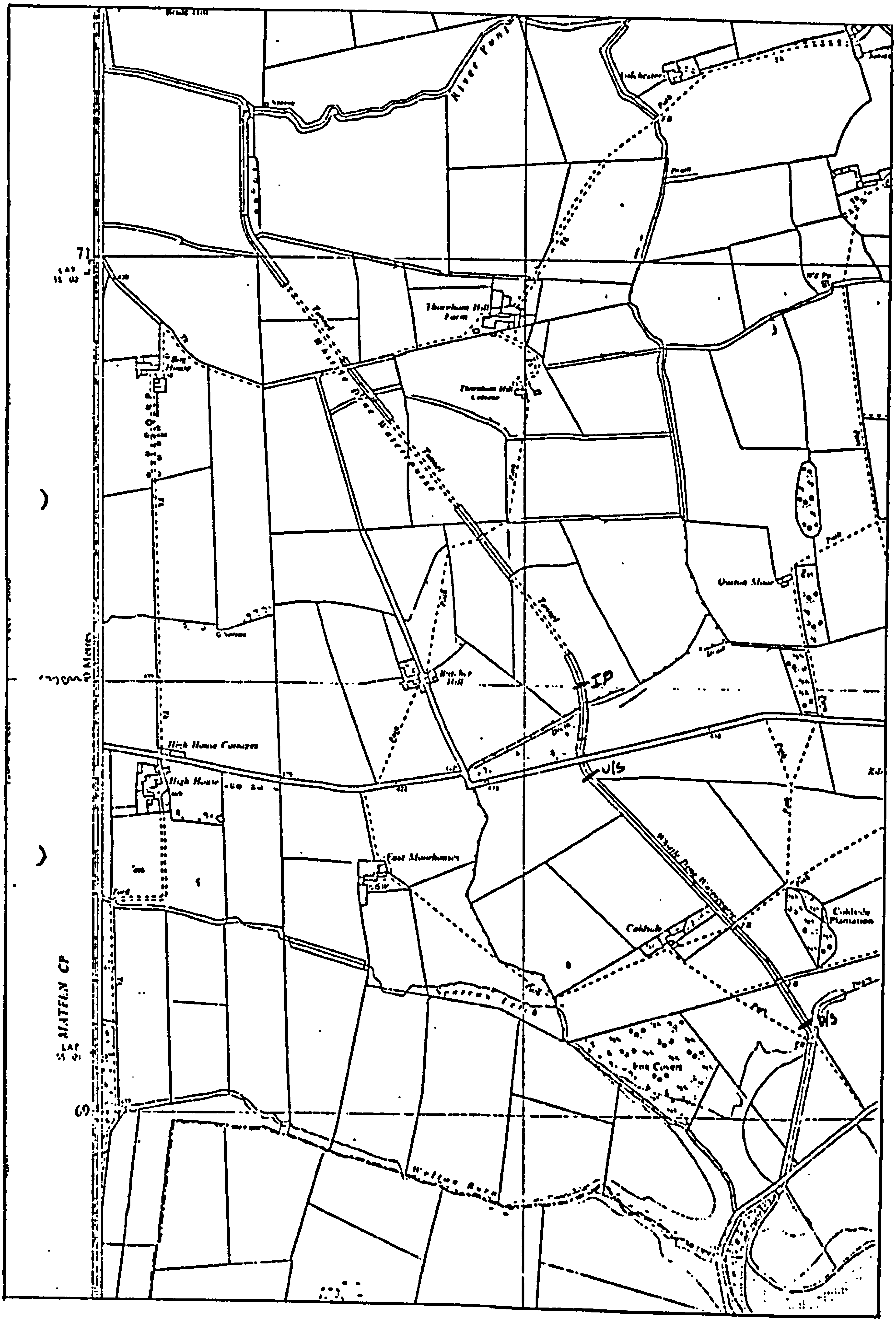


Figure 41: The Whittle Dene Watercourse
scale 1:10560

7.2 HYDRAULIC CHARACTERISTICS MEASUREMENT:

The water velocity was measured by a dilution method and a conductivity technique.

The chemical substance used as a tracer was sodium chloride (NaCl) with solubility of 360 g/l at 15°C. For concentrations up to 50 mg/l, the relation of its conductivity to concentration is substantially linear. The minimum concentration measurable with ±1% accuracy is 2.0 mg/l.

As discussed by Hubbard et al. (1982), following the injection of the tracer salt (or sodium sulphite solution in the case of the disturbed equilibrium method) in the centre of the stream, a considerable reach length may be required to complete lateral mixing. The following equation is suggested to estimate the length of the channel necessary for complete lateral mixing from a single point mid-channel injection (Hubbard et al.,1982):

$$L_m = 0.1 \frac{UW^2}{E_z} \qquad (159)$$

where E_z is the transverse mixing coefficient (m^2/s), given by

$$E_z = 0.2\ H\ u_* \qquad (160)$$

in which u_* is the shear velocity (m/s) defined by:

$$u_* = \sqrt{(g\ H\ S)} \qquad (161)$$

where U is the average water velocity (m/s), W is the channel width (m), H is the average depth (m), g is the acceleration of gravity (m/s^2) and S is the water surface slope in m/m.

This distance was estimated to be within the previously selected 300 m, so that the salt tracer would be completely mixed before it reached the first sampling site.

Field studies

A salt solution was prepared immediately prior to injection by dissolving about 3.0 kg of salt in an 8.0 litres container to produce a concentration of at least 2.0 mg/l at the downstream station.

The solution was then instantaneously injected at the centre of the flow and the electrical conductivity of the water was measured at 10 seconds intervals at the two sampling stations, during a period which includes the whole of the time taken for the injected solution pass the two stations. The conductivities were measured by two conductivity meters (PTI-58 and Jenway 4070) with automatic temperature compensation.

Since the relationship between conductivity and concentration is substantially linear, the traveltime of the peak concentration is given by:

$$t_p = T_p(n + 1) - T_p(n - 1) \qquad (162)$$

where t_p is the traveltime of the peak concentration, $T_p(n + 1)$ is the elapsed time to the peak concentration of the salt at the downstream station, and $T_p(n - 1)$ is the elapsed time to the peak concentration of the salt at the upstream station.

The average velocity of flow was then obtained by dividing the entire reach length by the traveltime of the peak salt concentration, as follows:

$$U = \frac{L}{t_p} \qquad (163)$$

The two conductivity meters were calibrated and checked for linearity before and after each experiment, according to the following procedure:

(i) the conductivity cell constant was adjusted according to the value given by the manufacturer;

(ii) the conductivity cell was then immersed in a demineralised water solution and adjusted for zero conductivity;

(iii) the conductivity cell was immersed, in a second step, into standard solutions with known concentrations of NaCl;

(iv) conductivity values were plotted against concentration values and a linear relationship should result, as shown in Figure 42;

The above procedure was considered to give the desired level of accuracy for the traveltime and average velocity measurements.

The depth of flow was measured in the centre of the channel cross section at about 200 m intervals, along the whole length of the study reach. A staff rule was used for these measurements, and the average depth was determined by computing the arithmetic mean of all observations.

The discharge could then be computed from velocity and depth measurements according to the continuity equation.

7.3 REAERATION RATE COEFFICIENT MEASUREMENT:

The reaeration rate coefficient was measured by the disturbed equilibrium technique, as described by Gameson and Truesdale (1959).

The method consists in the artificial removal of dissolved oxygen by the injection of a reducing chemical and observation of the DO concentration changes at two different sampling

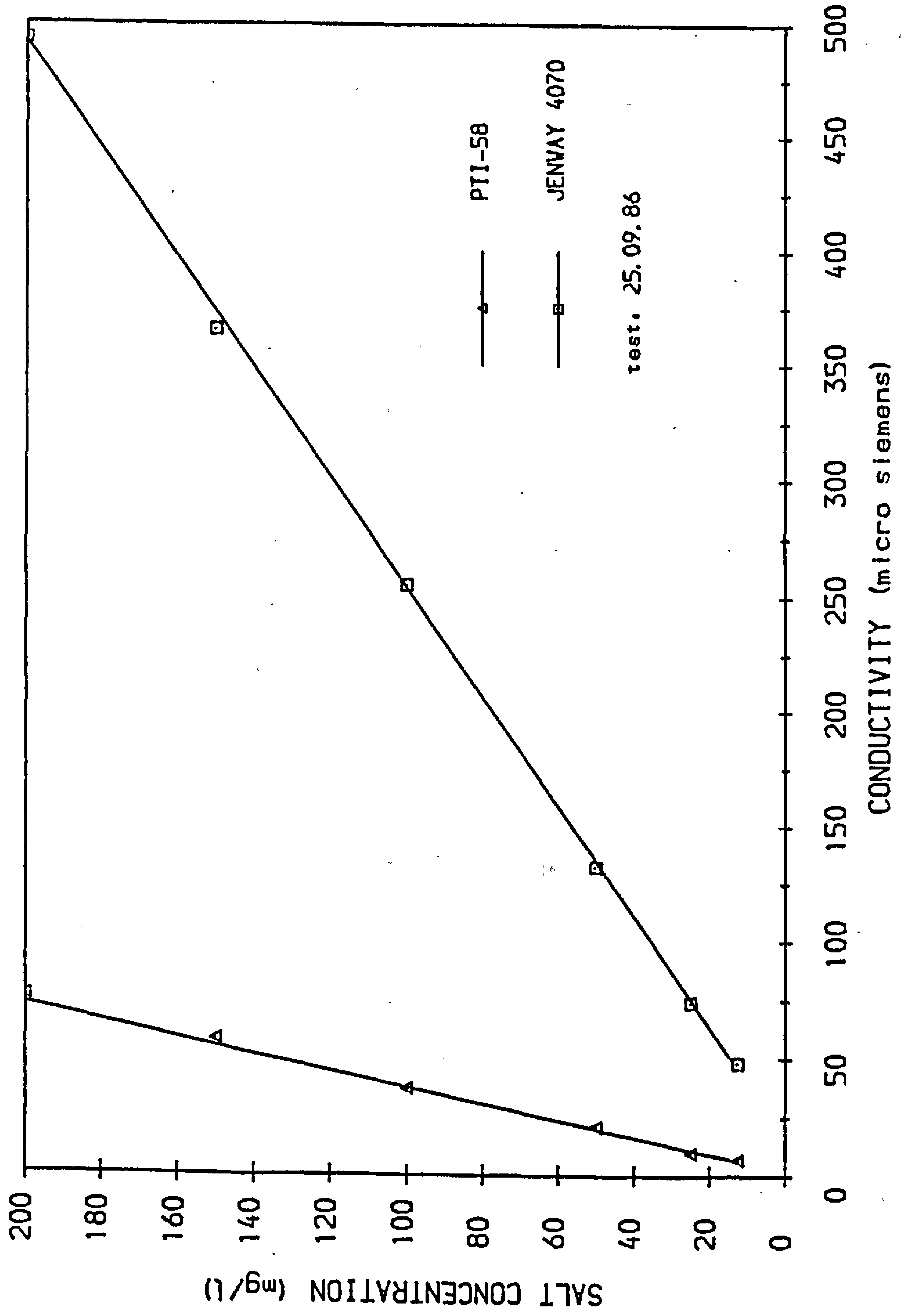


Figure 42: Linearity check for conductivity meters

stations during a certain length of time. A considerable oxygen depletion must be created to ensure that any error in measuring the integral of (C - C') is negligible relative to the accuracy in measuring the actual DO concentration. This can be achieved by a careful control over the quantity of sodium sulphite injected and the length of the study reach (Zogorski and Faust, 1973).

In order to create this oxygen deficit, a catalysed solution of sodium sulphite is introduced into the channel water. The quantity of Na_2SO_3 required to artificially remove a certain amount of DO is calculated from the following equation:

$$2Na_2SO_3 + O_2 + \text{catalyst} \longrightarrow 2Na_2SO_4 + 4H^+ \qquad (164)$$

The following expression was then used to calculate the required sodium sulphite dose:

$$\text{kg of } Na_2SO_3 \text{ per minute} = 0.4725.Q.D \qquad (165)$$

where Q is the stream discharge in m^3/s and D is the desired oxygen deficit in mg/l.

The required dose of cobaltous chloride was given by:

$$\text{g of } CoCl_2 \text{ per minute} = 60.0.Q.C_c \qquad (166)$$

where C_c is the desired concentration of $CoCl_2$ within the stream in mg/l (usually about 0.3 to 1.0 mg/l).

The dosing equipment consisted of two tanks of about 225 litres in volume each equipped with a discharge control valve. The sodium sulphite was dissolved and manually mixed in the two tanks previously filled with stream water. The initial mixing was done slowly and continuously to prevent the formation of large "cakes" of sodium sulphite on the bottom of the tanks.

Mixing of the sodium sulphite within the tanks was done immediately prior to injection.

The flow of the sodium sulphite solution discharged into the channel was controlled by a valve which was previously regulated to the desired flow rate of 24 l/min. The solution was injected by gravity directly in the centre of the flowing water in the channel. The sodium sulphite flow rate was maintained as constant as possible by transferring the solution from one tank to another in such a way that the level within the injection tank was kept constant. the time of injection was approximately estimated to be between 15 and 17 minutes in all tests.

The cobalt catalyst was added into the two tanks in a quantity to produce a concentration within the channel of about 0.5 mg/l.

The passage of the oxygen depleted water was monitored at the two selected sampling sites, about 724 m apart.

From the time of travel measurements, the elapsed time to the arrival of the leading and trailing edges of the oxygen depleted water could be estimated (refer to Hubbard et al.,1982 for details). Based on these times, samples were collected every three minutes during a period sufficient for the whole injected solution pass the station (estimated to be about 30 minutes).

Samples were collected either manually, or in a container in which the 250 ml standard bottles were immersed, being careful to avoid any bubble formation into the bottles. The DO was immediately fixed by the addition of 2 ml of manganous sulphate and 2 ml of sodium azide.

The oxygen content of the samples was later analysed in the laboratory by the Azide Modification of the Winkler Technique described in the Standard Methods (1985), using a micro burette with 0.02 ml precision.

Dissolved oxygen concentration values were then plotted against time, as shown in Figure 43. The reaeration rate coefficient was computed by the following equation:

$$K_2 = \frac{1}{t_p} \ln\left(\frac{N_1Q_1}{N_2Q_2}\right) \qquad (167)$$

where K_2 is the reaeration rate coefficient, t_p is the traveltime of the peak concentration, N is the area under the (C - C') versus time curve, and Q is the channel discharge. Subscripts 1 and 2 refer to the upstream and downstream sampling sites, respectively.

7.4 VELOCITY OF SOLIDS DISSOLUTION MEASUREMENT:

The velocity of benzoic acid dissolution was basically measured by the employment of the laboratory procedure, as described in Chapter 4.

The field procedure was therefore kept as simple as possible, and is described in the following:

(i) the solids were labelled and weighed in an analytical balance with 0.0001 g precision, to the nearest 1/1000g;

(ii) a set of ten floating soluble solids were exposed to the flowing water at the upstream sampling station and collected 724 m downstream, at the second sampling station;

(iii) from the 10 solids collected from the first run, eight of those were again exposed to the flowing water for the

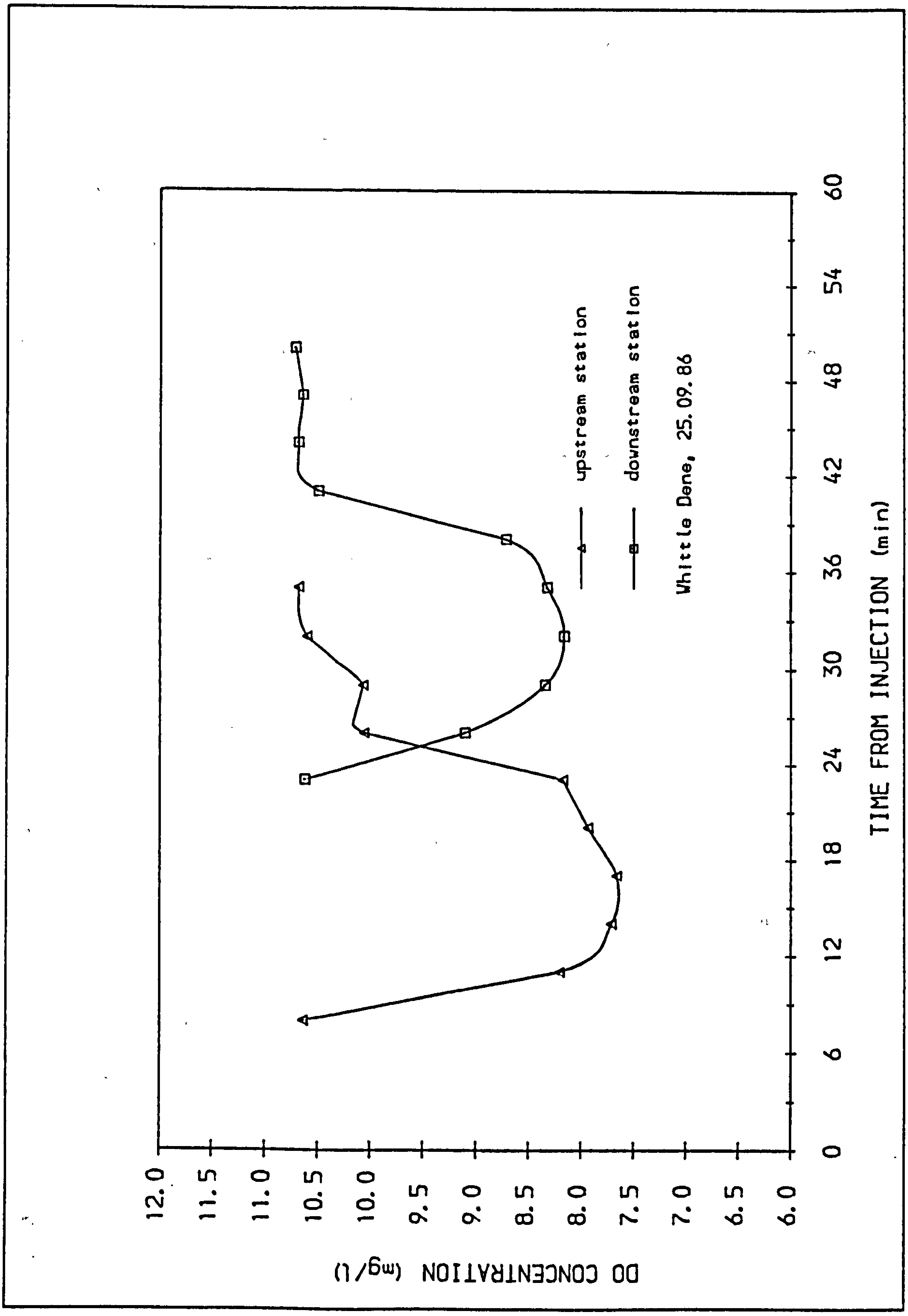


Figure 43: Typical disturbed equilibrium test

same 724 m, and then six, four and two solids in the next successive runs, totalizing 5 runs with replicate samples for each run;

(iv) the solids were stored into a common paper box and brought to the laboratory;

(v) the solids were left drying overnight at a constant temperature of 20°C;

(vi) the solids were weighed again in the following day and had their dissolution velocity determined by least squares analysis as already described (refer to Chapter 4);

7.5 RESULTS AND DISCUSSION:

The results obtained in these preliminary field tests are shown in Table 23 below. Predicted reaeration values computed from Churchill et al. (1962) equation - found to be the appropriate predictive model for the hydraulic characteristics of the Whittle Dene channel according to a method described by

Table 23: Preliminary field experimental results (Whittle Dene)

Date	U (m/s)	H (m)	Q (m^3/s)	$K_{2,20}$obs ($hour^{-1}$)	$K_{2,20}$pred* ($hour^{-1}$)	$V_s \times 10^{-6}$ (cm/min)	$K_{2,20}$pred** ($hour^{-1}$)	Temperature (°C)
10.09.86	0.71	0.78	1.38	1.0941	0.1473	96.0	2.225	11.8
16.09.86	0.98	0.88	2.16	0.2547	0.2420	103.0	3.271	11.9
18.09.86	0.83	0.87	1.81	0.1329	0.1602	98.0	2.585	11.3
25.09.86	0.82	0.92	1.89	5.3800	0.1305	106.0	2.685	12.5
30.09.86	0.79	0.87	1.72	0.0212	0.1403	100.0	2.492	13.2
13.10.86	0.83	0.82	1.70	-	0.1923	102.0	2.766	11.2
14.10.86	0.84	0.81	1.70	-	0.2063	100.0	2.764	11.3
15.10.86	0.89	0.80	1.78	-	0.2505	101.0	3.001	11.3
16.10.86	0.82	0.83	1.70	-	0.1793	101.0	2.724	11.4

$K_{2,20}$pred* is the reaeration coefficient predicted by Churchill's et al. (1962) equation
$K_{2,20}$pred** is the reaeration coefficient predicted by the K_2/V_s relationship

Covar (1976) - and from the derived K_2/V_s relationship were also included.

The most significant correlations among the relevant hydraulic variables, predicted and observed reaeration coefficients were then obtained, and are as follows:

Table 24: Correlation coefficients (Whittle Dene)

VARIABLE	velocity	depth	discharge	K_2obs	K_2pred*	K_2pred**
depth	0.324					
discharge	0.898	0.705				
K_2obs	-0.134	0.459	0.066			
K_2pred*	0.781	-0.332	0.429	-0.440		
K_2pred**	0.979	0.228	0.835	-0.040	0.829	
V_s	0.534	0.651	0.690	0.670	0.132	0.596

It is clearly shown that although no significant velocity and depth changes have been verified in the five disturbed equilibrium tests, the observed K_2 values varied widely. Very poor correlations have been obtained between K_2obs and the three hydraulic characteristics (velocity, depth and discharge), and also between K_2obs and K_2pred*. It appears that only the K_2 values observed in the second and third tests are in some agreement with the predicted values from Churchill's et al. (1962) equation.

As it has been discussed in Chapter 2, the disturbed equilibrium method for the measurement of the reaeration rate coefficient can be successfully applied if careful consideration of its main assumptions and inherited limitations are taken into account.

Although every effort has been made in order to improve as much as possible the actual data collection with the available equipment, no practical attempt has been made to verify the complete vertical and horizontal mixing of the oxygen depleted water, which must occur before the first sampling point is reached. The assumption that all sources and sinks of DO (except atmosphere reaeration) are constant and not affected by the sulphite for the reach during the period of measurement has not been practically verified either.

Problems with the injection equipment, especially related to the maintenance of constant sulphite flow rate have been experienced in the last half of the injection period and should be considered as an important source of error in these preliminary experiments.

It appears that the failure to comply exactly with the main assumptions concerning the application of the disturbed equilibrium technique plus the introduction of both procedural and random experimental errors (as listed by Hovis et al.,1982), led to the acquisition of rather inaccurate data.

Apart from the necessary improvements concerning the injection equipment and sampling procedure for future disturbed equilibrium tests, it seems that velocity monitoring based on time of travel measurements only is not adequate for the level of study required. Cross sectional velocity measurements both at injection and at the two sampling sites are highly desirable.

These preliminary tests also suggest that the velocity of solids dissolution parameter correlates reasonably well with the three relevant hydraulic variables, as it was previously observed in the laboratory studies. It is shown however, that a poor correlation has been verified between V_s and the reaeration coefficient computed by Churchill's et al. equation.

The reaeration rate coefficient computed from velocity of solids dissolution measurements is, on the other hand, highly correlated with both the hydraulic variables and K_2pred*, thus indicating that the relationship developed between K_2 and V_s from laboratory data might be successfully employed to other flow situations. The above result must be however cautiously considered since it is based on a few data points only. Further tests are needed to better clarify this evidence.

7.6 SUMMARY AND CONCLUSIONS:

A series of nine field tests have been carried out, in a preliminary basis, to investigate the following:

(i) velocity of benzoic acid dissolution response when the floating soluble solids method is applied to totally different flow conditions from those found in the laboratory;

(ii) if the disturbed equilibrium and the floating soluble solids methods are comparable in terms of the observed reaeration rate coefficient;

The results obtained allow us to conclude that:

(i) reaeration measurements by the disturbed equilibrium technique were found to be inaccurate due to the failure in complying with the main assumptions concerning the application of the method;

(ii) sodium sulphite injection equipment and procedure, water sampling and water velocity monitoring must be improved and modified, so that the disturbed equilibrium technique can be successfully applied;

(iii) the velocity of solids dissolution parameter was found to be a function of the hydraulic characteristics of the channel, as previously verified in the laboratory;

(iv) the reaeration rate coefficient predicted from velocity of solids dissolution measurements is in good agreement with the measured hydraulic variables, and as a consequence, it is also in agreement with the predicted K_2 values computed from Churchill's et al. equation;

(v) further studies are needed to better evaluate the application of the floating soluble solids method for the measurement of K_2 in small streams;

CHAPTER 8

Field Measurement of K_2 and V_s

Subsequent Tests

Subsequent field experiments have been planned based on the conclusions drawn from the preliminary tests. Another concrete lined channel has been selected with equipment and procedure modifications being introduced in an attempt to improve the accuracy of the measured reaeration rate coefficient.

Measured reaeration rates by the floating soluble solids method are compared to both disturbed equilibrium and steady state propane gas tracer methods results, and also to empirical predictive equations.

8.1 THE HALLINGTON CHANNEL:

The Hallington channel is another rough (Manning's roughness coefficient n=0.022), deeply pitted, concrete lined channel owned by the Newcastle and Gateshead Water Company, which carries water from the Hallington Reservoir to the Whittle Dene channel, and then to the Great Northern Reservoir near Harlow Hill.

This channel runs through farm lands for about 2600 m until it reaches the Fairspring (as in Figure 44), which in turn makes the connection to the Whittle Dene channel. It is located about 40 km north-west from Newcastle upon Tyne.

The particular reach of interest selected for these experiments is about 630 m long, 2.50 m wide, reasonably clean and uniform. Its bed slope has been determined from level measurements and estimated to be 0.00168 m/m.

Selected sampling sections were located 320 m apart, and the injection site was located about 310 m upstream of the first sampling station, just besides the South Farm, as indicated in Figure 44.

Various incoming water flow points (spring water) have been identified both upstream and downstream of the selected study reach. In order to avoid discharge variations within the latter, and also because of the limited budget available for these field test, it has been decided not to use the former stretches.

Submersed waterweeds growth (mainly *Potamogeton* and *Elodea*) and sand deposits have been observed all along the 2600 m of channel length, but which, as verified later, did not significantly affect the reaeration measurements.

8.2 EQUIPMENT AND PROCEDURE MODIFICATIONS:

Various modifications have been introduced in an attempt to reduce the experimental error in the reaeration rate coefficient measurement.

The first step in planning the experiments, after the study reach had been selected, was to make a practical evaluation of its hydraulic characteristics.

Diurnal DO variations have been also observed during the months of June and July of 1987, when the actual reaeration rate measurements by the disturbed equilibrium technique were taking place, in order to verify the effect of primary producers on the

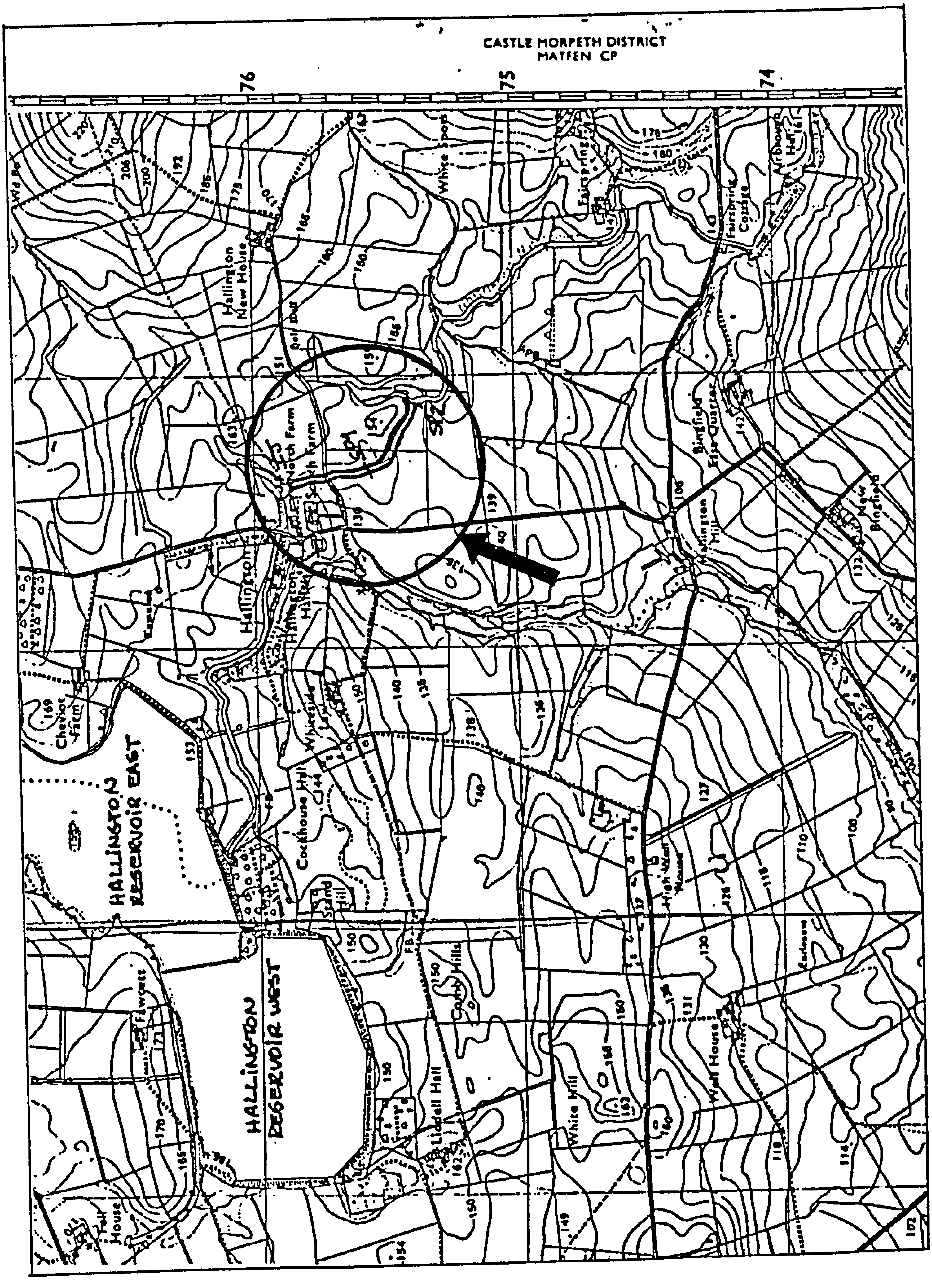


Figure 44: The Hallington channel

measurement of K_2 within the selected study reach.

Carefully planned disturbed equilibrium experiments were then followed by the propane gas tracer tests in order to attempt some sort of comparison between these two methods and the floating soluble solids method, in terms of the measured K_2 value.

8.2.1 Time of Travel Measurement:

Because the impossibility of using a dye tracer (such as Rhodamine-WT) for the time of travel measurements, due to the Newcastle and Gateshead Water Company restrictions, sodium chloride was again used for such measurements.

The salt solution was prepared and injected according to the procedure previously described in section 7.2, but in these subsequent studies data have been collected to produce a full suite of time of travel information, so that the study included the following:

(i) independent measurement of stream discharge at the injection and at the two sampling sites with a braystroke current meter;

(ii) measurement of the entire salt tracer curve, or until a concentration (conductivity) equal to or less than 10% of the peak was reached (refer to Figure 45);

(iii) measurement of the salt tracer curve made with conductivity meters at the centre of the flow;

Sufficient data was then provided to determine the time of travel of the leading and trailing edges, peak and centroid of a

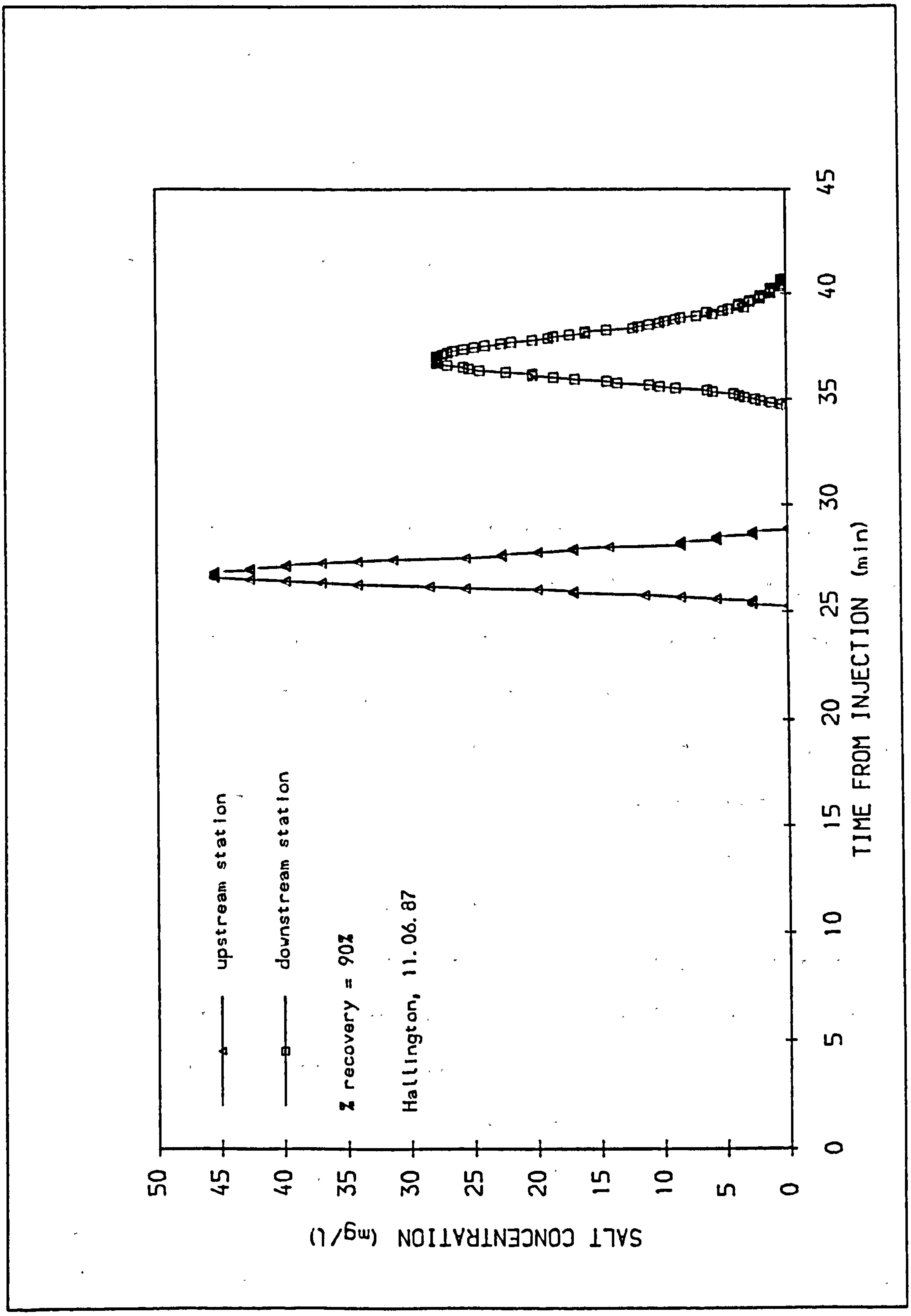


Figure 45: Typical salt tracer curves for traveltime information

solute for a particular stream discharge (refer to Hubbard et al., 1982 for detailed information).

Stream velocity and traveltime were then related to the stream discharge by the following equation:

$$t = 8.41\ Q^{-0.275} \tag{168}$$

which is represented by a straight line when the time of travel is plotted against discharge in logarithmic scales, as shown in Figure 46.

8.2.2 Water Quality:

Water quality data collected in the study area from March and July of 1987 are presented in Table 25. Data collected at both sampling sites indicate that the channel water is of good standard and not subjected to pollution.

Physical water quality characteristics measured during the study were total and suspended solids, water temperature, colour and turbidity, along with visual observations of solids, floating material and deposits.

Suspended solids are generally related to stream turbidity and its several sources within the Hallington channel were identified to be, as follows:

(i) sediment washed off the watershed;

(ii) sediment scoured from the stream bed at particular locations;

(iii) particulate matter discharged by the reservoir upstream of the channel;

Suspended solids concentrations within the stream vary as new

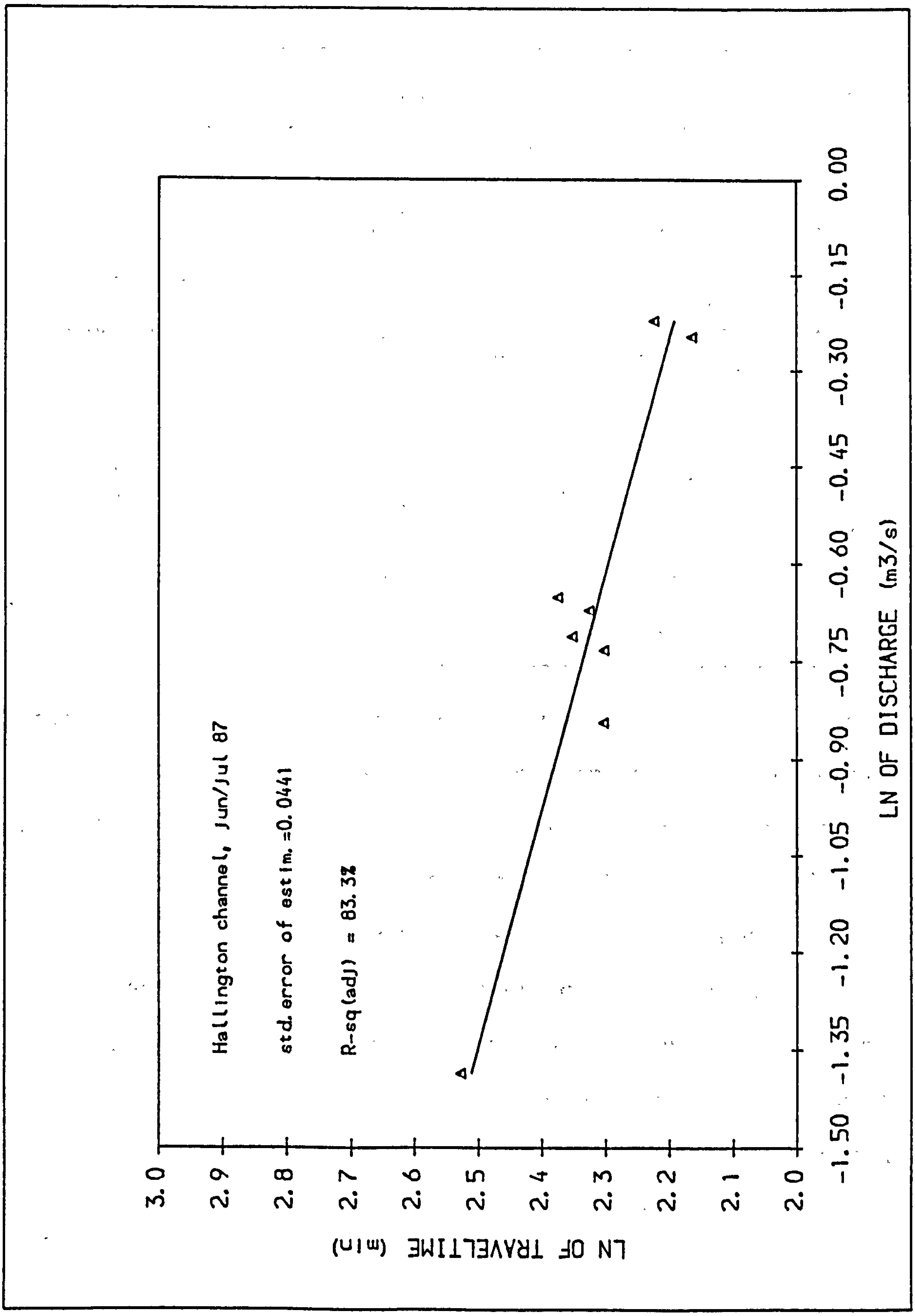


Figure 46: Traveltime versus discharge (Hallington channel)

Table 25: Chemical, physical and bacteriological analyses Hallington channel

Analysis	March	May	June	July
Colour (Hazen)	1.3	1.7	1.8	1.5
Turbidity (NTU)	1.5	1.9	2.3	1.7
Susp.solids (mg/l)	2.0	2.2	2.8	2.4
Total solids(mg/l)	144	160	196	152
Hardness (mg/l of $CaCO_3$)	220	231	227	210
pH	7.6	7.4	7.7	7.5
Temperature (^oC)	4.0	10-12	12-13	15-16
DO (mg/l)	14.2	9.4-13.4	8.9-10.1	8.3-9.0
$BOD_{5,20}$(mg/l)	4.0	3.4	3.8	3.6
Total nitrogen (mg/l)	4.1	3.1	3.2	2.8
NH_3-N (mg/l)	1.1	-	1.0	-
NO_3-N (mg/l)	3.1	1.6	0.6	0.3
Phosphates (mg/l)	-	-	-	-
Total coliforms (/100 ml)	40	50	58	43
F.Streptococci (/100 ml)	8	12	17	10

sources are added, as particles are deposited or resuspended, and as organic matter is produced and consumed. Its concentration within the channel water was found to be practically constant, ranging from 2.0 to 3.0 mg/l. Turbidity and colour were also found to be very low, ranging from 1.5 to 2.3 NTU, and from 1.3 to 1.9 Hazen, respectively.

Surface water temperature varies continually in response to changes in solar radiation and changing seasons. Temperature is highest at midday and lowest at early morning hours. Water temperature in the Hallington channel varied from 9.0 to 17°C during the study period.

Chemical water quality characteristics measured during the study were pH, DO, BOD, hardness and nutrients.

The pH of most natural waters ranges from 6.0 to 8.5 units.

Where photosynthesis by aquatic organisms takes up dissolved carbon dioxide during the daylight hours, pH may fluctuate, and the maximum pH value may sometimes reach as high as 9.0 units. Continuous monitoring of pH during 24 hours surveys revealed no significant variations, probably due to the low primary productivity at the time measurements were taken (June and July 1987).

The DO concentration of flowing water is highly variable. Oxygen in streams is consumed by bacterial decomposition of suspended, dissolved, and deposited organic matter, oxidation of ammonia by nitrifying bacteria, and the respiration of aquatic organisms. Oxygen is replenished in natural water primarily by reaeration, and photosynthesis.

Dissolved oxygen concentration of the Hallington channel was measured at about 2 hours intervals during each 24 hour sampling period, together with temperature and pH monitoring. Dissolved oxygen concentrations within the channel water, during the months of June and July (1987), ranged from a minimum of 8.3 to a maximum of 10.1 mg/l. Mean daily DO profiles are shown in Figures 47 and 48.

The DO concentration was generally lowest in the early morning hours due to the cumulative night time respiration and absence of production. Differences between night time and midday DO concentrations at the two sampling sites indicate that photosynthetic activity was not significant during the period of study. Community respiration always exceeded photosyntetic activity. According to Duffer and Dorris (1966), unpolluted

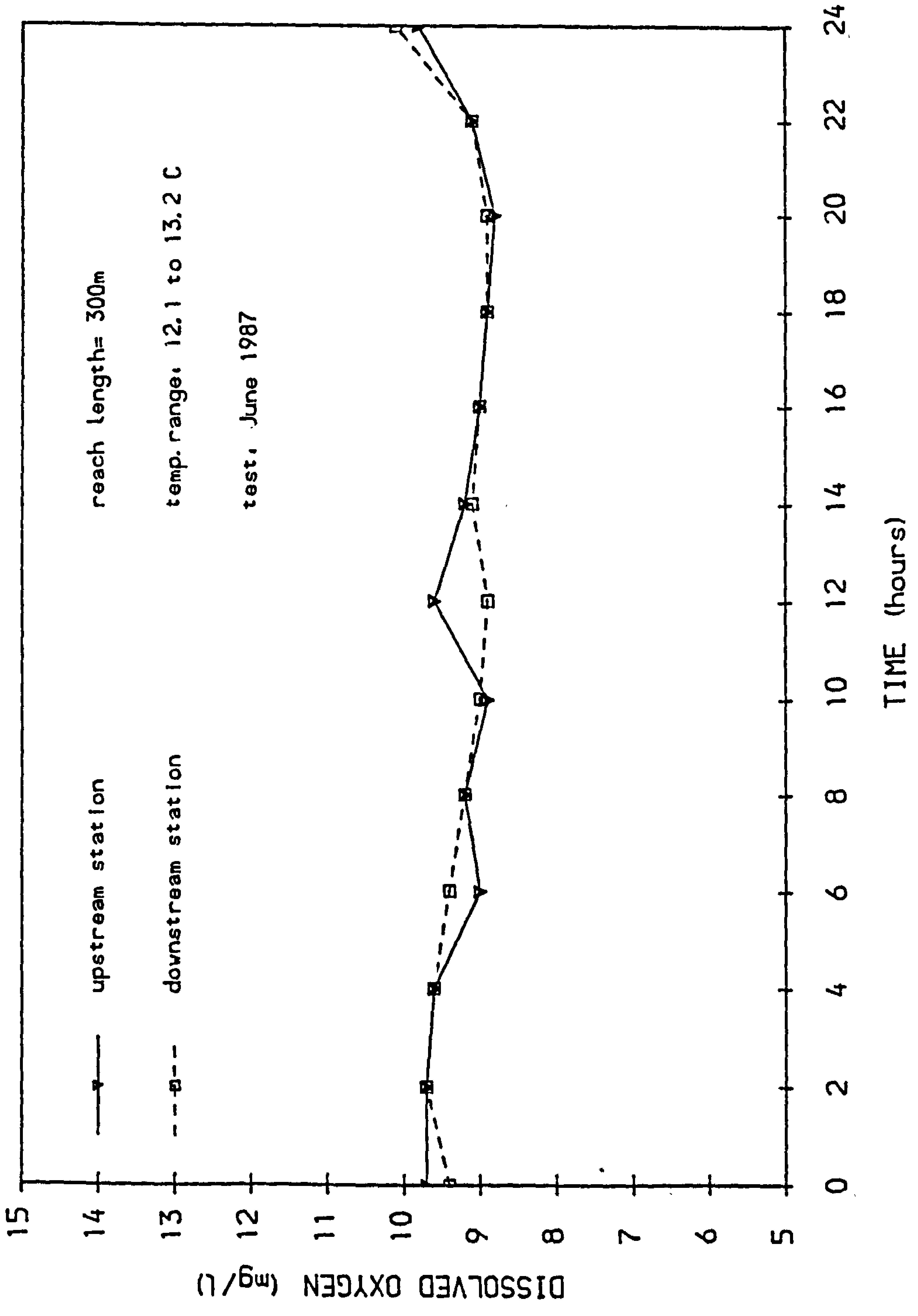


Figure 47: Diurnal curve variation (June 1987)

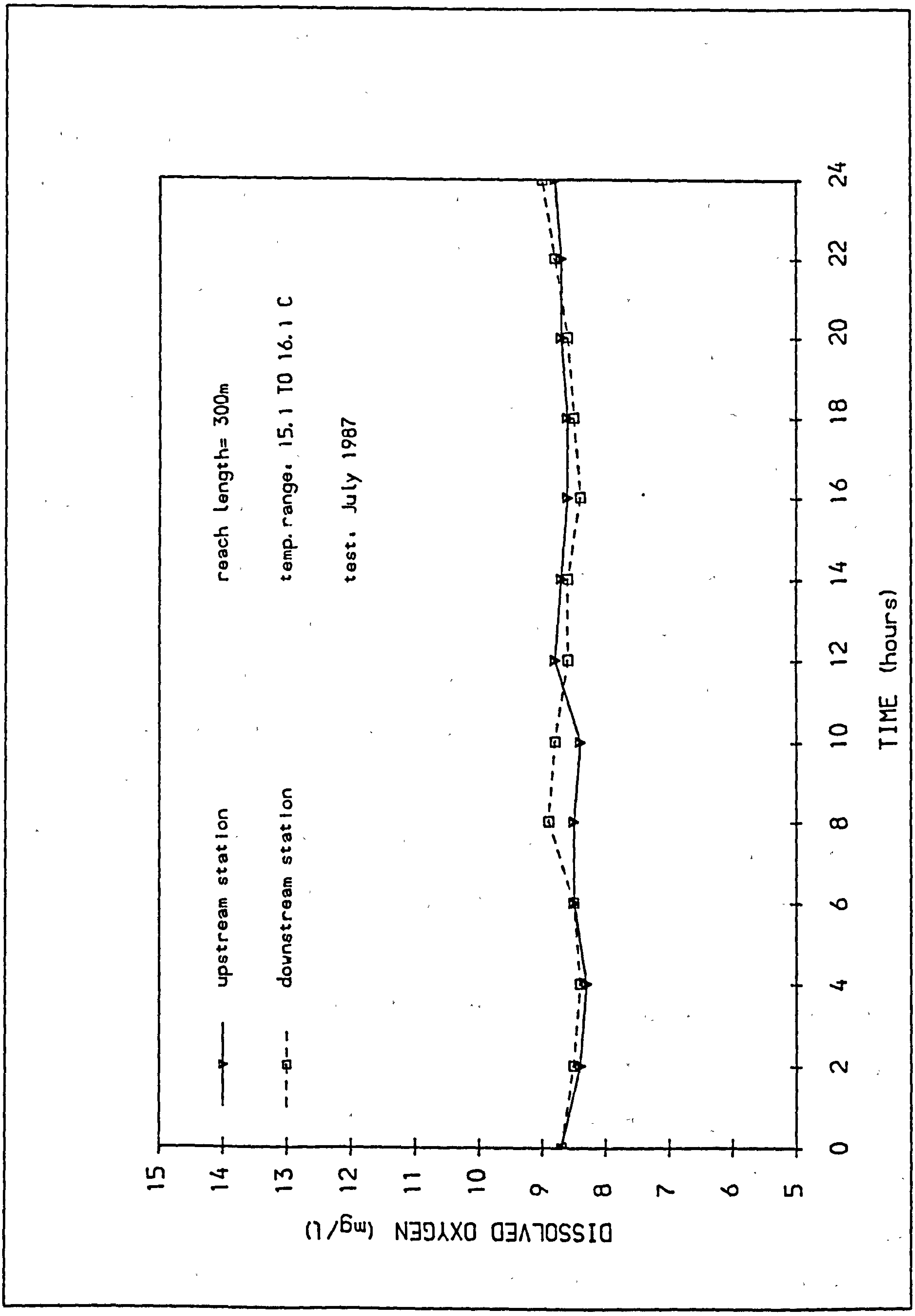


Figure 48: Diurnal curve variation (July 1987)

streams generally have lower productivity. The ratio of productivity to respiration (P:R ratio) within the study reach was found to be as low as 0.40, following a computation procedure described by Vollenweider (1969). Low primary productivity values have apparently resulted from small populations of benthic producers in the sand banks (agglomeration of organic matter, silt and sand where dead vegetation seemed to occupy most of its volume) generally located at areas of low velocity flows. These sand banks were the substrate for higher rooted plants (*Potamogeton* and *Elodea*), apart from the fact that aquatic life finds in these obstructions a suitable place for breeding, giving rise to the decomposition cycle where anaerobic processes develop a few centimetres of the mud surface. Worms, molluscs and invertebrates were satisfactory living attached to the plants or to the mud itself.

No significant contributions to the oxygen balance were verified due to either macrophytes or periphyton within the selected study reach.

The biochemical oxygen demand is a two-stage reaction defining the quantity of oxygen used by organisms in the water column as they consume organic material. Demands can be defined for any period of time, and the maximum quantity of DO required for the complete assimilation of organic material in a given volume of water is defined as the ultimate biochemical oxygen demand, herein calculated to be about 17 mg/l.

The decay of organic material is generally defined by a first order reaction model expressed by the following equation:

$$L_t = L_0 \exp(-K_1 t) \qquad (169)$$

where L_t is the concentration of BOD remaining after t days, L_0 is the initial concentration of BOD at time zero, K_1 is the first order BOD decay rate, and t is the time.

The 5-day biochemical oxygen demand for the study reach was found to be as low as 3 mg/l and the decay rate was estimated to be about 0.087 $days^{-1}$.

It is well known that plants, including algae, require carbon, nitrogen, phosphorus and potassium, as well as trace amounts of other elements to grow. Forms of nitrogen dissolved in water include, organic nitrogen, ionised ammonia (NH_4^+), unionised ammonia (NH_3), nitrite, and nitrate. Of these forms, nitrate is the most readily available for plant growth and is the predominant form present in streams. Forms of phosphorus in water include orthophosphate and the bound phosphate in soluble form. Dissolved forms of nitrate and phosphate are readily taken up by plants and their concentrations in natural water are usually low.

Nutrient concentrations within the channel water were found to be rather low due to the non-existence of pollution sources. Ammonia-nitrogen concentrations ranged from 0.0 to 1.1 mg/l, while NO_3-N concentrations ranged from 0.6 to 3.0 mg/l. PO_4-P was not detected. The presence of a reservoir just upstream of the channel seems to contribute to the low availability of nutrients within the channel water.

Microbiological analyses have been also carried out, and a total coliform count of about 50/100 ml of sample in average was found, while *F.streptococci* count was only 15/100 ml of sample in average. These bacteriological counts were mainly due to land drainage and agricultural runoff from the neighbouring farms.

8.2.3 Reaeration Rate Coefficient Measurement:

The reaeration rate coefficient was herein measured by three different methods, namely the disturbed equilibrium, propane gas tracer and floating soluble solids techniques. Five disturbed equilibrium tests have been carried out at a constant discharge of about 0.50 m^3/s. Three propane gas tracer tests followed the disturbed equilibrium experiments and were carried out at discharges varying from 0.25 to 0.75 m^3/s. Velocity of solids dissolution has been measured for the eight tests carried out from June to August of 1987.

8.2.3.1 Disturbed Equilibrium Method:

Some modifications have been introduced for the measurement of K_2 by the disturbed equilibrium method based on the conclusions drawn from the previous tests (Chapter 7), and are mainly related to the dosing equipment.

The dosing equipment consisted in the same two tanks (225 litres in volume) used before, connected to a constant head pump powered by a portable generator, which discharged about 25 l/min of sodium sulphite into the channel water through two injection points (connected to the pump and made from PVC). This was modified to ensure a constant dose of sulphite into the water and also to avoid having to make the injection an inconveniently long distance (about 1500 m) upstream if a single point injection had been used.

The cobalt catalyst was separately injected through a Mariotte vessel (see Cobb, 1967), at a flow rate of 60 ml/min, in a quantity sufficient to produce a concentration within the channel water between 0.3 to 0.5 mg/l.

Water sampling, DO analysis and K_2 computation were carried out as described in the preliminary tests (section 7.3).

8.2.3.2 Propane Gas Tracer Method:

A long duration method has been selected for the gas tracer measurements (refer to Yotsukura et al.,1983) since both the hydraulics and gas transfer were expected to be steady during the test.

Because of the restriction imposed by the Water Company concerning the use of dye tracers in its aqueducts, the field procedure has been slightly modified in comparison to that described by Yotsukura et al. (1983). An instantaneous injection of NaCl at the beginning of a long duration injection of the hydrocarbon gas was used instead of the commonly used dye tracer (Rhodamine WT).

The steady state method, as described in Chapter 2, combines an instantaneous injection of a dye tracer (salt was used in these particular tests) with a long duration injection of propane gas. The gas injection lasts long enough to allow collection of steady state data for gas concentration at the two measurement cross sections. Only salt concentrations were determined (using conductivity meters) while the salt was passing. When the salt concentration declined to approximately 2% of the peak concentration, the gas concentration will be essentially at steady state. The salt measurements were then stopped and gas sampling is initiated and continued as long as desired during the steady state period. Refer to Figure 7 in Chapter 2 for a diagrammatic explanation of the method. Discharge measurements are also taken at each cross section (injection and the two sampling sites).

The propane gas and salt quantities for the modified propane gas tracer technique were estimated based on previous disturbed equilibrium and hydraulic characteristics measurements, and in accord to a procedure described by Rathbun (1979).

The commercially available propane gas was injected into the channel water by bubbling the gas through a porous diffuser, as shown in Plate 4. The diffuser was manufactured by Porvair Ltd., and made from Vyon F material, a porous permeable plastic membrane (high density polyethylene). the structure of Vyon materials provides a volume porosity in the order 35%. Because of this characteristic, the diffuser is able to allow flow rates much higher than their pore size indicates. The diffuser was about 25 cm long, 2.5 cm in outside diameter, 2.5 mm thick, with average pore size of 60 microns and minimum tensile strength of about 40 kgf/cm^2. The tube was mounted in a frame and placed on the bottom of the stream at the centre of flow.

Propane was fed directly from a high pressure cylinder through a two-stage regulating valve and a rotameter for the monitoring of propane gas flow rate.

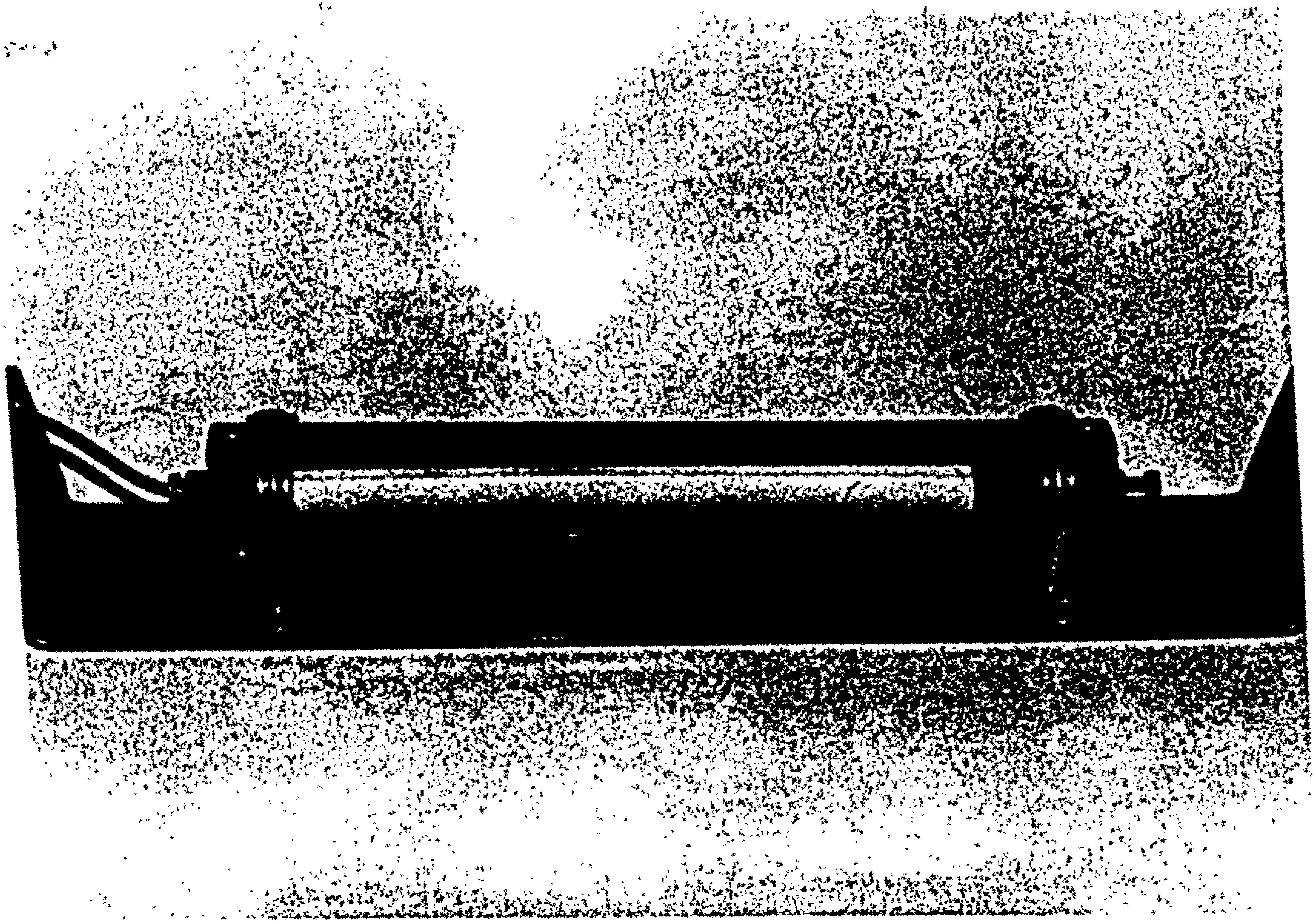


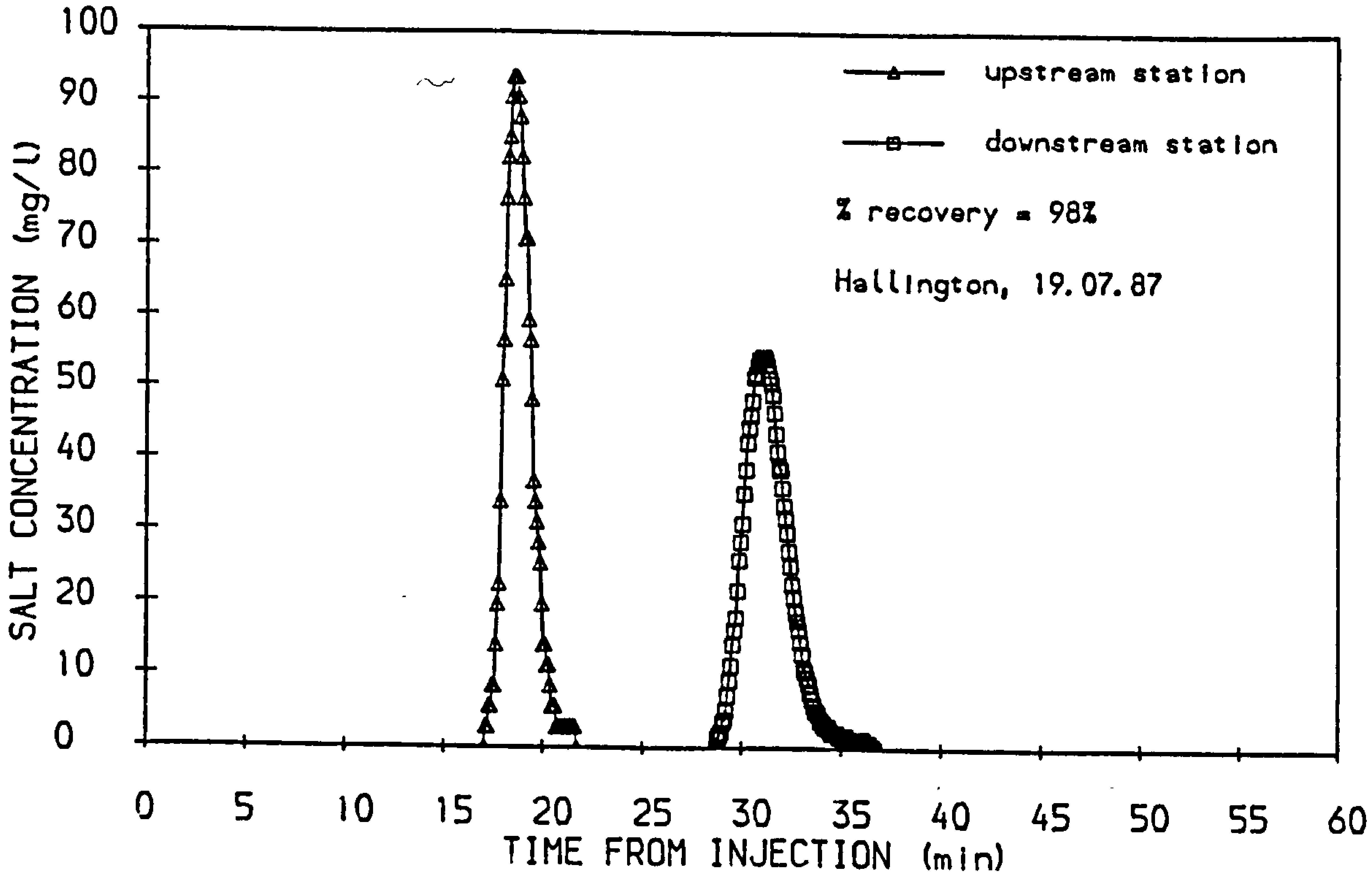
PLATE 4: PROPANE GAS DIFFUSER

Propane gas flow rate and the length of the injection period were adjusted to give a peak propane concentration at the downstream end of the measurement reach of at least 10 µg/l, due to the poor sensibility of the GC machine response to detect hydrocarbon concentrations lower than this value.

The quantity of propane required to give this concentration is a function of the combination of water discharge, reaeration coefficient, longitudinal dispersion coefficient, traveltime, flow accrual, water temperature, and the efficiency of the absorption process which in turn depends on the flow rate of propane through the diffuser, the depth of water over the diffuser and the flow velocity at the injection point (refer to Rathbun, 1979).

A total of 750 g of propane was injected during each test over a period of 35 to 40 minutes at a flow rate of 20 l/min.

Samples for gas analysis were obtained by allowing the water to flow slowly into a 60 ml glass bottle at three minutes intervals during 30 minutes, so that they filled with a minimum amount of turbulence. One ml of formalin was added to each sample bottle to avoid biodegradation, and the vials were then capped with Teflon lined septa, stored and transported to the laboratory for analysis. Replicate samples were collected at each 3 minutes at the centre of the flow, so that a total of 42 water samples were analysed by the chromatographic technique described in Chapter 5. The collected samples were kept at 4°C until analysis to retard any possible biological degradation. The three steady state propane gas tracer tests are shown below.



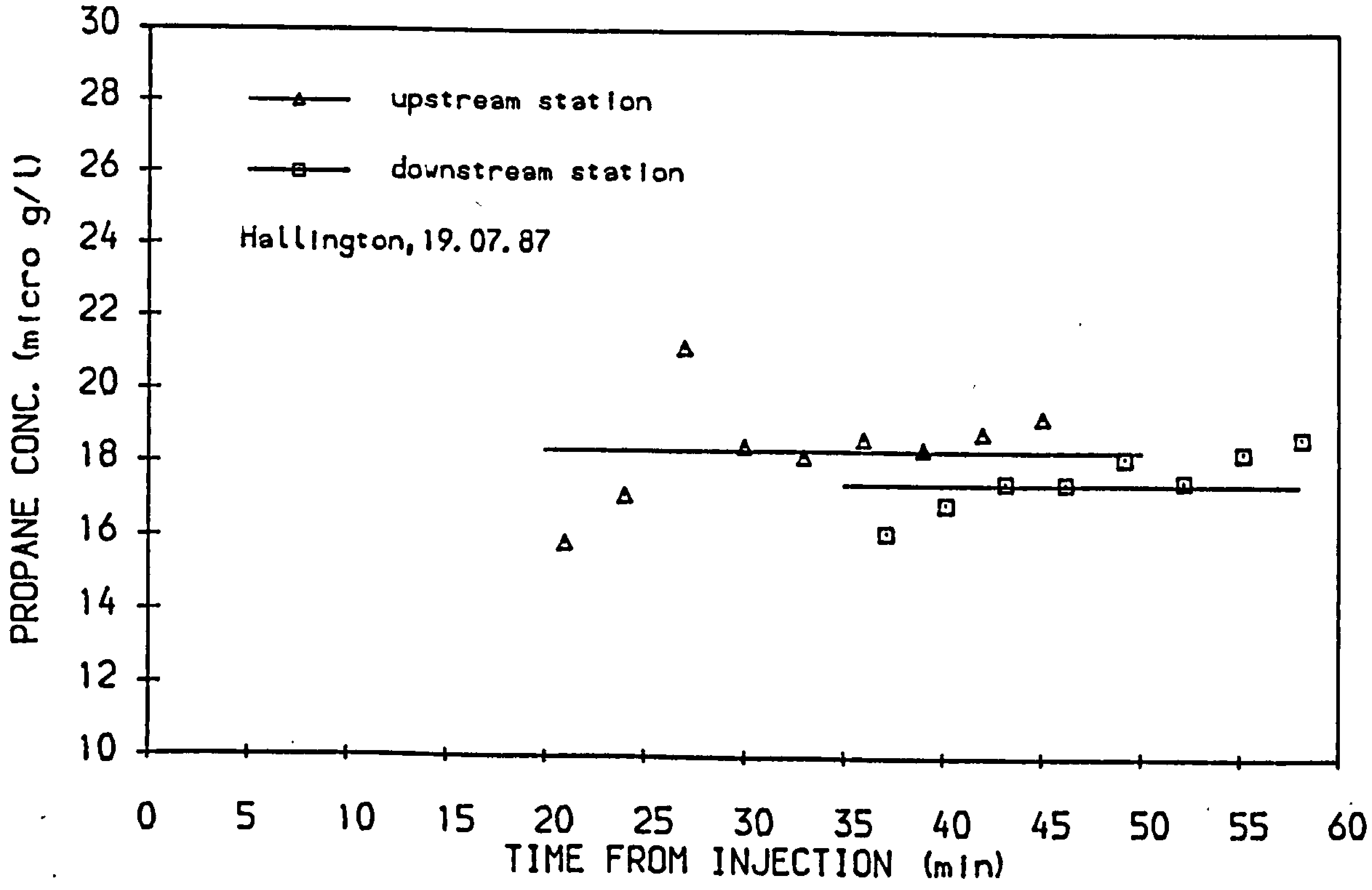
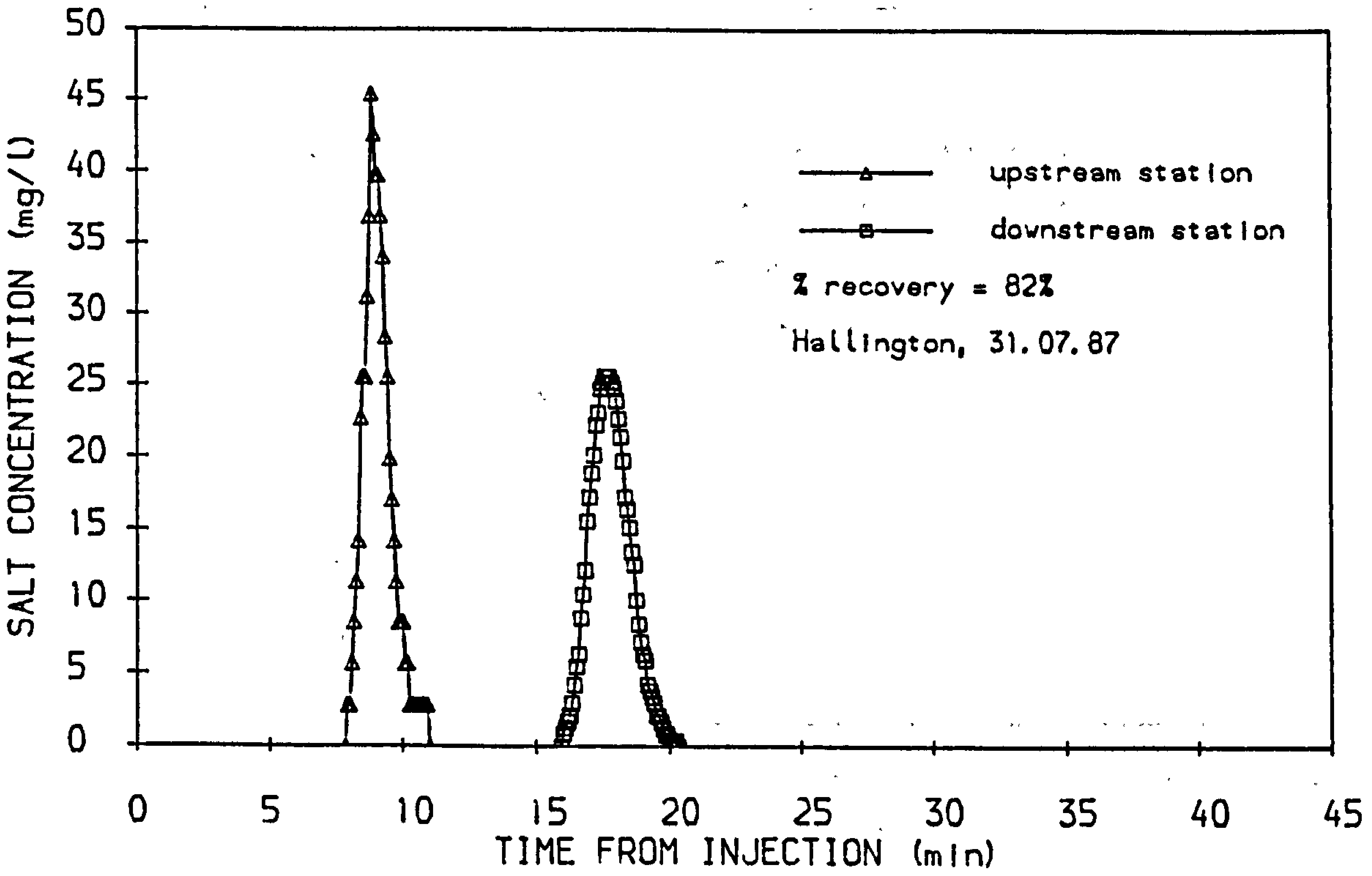


Figure 49: Steady state propane gas tracer experiment
Hallington channel (Jul/Aug 87)



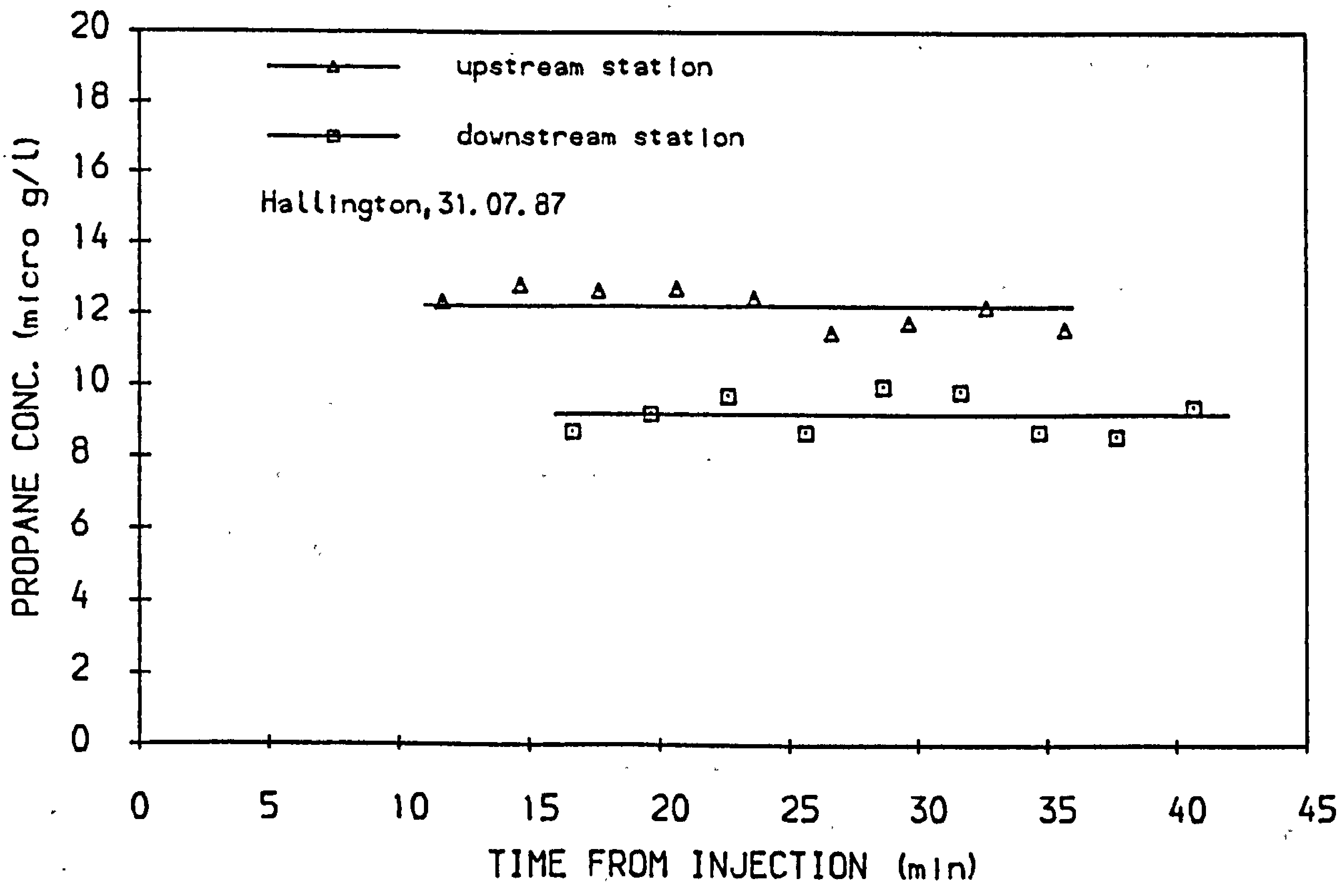
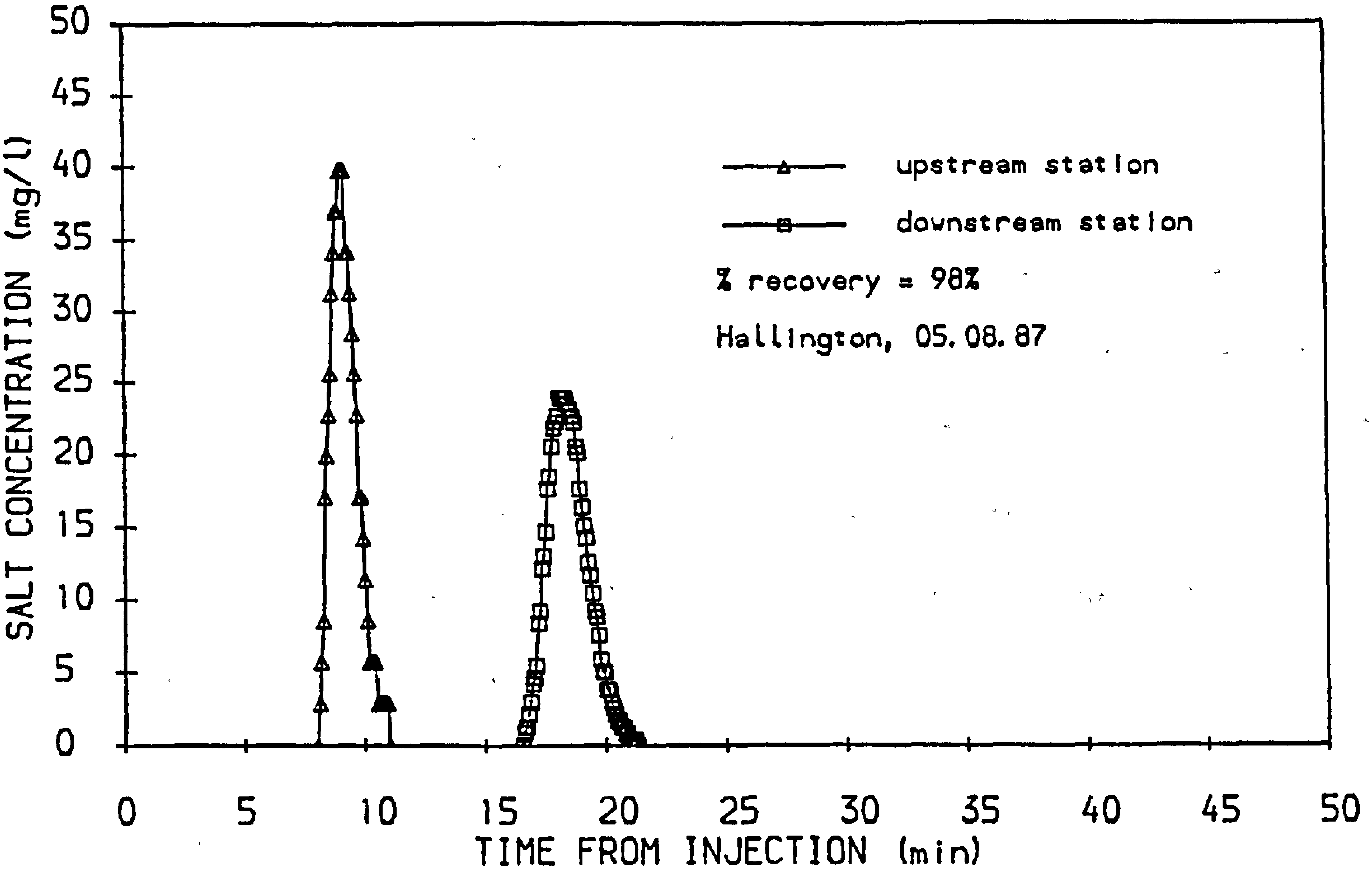


Figure 50: Steady state propane gas tracer experiment Hallington channel (Jul/Aug 1987)



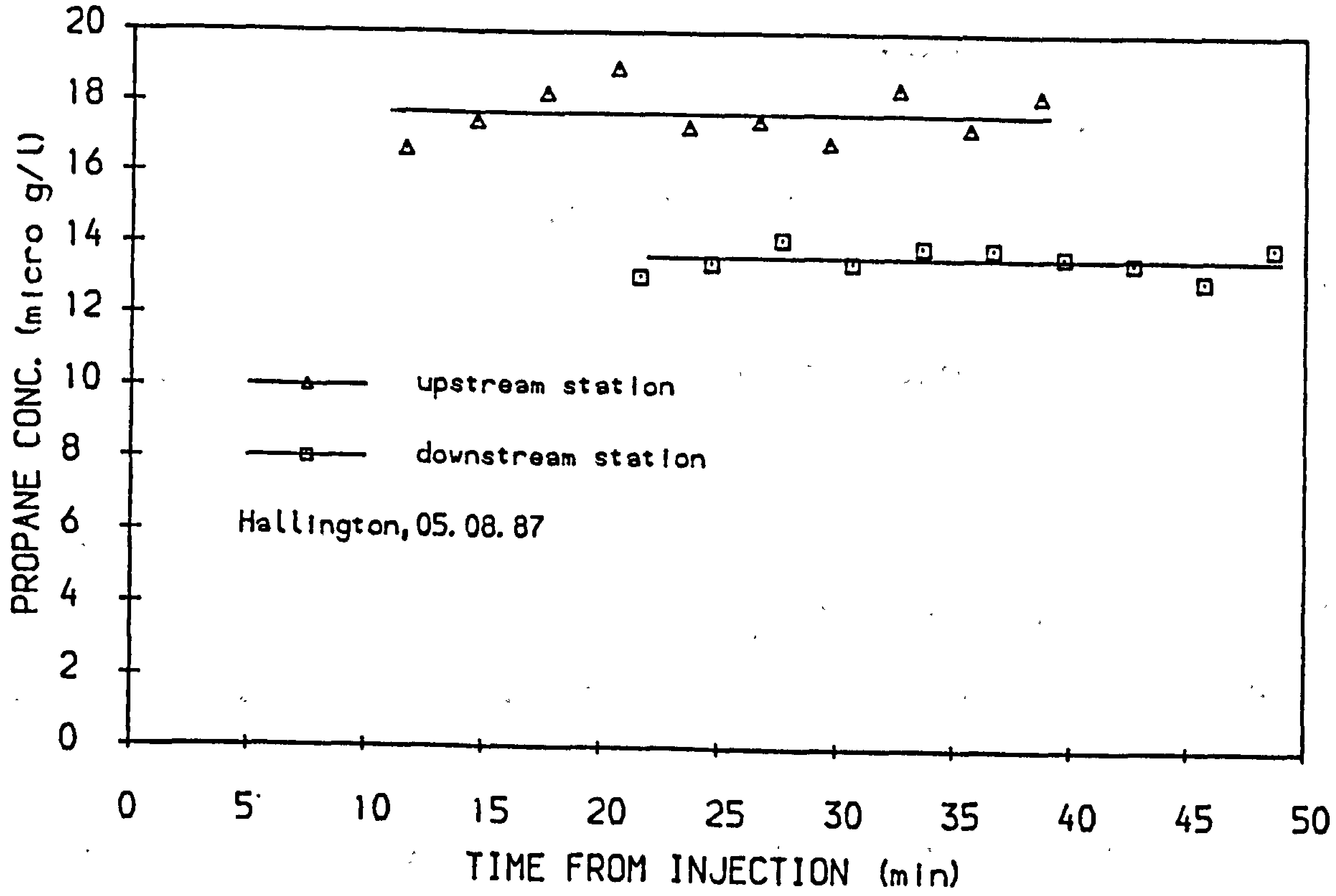


Figure 51: Steady state propane gas tracer experiment Hallington channel (Jul/Aug 1987)

The reach averaged desorption coefficient K_p is calculated from:

$$\frac{(CQ)_1}{(CQ)_2} = \exp\ [-K_p(\bar{t}_2 - \bar{t}_1)] \qquad (170)$$

where C is the steady state propane gas concentration, $\bar{t}$ is the traveltime determined by the centroids of the salt tracer concentration curves, and the subscripts 1 and 2 refer to the upstream and downstream sampling sites, respectively.

The reaeration coefficient is then computed from the following equation (as in Chapter 2):

$$K_2 = \frac{K_p}{1.36} \qquad (171)$$

where K_2 is the reaeration rate coefficient and K_p is the propane gas desorption coefficient.

Temperature corrections on the reaeration rate coefficient are made by the following expression, as in Chapter 3:

$$K_{2,20} = K_{2,T} \times (1.0241)^{20-T} \qquad (172)$$

where $K_{2,20}$ is the reaeration rate coefficient at 20°C and $K_{2,T}$ is the reaeration rate measured at a T temperature.

8.3 RESULTS AND DISCUSSION:

The results obtained in these subsequent field experiments are summarised in Table 26. The first five $K_{2,20}$obs values were measured by a disturbed equilibrium technique, while the last three values were measured by a steady state propane gas tracer technique. Predicted reaeration values computed from Owens et al. (1964) equation - found to be the appropriate predictive

Table 26: Subsequent field experimental results (Hallington channel)

Date	U (m/s)	H (m)	Q (m^3/s)	$K_{2,20}obs$ ($hour^{-1}$)	$K_{2,20}pred*$ ($hour^{-1}$)	$V_s x10^{-6}$ (cm/min)	$K_{2,20}pred**$ ($hour^{-1}$)	Temperature (°C)
09.06.87	0.65	0.33	0.52	1.7919	1.4662	75.0	2.095	12.7
11.06.87	0.63	0.33	0.51	0.6410	1.4331	71.0	1.913	12.8
16.06.87	0.64	0.31	0.49	1.1328	1.6173	78.0	2.171	12.6
18.06.87	0.63	0.30	0.47	1.8660	1.6933	73.0	2.011	12.8
26.06.87	0.58	0.28	0.43	1.0324	1.7986	74.0	1.881	13.1
19.07.87	0.50	0.23	0.25	1.7189	2.2772	69.0	1.536	17.2
31.07.87	0.75	0.45	0.78	2.7960	0.9459	96.0	2.905	12.2
05.08.87	0.75	0.43	0.73	2.0721	1.0242	78.0	2.393	15.6

$K_{2,20}pred*$ is the reaeration rate coefficient computed from Owens et al. (1964) equation
$K_{2,20}pred**$ is the reaeration rate coefficient computed from the K_2/V_s equation

model for the Hallington channel hydraulic characteristics according to Covar's (1976) method - and from velocity of solids dissolution measurements, are also presented.

A correlation table was then obtained and is shown below:

Table 27: Correlation coefficients (Hallington)

VARIABLE	velocity	depth	discharge	K_2obs	K_2pred*	$K_2pred**$
depth	0.848					
discharge	0.987	0.905				
K_2obs	0.534	0.432	0.551			
K_2pred*	-0.981	-0.877	-0.987	-0.453		
$K_2pred**$	0.921	0.837	0.942	0.664	-0.900	
V_s	0.740	0.747	0.796	0.699	-0.729	0.941

It is clear that considerable improvement has been achieved not only related to the hydraulic characteristics measurements, revealed by the high correlation coefficients between the relevant variables (velocity, depth and discharge), but also in the actual reaeration measurements.

With the exception of the second test, the measured reaeration rates by the disturbed equilibrium appear to be in reasonable agreement both with the predicted reaeration values computed from Owens et al. (1964) equation and the channel hydraulic characteristics.

On the other hand, the measured K_2 values by the steady state propane gas tracer method are in total disagreement with K_2pred*. Negative correlations were however obtained between K_2pred* and both velocity and discharge, which does not seem to be in accord with current theories of oxygen transfer from the atmosphere into the water. In this case, it appears that the observed K_2 values are more reliable than the predicted values, despite the errors involved in its measurement.

It should be herein mentioned that, as recommended by Yotsukura et al.(1983) and also by Holley and Yotsukura (1984), it is always advisable to consider the value of the non-dimensional group ($K_t\Delta t$) as a measure of the amplification or attenuation of the errors involved in the other variables when planning field experiments.

It was soon realised that the condition of ($K_t\Delta t$) ≥ 1 would not be observed for the selected study reach. By the estimation of the reaeration rate coefficients from predictive models, and also from previous traveltime measurements, it was observed that the maximum value which could be obtained for ($K_t\Delta t$) was about 0.30.

It is recognised that the errors in measuring individual variables (e.g. concentrations) will in this case be amplified, and consequently the rate coefficients obtained are not the most accurate. The fact is that many limitations, such as the impossibility of using Rhodamine-WT dye tracer in the Water Company's aqueducts, lack of appropriate sampling equipment (e.g. flow through sampling system), personnel and time, and the higher costs involved in selecting a longer reach (of about 1500 m instead of the 600 m selected), were imposed for the accomplishment of these tests and had to be carefully considered before their beginning. Alternatives had to be found (such as the use of a salt tracer) in order to improve as much as possible the actual data collection. Although the values obtained for the reaeration rate coefficient cannot be considered as accurate as they would be if the ($K_t\Delta t$) group was near about 1.0, they do provide a reliable means of comparison between the different methods employed.

Velocity of solids dissolution values are in good agreement with both the hydraulic variables and the observed K_2 values, statistically confirmed by a correlation coefficient of about 0.75. These results thus appear to further confirm the tendency verified both in the laboratory and preliminary field tests that V_s is a function of turbulence of water and that it correlates reasonably well with K_2.

It was also verified that when the overall laboratory data were combined with the subsequent field test data, the correlation between the K_2/V_s ratio and the turbulence parameter Re/h has proven to be as strong as it was previously observed (r=0.89) in the laboratory. Referring to Figure 51, it is shown that although data scatter is observed at higher values of both K_2/V_s and Re/h, the model developed from laboratory data can reasonably predict reaeration rates at diverse flow situations. It should be noted that the three values within the 95% confidence interval of the model correspond to those

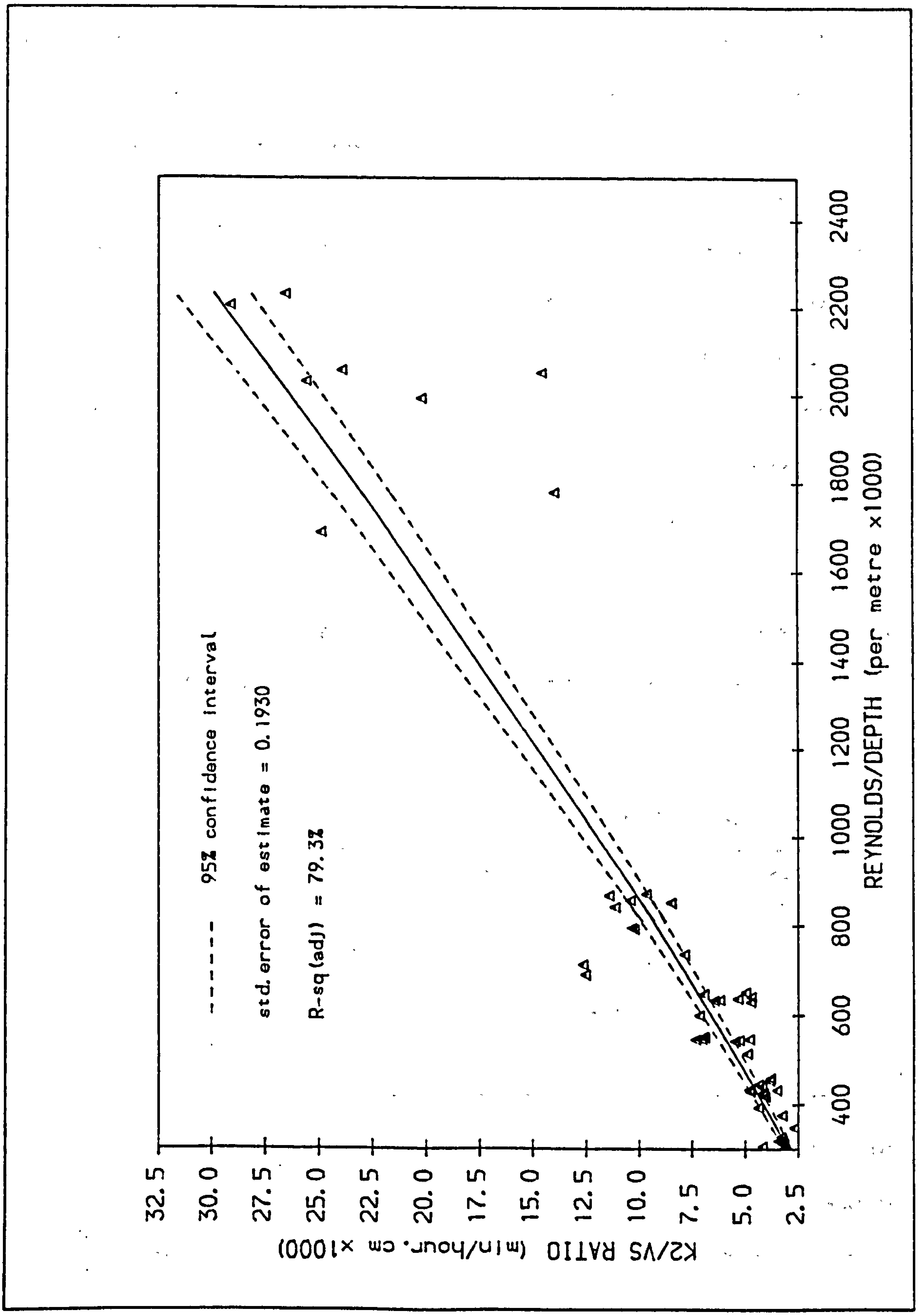


Figure 52: Laboratory and subsequent field test combined data

measured by the modified propane gas tracer technique, and that the scatter observed is most probably due to the higher variability of field data, especially if the disturbed equilibrium method is being considered.

The modified gas tracer technique, usually considered to be the most accurate technique (with the exception of the radioactive tracer technique), gave rise to reaeration rate coefficients which are in reasonable agreement with K_2pred**, both in terms of correlation and order of magnitude, as discussed above and shown in Figure 52. This fact appears to give further support to the application of the floating soluble solids method in small streams.

In a second phase of data analysis, the preliminary and subsequent test results were combined, and the following correlations have been obtained:

Table 28: Correlation coefficients (Whittle Dene + Hallington)

VARIABLE	velocity	depth	discharge	K_2obs	K_2pred*	K_2pred**
depth	0.863					
discharge	0.921	0.984				
K_2obs	-0.026	-0.010	-0.034			
K_2pred*	-0.888	-0.965	-0.948	-0.002		
K_2pred**	0.958	0.763	0.826	0.089	-0.809	
V_s	0.884	0.947	0.944	0.142	-0.945	0.873

The above table shows that although a poor and unreliable evidence of an association between both K_2obs and K_2pred* has been obtained in relation to the three measured hydraulic variables, the reaeration rate coefficient computed from velocity of solids dissolution is highly correlated with these variables.

The above can be further confirmed if K_2pred** is plotted against the energy dissipated expressed by the product of velocity and slope (SU), as shown in Figure 53. A rather strong correlation coefficient is obtained between K_2pred** and (SU), estimated to be equal to 0.955, as indicated in the plot. The straight line fitted through the data by least square analysis indicates that the relationship between K_2 and the energy dissipated is of the type:

$$K_{2,20} = 0.537\ (SU) \qquad (173)$$

where the C = 0.537 value is known as the escape coefficient, as defined by Tsivoglou and Wallace (1972).

The escape coefficient is not a single universal constant, but must be expected to differ somewhat from one stream to another and even from one segment to another in the same stream. It is by nature a mixing coefficient that connects gas transfer with surface replacement and turbulence. It is affected by a wide variety of physical and hydraulic conditions that influence the quality and intensity of mixing. According to Tsivoglou and Neal (1976), each stream must be regarded as unique and different from all others, and the hydrodynamic fine structure created by topographic features is reflected in the magnitude of the escape coefficient.

The escape coefficient is expected to be lower in relatively large and deep channels (with discharge between 28 to 85 m^3/s), and higher in small streams having flows in the 0.71 to 1.42 m^3/s range. The presence of pollutants also affects the magnitude of C, as reported by Tsivoglou and Wallace (1972),

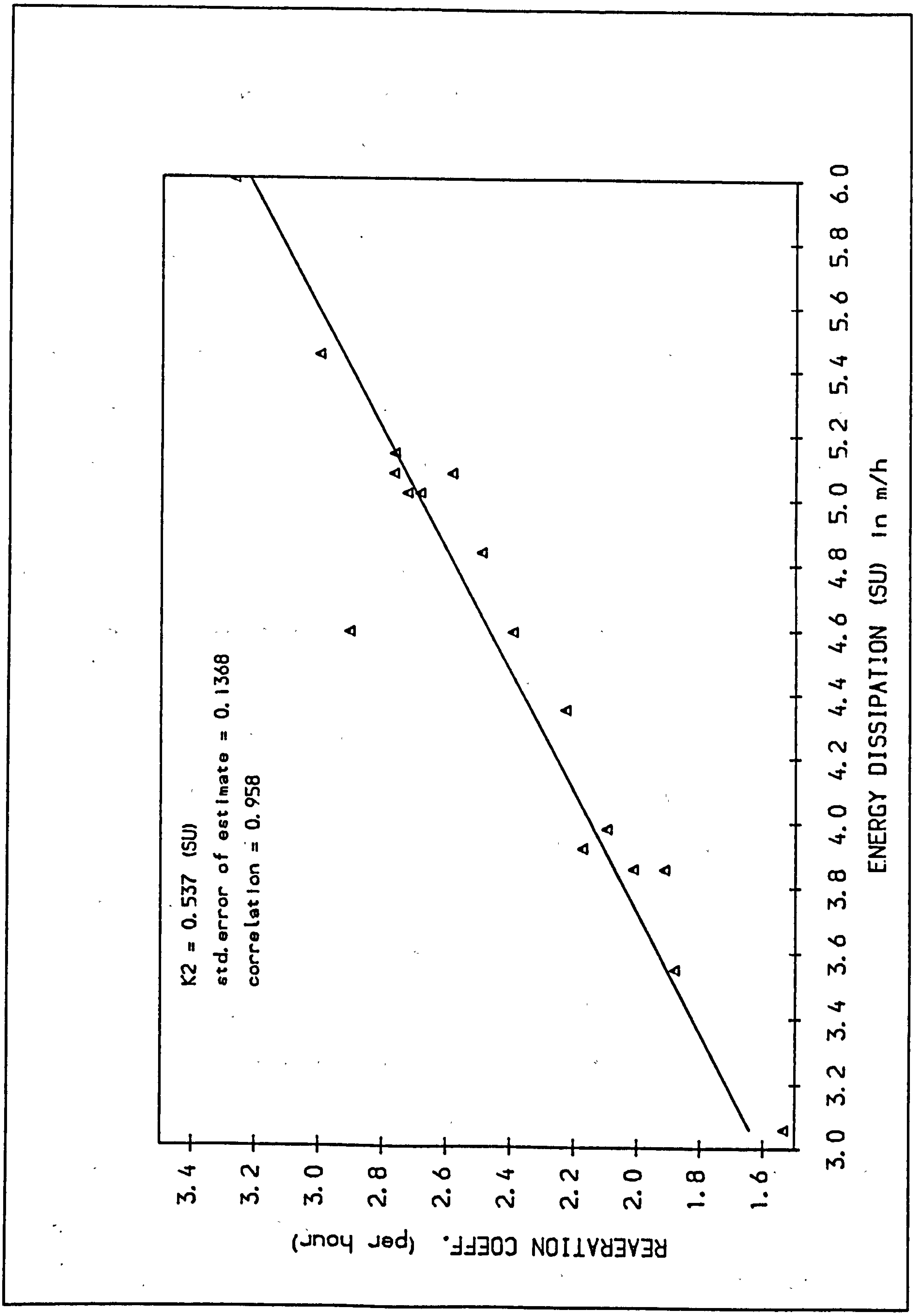


Figure 53: Combined field data
(reaeration as a function of the energy dissipated)

which increases as the pollution level decreases in a particular stream.

Typical values of C are between 0.131 and 0.200 per metre as reported by Tsivoglou and Neal (1976), but values as high as 0.49/m and 0.59/m have also been observed. Grant (1976,1978) found C to be equal to 0.364/m in average for 10 small streams in Wisconsin, U.S.A., and between 0.190 and 0.200 for the Rock River, Wisconsin and Illinois, U.S.A. Shindala and Truax (1980) reported an escape coefficient of 0.196/m for discharges ranging from 0.30 to 8.00 m^3/s and 0.263/m for discharges less than 0.30 m^3/s in analysing radioactive tracer studies from 7 different states in the U.S.A.

It may therefore be concluded that although the herein obtained escape coefficient (as an average for the two studied channels) appears to be unusually high when it is compared with previously reported values, it is not in disagreement with the theory behind it, in terms of channel hydrodynamic features and water quality.

It is within this context that the above energy dissipation model (equation 173), developed from velocity of solids dissolution measurements, appears to further confirm the previously obtained relationship between K_2 and V_s as suitable for application in totally diverse flow situations than those found in the laboratory.

A summary analysis of the overall laboratory and field data suggests that the floating soluble solids method appears to be at least as reliable as previously reported methods for the determination of reaeration rates in small streams, and the following aspects seem to be worth considering:

(i) the floating soluble method does not require any sophisticated equipment other than an analytical balance;

(ii) since the solids can be exposed to the water surface for any desired reach length, the condition of a mixing length is not required as it is when other methods are employed;

(iii) it seems that the solids technique is therefore subjected to less procedural and random errors than the other methods herein reported;

8.4 SUMMARY AND CONCLUSIONS:

Subsequent field tests were carried out in order to measure the reaeration rate coefficient in a long concrete lined channel and compare three different methods used for its measurement: the disturbed equilibrium, modified gas tracer and floating soluble solids methods.

It has been concluded that the disturbed equilibrium technique gives reasonably satisfactory results when correctly applied. The equipment and procedural modifications introduced resulted in a considerable improvement in terms of the actual reaeration coefficient measurement.

The steady-state propane gas tracer method has been successfully applied for the measurement of K_2 in the Hallington channel. Although the requirement that $(K_t \Delta t) \geq 1$ has not been satisfied, it appears that the measured K_2 values are well correlated with the three hydraulic variables, and also with previously reported K_2 values measured at similar hydraulic conditions (Zizon et al.,1978).

Reaeration coefficient values predicted from Owens et al. (1964) equation are negatively correlated with both velocity and depth, and do not seem to be in agreement with current gas absorption theories.

The evidence that the K_2/V_s relationship, developed from laboratory data, might be successfully employed in diverse flow situations has been herein confirmed. Combined laboratory and subsequent field test data correlations appear to support this evidence.

The reaeration rate coefficient measured by the floating soluble solids technique is strongly correlated with the energy dissipation rate, when both preliminary and subsequent field data are combined. The relationship obtained between these two variables is not in disagreement with previously reported energy dissipation models and seems to further support the use of the K_2/V_s relationship as a reliable means for the determination of reaeration rates in small streams.

The major advantage of the floating soluble solids method over previously reported techniques is that it does not require any sophisticated equipment or elaborated sampling schemes and analysis. Solids are exposed to the water surface for any desired time or reach length and it is not necessary to account for any mixing length. It seems that the solids technique is less subjected to both procedural and random errors inherent of all experimental procedures.

CHAPTER 9

General Summary and Conclusions

9.1 BACKGROUND TO THE REPORTED RESEARCH:

(i) the process of atmospheric reaeration in streams is usually described by the gas transfer equation, Equation (1);

(ii) the reaeration rate coefficient is primarily a function of water turbulence;

(ii.1) conceptual and empirical predictive models have been developed for the computation of the reaeration coefficient;

(ii.1.1) conceptual models usually relate the reaeration coefficient to the turbulence characteristics of the water in terms of rate of surface renewal, film thickness, rate of energy dissipated, and so on;

(ii.1.2) empirical predictive models relate these parameters to measure hydraulic variables so that the conceptual models are simplified to be applicable in natural streams;

(ii.1.3) both conceptual and empirical models were developed from data collected for specific ranges of those hydraulic and physical characteristics which have a bearing on the gas transfer process; outside of their range, they often give widely different estimates of K_2;

(ii.1.4) misinterpretation or poor estimation of reaeration can seriously affect the calculation of the oxygen balance and result in an improper determination of the required degree of waste treatment;

(iii) development of several methods for the measurement of reaeration rates in natural streams;

(iii.1) oxygen balance technique - based on Streeter and Phelps (1925) model, is subjected to potentially large errors associated with the many sources and sinks of oxygen which must be evaluated;

(iii.2) disturbed equilibrium technique - limited to streams with no temporal variation of natural DO concentration and no sources and sinks which depend on DO concentration, if it can be verified that there is no residual sulphite;

(iii.3) radioactive tracer technique - known to be the most accurate method for the measurement of K_2 in natural streams; its application is however limited because of problems concerning radiation exposure received by both technical personnel and the public along the stream, and also because of the sophisticated equipment needed;

(iii.4) modified gas tracer technique - apparently the best alternative for the measurement of K_2 in streams, but it is still being investigated and problems concerning its accuracy have been reported; it also requires sophisticated equipment and relatively high costs might be involved in its application;

(iii.5) floating soluble solids technique - developed under the assumption that the solids dissolution is increased by turbulent eddies which are randomly renewed at the water surface; strong correlations have been verified between solids dissolution and reaeration processes; it needs to be thoroughly investigated since it appears to offer a simple and reliable method for the measurement of reaeration rates in small streams;

9.2 THE REPORTED RESEARCH:

9.2.1 Laboratory Studies:

(i) preliminary studies were conducted in an attempt to identify the appropriate soluble solid and its configuration, floating device, and also to select the best methods for the measurement and computation of both K_2 and V_s;

(ii) overall results obtained in these preliminary studies revealed a strong correlation between the velocity of benzoic acid dissolution and the oxygen transfer coefficient, which was statistically confirmed by a correlation coefficient $r = 0.957$;

(iii) although no attempt was made at that time to quantify the $K_L - V_s$ relationship, further studies were then planned to investigate the individual and combined effects of three hydraulic factors (velocity, depth and roughness) upon three different processes, namely reaeration, propane gas desorption and solids dissolution at the water surface;

(iv) from statistical experimental design and analysis techniques, it was possible to show how the selected response variables (K_2, K_L, K_p and V_s) were affected by a set of hydraulic variables over a specified region, and thus indirect assess both the modified gas tracer and floating soluble solids techniques for the determination of reaeration rates in streams;

(v) velocity and depth were found to be the most important effects to be taken into consideration, while the roughness effect was found to be irrelevant for the range of hydraulic conditions studied;

(vi) the interaction effect of velocity and depth has then been further studied by response surface methodology which revealed that both K_2 and K_p are less depth-dependent at low velocity levels than at higher velocity levels;

(vi.1) the above finding was substantiated by the analysis of natural river data, and also by the analysis of energy dissipation response to the same hydraulic conditions as before, which suggests a weaker depth-dependence of both K_2obs and the rate of energy dissipated at low turbulence levels and a stronger depth-dependence at higher turbulence levels;

(vi.2) the K_2 - energy dissipation relationship appears to be in reasonable agreement with the related theory and the models reported in the literature;

(vii) the assumption that the K_2/K_p ratio is constant and independent of turbulence intensity and mixing has been herein confirmed and estimated to be equal to 1.365 ± 0.03; response surfaces obtained for both K_2 and K_p strongly supports the above statement;

(viii) the physical processes of both oxygen absorption and benzoic acid dissolution appear to be ruled by the same diffusion processes, so that physical mass transport determines the overall reaction rate; the main resistance to both processes is in the liquid phase, so that agitation has a considerable effect on the overall mass transfer coefficient (revealed by the strong effect of the velocity factor on both K_L and V_S);

(ix) subsequent laboratory studies showed however, that there is a limiting factor between oxygen absorption and solids dissolution processes, most probably related to the surface area of contact between the two phases, either gas-liquid or solid-liquid;

(x) combined laboratory data (preliminary + subsequent tests) reveals a good agreement between both K_2 and K_L with V_S, statistically confirmed by a correlation coefficient of 0.71 and 0.80, respectively;

(xi) the ratio between K_L/V_S was found to be dependent of turbulent and mixing conditions of the particular experimental system, as demonstrated above, and mathematically expressed by:

$$\frac{K_L}{V_S} = 9.279\times10^{-3}\ Re^{1.01}$$

(xii) the above expression could then be statistically improved by substituting the oxygen mass transfer coefficient by the reaeration rate coefficient, so that the following mathematical equation resulted:

$$\frac{K_2}{V_S} = 1.534\times10^{-3}\ \left(\frac{Re}{H}\right)^{1.15}$$

9.2.2 Field Studies:

(i) preliminary field studies were conducted to test the floating soluble solids method in less artificial conditions than those found in the laboratory, and also to acquire some experience both on the measurement of channel hydraulic characteristics and of the reaeration rate coefficient by the disturbed equilibrium method;

(ii) the inability to comply with the main assumptions and inherited limitations of the disturbed equilibrium method, resulted in doubtful and inaccurate measured K_2 values;

(ii.1) injection equipment, sampling procedure and water velocity monitoring should be improved and modified so that the disturbed equilibrium method could be satisfactorily applied;

(iii) velocity of benzoic acid dissolution was found to correlate well with velocity and discharge, as previously verified in the laboratory;

(iv) reaeration rates predicted from velocity of solids dissolution measurements are strongly correlated with both velocity and discharge ($r=0.90$), and also with the reaeration rates predicted from Churchill et al. (1962) equation ($r=0.829$);

(v) subsequent field studies were then carried out in a different concrete lined channel to verify the above evidence by improving both reaeration measurement technique procedures and hydraulic characteristics monitoring;

(vi) considerable improvement was achieved by the introduction of equipment and procedural modifications in relation to preliminary field tests;

(vii) measured reaeration rates by the disturbed equilibrium technique are in good agreement with the predicted values computed from Owens et al. (1964) equation, and also with the three measured hydraulic factors (velocity, depth and discharge);

(viii) predicted K_2 values computed from Owens et al. equation are however, negatively correlated with both velocity and discharge, which does not appear to be in accordance with current gas/liquid transfer theory;

(ix) it has been concluded that observed K_2 values are more reliable than the predicted reaeration rates by Owens et al. equation, despite the errors involved in its measurement;

(x) velocity of solids dissolution values are well correlated both with hydraulic variables and observed K_2 values, statistically confirmed by a correlation coefficient of $r = 0.699$;

(x.1) as a consequence, the reaeration rate coefficient values predicted from the velocity of solids dissolution measurement appear to be even more strongly correlated with the hydraulic variables ($r=0.90$) and reasonably well correlated with the observed K_2 value ($r=0.664$);

(xi) combined laboratory and subsequent field test data showed that the K_2/V_s relationship developed from laboratory data can be satisfactorily applied to diverse flow situations; a correlation coefficient $r = 0.89$ was obtained between K_2/V_s and Re/H when the combined data is considered;

(xii) a combination of preliminary and subsequent field test data suggests a rather strong correlation between the reaeration rate coefficient predicted from velocity of solids dissolution and the measured hydraulic variables;

(xii.1) this is further confirmed by the even stronger correlation coefficient obtained between the reaeration rate values (measured from V_s) and the energy dissipation rate ($r=0.955$);

(xii.2) the above relationship has been mathematically expressed by:

$$K_2 = 0.537\ (SU)$$

which is not in disagreement with previously reported energy dissipation models;

(xiii) it is therefore suggested that the floating soluble solid method appears to be at least as reliable as the previously reported direct and independent methods for the measurement of reaeration rates in small streams, with the main advantage that it does not require any sophisticated equipment nor elaborated sampling procedure and analysis;

(xiv) the floating soluble solids method is therefore capable of providing fast and reliable estimates of the reaeration rate coefficient for small streams with steady flow hydraulics;

9.3 SUGGESTIONS FOR FURTHER RESEARCH:

(i) it is necessary to further investigate the relationship which express the K_2/V_s ratio as a function of turbulence by conducting more comparative studies, especially with the modified gas tracer technique;

(ii) the effect of temperature on the velocity of benzoic acid dissolution require to be tested, although some evidence exists concerning the non-significant effect of temperature on the solubility of benzoic acid floating in a turbulent system in the 15 - 25°C;

(iii) it seems worth testing another chemical compounds as floating soluble solids which are originally insoluble but become soluble in the water in the presence of oxygen (e.g. $CuCl_2$, although toxicity of copper is a problem);

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APPENDICES A.1

LABORATORY EXPERIMENTS

DISSOLVED OXYGEN (mg/l)

METER	WINKLER	METER	WINKLER	METER	WINKLER	METER	WINKLER
1.1	1.6	1.0	1.5	1.0	1.1	1.0	2.0
2.0	2.8	3.7	3.9	2.7	2.8	3.9	4.8
2.7	3.6	5.4	5.5	3.8	3.9	5.5	6.1
3.9	5.1	6.9	6.9	5.2	5.4	7.1	7.9
4.9	6.1	7.6	7.7	6.1	6.2	7.9	8.4
1.1	1.4	1.0	1.5	0.9	1.6	1.0	1.2
2.8	3.1	2.9	3.0	3.7	4.5	2.5	3.0
4.1	4.5	4.4	4.4	5.2	6.0	3.7	4.0
5.9	6.2	6.2	6.0	6.5	7.6	5.6	5.8
7.0	7.4	7.1	7.1	7.2	8.3	6.9	7.2

regression equation: DO METER = -0.4636 + 1.000 WINKLER
standard deviation of coefficient = 0.0197
correlation = 0.989
90% confidence interval for beta is (0.9672,1.0329)
there is no evidence against the hypothesis that beta = 1.000

APPENDICES A.2

LABORATORY EXPERIMENTS - JULY 1986

MEMBRANE ELECTRODE VS. WINKLER TECHNIQUE

MEMBRANE ELECTRODE					WINKLER TECHNIQUE				
INITIAL CONC.			REAERATION COEFF.		INITIAL CONC.			REAERATION COEFF.	
OBS.	ESTIM.	STD.DEV.	ESTIM.	STD.DEV.	OBS.	ESTIM.	STD.DEV.	ESTIM.	STD.DEV.
1.1	1.123	0.0160	0.00394	0.000033	1.6	1.624	0.0444	0.00585	0.000104
1.1	1.063	0.0251	0.00856	0.000071	1.4	1.359	0.0806	0.00953	0.000246
1.0	1.002	0.0524	0.01677	0.000260	1.5	1.466	0.1250	0.01677	0.000721
0.9	1.347	0.2050	0.01195	0.000759	1.6	1.614	0.0972	0.01769	0.000546
1.0	0.944	0.0272	0.01105	0.000096	1.5	1.413	0.1140	0.01000	0.000394
1.0	1.232	0.0781	0.00752	0.000228	1.1	1.476	0.2330	0.01038	0.000814
1.0	1.196	0.0749	0.01472	0.000315	2.0	1.992	0.1722	0.01827	0.001053
1.0	0.916	0.0598	0.00801	0.000161	1.2	1.201	0.1640	0.00865	0.000458
1.0	1.020	0.0229	0.00486	0.000049	1.4	1.377	0.1005	0.00631	0.000232
1.0	1.123	0.1123	0.02310	0.000697	1.9	1.880	0.1168	0.02567	0.000974
0.6	0.498	0.0673	0.01692	0.000294	1.1	1.039	0.2757	0.01789	0.001479
0.5	0.624	0.0624	0.00868	0.000170	0.9	0.978	0.1035	000967	0.000307

units are in mg/l and per min

APPENDICES A.3

LABORATORY EXPERIMENTS

DEAERATION TESTS

30.06.86			21.07.86			31.07.86		
TIME (hours)	DO (mg/l)	TEMP. (C)	TIME (hours)	DO (mg/l)	TEMP. (C)	TIME (hours)	DO (mg/)	TEMP. (C)
0.0	8.6	22.8	0.0	8.5	23.4	0.0	8.6	23.1
1.0	8.6	22.8	1.0	8.4	23.4	1.0	8.5	23.2
2.0	8.6	22.9	2.0	8.4	23.5	2.0	8.5	23.2
3.0	8.5	22.9	3.0	8.4	23.5	3.0	8.5	23.3
4.0	8.5	23.0	4.0	8.5	23.5	4.0	8.4	23.4
5.0	8.5	23.1	5.0	8.4	23.7	5.0	8.4	23.4
6.0	8.6	23.1	6.0	8.4	23.8	6.0	8.4	23.5
8.0	8.6	23.2	8.0	8.3	23.8	8.0	8.3	23.6
10.0	8.5	23.3	10.0	8.3	23.9	10.0	8.3	23.8
24.0	8.5	23.1	24.0	8.4	23.5	24.0	8.4	23.4
36.0	8.4	23.6	36.0	8.3	23.8	36.0	8.3	23.9
mean	8.5	23.1	*	8.4	23.6	*	8.4	23.4
td.dev.	0.007	0.022	*	0.007	0.024	*	0.009	0.025

APPENDICES A.4

LABORATORY EXPERIMENTS - JULY 1986

DATE OF EXPER.	VEL. DISS. in cm/min	STANDARD DEVIATION (1E-06)	K2 in per min	STANDARD DEVIATION (1E-03)	EXCHANGE COEFF. in cm/min
10.07.86	0.000088	2.0426	0.00394	0.033	0.048
08.07.86	0.000117	3.7242	0.00856	0.071	0.105
02.07.86	0.000209	6.3558	0.01677	0.260	0.206
17.07.86	0.000144	1.8948	0.01195	0.759	0.119
15.07.86	0.000135	2.4682	0.01105	0.096	0.111
16.07.86	0.000103	2.7389	0.00752	0.228	0.075
23.07.86	0.000167	2.5051	0.01472	0.315	0.206
24.07.86	0.000118	2.1494	0.00801	0.161	0.112
25.07.86	0.000089	1.3652	0.00486	0.049	0.068
28.07.86	0.000177	5.2884	0.02310	0.697	0.184
29.07.86	0.000142	3.0547	0.01692	0.294	0.135
30.07.86	0.000095	2.5104	0.00868	0.170	0.069
mean	0.000130	3.0081	0.01134	0.261	0.120
std.dev.	0.000038	*	0.00562	*	0.054

APPENDICES B.1

GC MACHINE RESPONSE - ACCURACY OBTAINED

	ASSIGNED CONCENTRATIONS									
	30.0		22.5		15.0		7.5		3.0	
	OBSERVED CONCENTRATIONS									
	R	L	R	L	R	L	R	L	R	L
	29.7	29.8	23.1	22.1	14.8	16.1	7.2	6.5	3.3	3.4
	29.7	31.4	22.8	20.8	15.2	13.8	7.3	7.9	3.0	4.1
	29.2	29.3	23.9	23.9	14.4	13.9	7.6	7.4	3.0	3.4
	30.0	30.3	22.3	21.7	15.2	15.6	7.3	7.1	3.1	3.2
	29.9	29.9	23.4	22.7	13.8	15.1	7.5	7.2	3.5	3.1
	29.9	29.2	22.1	23.5	15.3	14.9	8.2	7.4	2.3	2.9
	30.4	30.2	22.9	23.2	13.5	13.4	7.1	7.3	4.2	4.1
	29.1	33.7	23.6	25.2	15.2	17.6	4.2	9.4	3.1	4.8
	26.3	31.3	22.1	26.6	13.7	15.9	7.7	7.4	3.0	2.5
	29.3	29.5	22.7	23.2	16.2	14.9	6.7	7.7	2.9	2.7
	29.0	30.4	23.6	22.6	15.1	13.8	7.3	7.5	2.9	3.8
mean	29.3	30.5	22.9	23.2	14.8	15.0	7.1	7.5	3.1	3.5
std.dev.	1.09	1.30	0.63	1.61	0.83	1.26	1.0	0.7	0.5	0.7
c.v.	0.04	0.04	0.03	0.07	0.06	0.08	0.1	0.1	0.2	0.2

* all values are expressed in micro g/l

APPENDICES C.1

FORTRAN PROGRAM

```
C
C     ==============================================================
C       MULTI-VARIATE ANALYSIS OF VARIANCE FOR A GENERAL FACTORIAL
C       DESIGN AND ITS PARTICULAR CASE, THE 2**3 FACTORIAL DESIGN
C     ==============================================================
C
C       DIMENSIONING VARIABLES
C
      DIMENSION A(10,10),Y1(10),Y2(5),Y3(5),Y4(5),Y5(5),Y6(5),Y7(5)
      DIMENSION Y8(5),AVG(10),AVI(5),AVJ(5),AVK(5),ALPHA(5),BETA(5)
      DIMENSION GAMA(5),AVIJ(5),AVIK(5),AVJK(5),AB(5),AG(5),BG(5)
      DIMENSION ABG(10),PRED(10),RES(10,10)
      CHARACTER*30 NAME(9)
      CHARACTER*30 FACTOR(10)
C
      OPEN(5,FILE='C:\FORTDAT\INP1.BAT',ACCESS='SEQUENTIAL',STATUS=
     #'OLD')
      OPEN(6,FILE='C:\FORTDAT\INP2.BAT',ACCESS='SEQUENTIAL',STATUS=
     #'OLD')
      OPEN(7,FILE='C:\FORTDAT\INP3.BAT',ACCESS='SEQUENTIAL',STATUS=
     #'OLD')
      OPEN(8,FILE='C:\FORTDAT\OUT.BAT',ACCESS='SEQUENTIAL')
C
C     DATA IS ENTERED AS IN YATE'S ALGORITHIM
C
      DO 10 I=1,8
         READ(5,1000) A(I,1),A(I,2),A(I,3)
 10   CONTINUE
 1000 FORMAT(3F10.6)
C
C     ENTER NO. OF I,J AND K LEVELS AND NO. OF REPLICATES
C
      A1=2.0
      B=2.0
      C=2.0
      REPL=3.0
C
C     ==============================================================
C       MAIN AND INTERACTION TOTALS
C     ==============================================================
C
C      Yijk.
C
      DO 30 I=1,8
       Y1(I)=A(I,1)+A(I,2)+A(I,3)
 30   CONTINUE
C
C      Yij..
C
```

```
      Y2(1)=Y1(1)+Y1(2)
      Y2(2)=Y1(3)+Y1(4)
      Y2(3)=Y1(5)+Y1(6)
      Y2(4)=Y1(7)+Y1(8)
C
C      Yi.k.
C
      Y3(1)=Y1(1)+Y1(3)
      Y3(2)=Y1(2)+Y1(4)
      Y3(3)=Y1(5)+Y1(7)
      Y3(4)=Y1(6)+Y1(8)
C
C      Y.jk.
C
      Y4(1)=Y1(1)+Y1(5)
      Y4(2)=Y1(2)+Y1(6)
      Y4(3)=Y1(3)+Y1(7)
      Y4(4)=Y1(4)+Y1(8)
C
C      Yi...
C
      Y5(1)=Y1(1)+Y1(2)+Y1(3)+Y1(4)
      Y5(2)=Y1(5)+Y1(6)+Y1(7)+Y1(8)
C
C      Y.j..
C
      Y6(1)=Y4(1)+Y4(2)
      Y6(2)=Y4(3)+Y4(4)
C
C      Y..k.
C
      Y7(1)=Y4(1)+Y4(3)
      Y7(2)=Y4(2)+Y4(4)
C
C      Y....
C
      Y8(1)=Y7(1)+Y7(2)
C
C     ==============================================================
C       SUM OF SQUARES
C     ==============================================================
C
C       MAIN EFFECTS
C       ------------
C
      PARAM=((ABS(Y8(1)))**2.0)/(A1*B*C*REPL)
C
C       ROUGHNESS
C
      S1=0.0
      DO 40 I=1,2
       S1=S1+((ABS(Y5(I)))**2.0)/(B*C*REPL)
   40 CONTINUE
      SSR=S1-PARAM
C
```

```
C         DEPTH
C
       S2=0.0
       DO 50 I=1,2
        S2=S2+((ABS(Y6(I)))**2.0)/(A1*C*REPL)
  50   CONTINUE
       SSD=S2-PARAM
C
C         VELOCITY
C
       S3=0.0
       DO 60 I=1,2
        S3=S3+((ABS(Y7(I)))**2.0)/(A1*B*REPL)
  60   CONTINUE
       SSV=S3-PARAM
C
C         TWO-FACTOR INTERACTION EFFECTS
C         ----------------------------
C
C         ROUGHNESS X DEPTH
C
       S4=0.0
       DO 70 I=1,4
        S4=S4+((ABS(Y2(I)))**2.0)/(C*REPL)
  70   CONTINUE
       SSRD=S4-PARAM-SSR-SSD
C
C         ROUGHNESS X VELOCITY
C
       S5=0.0
       DO 80 I=1,4
        S5=S5+((ABS(Y3(I)))**2.0)/(B*REPL)
  80   CONTINUE
       SSRV=S5-PARAM-SSR-SSV
C
C         DEPTH X VELOCITY
C
       S6=0.0
       DO 90 I=1,4
        S6=S6+((ABS(Y4(I)))**2.0)/(A1*REPL)
  90   CONTINUE
       SSDV=S6-PARAM-SSD-SSV
C
C         THREE-FACTOR INTERACTION EFFECT
C         -----------------------------
C
C         ROUGHNESS X DEPTH X VELOCITY
C
       S7=0.0
       DO 100 I=1,8
        S7=S7+((ABS(Y1(I)))**2.0)/(REPL)
 100   CONTINUE
       SS3F=S7-PARAM-SSR-SSD-SSV-SSRD-SSRV-SSDV
C
C         TOTAL AND ERROR SUM OF SQUARES
C         ----------------------------
```

```
C
      S8=0.0
      DO 110 I=1,8
       DO 120 J=1,3
        S8=S8+((ABS(A(I,J)))**2.0)
  120  CONTINUE
  110 CONTINUE
      SST=S8-PARAM
      SSE=SST-(S7-PARAM)
C
C       DEGREES OF FREEDOM
C       ------------------
C
      DFR=A1-1.0
      DFD=B-1.0
      DFV=C-1.0
      DFRD=(A1-1.0)*(B-1.0)
      DFRV=(A1-1.0)*(C-1.0)
      DFDV=(B-1.0)*(C-1.0)
      DF3F=(A1-1.0)*(B-1.0)*(C-1.0)
      DFE=A1*B*C*(REPL-1.0)
      DFT=A1*B*C*REPL-1.0
C
C       MEAN SQUARES
C       ------------
C
      SQR=SSR/DFR
      SQD=SSD/DFD
      SQV=SSV/DFV
      SQRD=SSRD/DFRD
      SQRV=SSRV/DFRV
      SQDV=SSDV/DFDV
      SQ3F=SS3F/DF3F
      SQE=SSE/DFE
C
C        F RATIOS
C        --------
C
      FR=SQR/SQE
      FD=SQD/SQE
      FV=SQV/SQE
      FRD=SQRD/SQE
      FRV=SQRV/SQE
      FDV=SQDV/SQE
      F3F=SQ3F/SQE
C
C     ==============================================================
C       DECOMPOSITION OF OBSERVATIONS
C     ==============================================================
C
C       AVERAGE Yijk. AND OVERALL MEAN Y....
C       ------------------------------------
C
      S9=0.0
      DO 130 I=1,8
       AVG(I)=(A(I,1)+A(I,2)+A(I,3))/3.0
```

```
       S9=S9+AVG(I)
 130  CONTINUE
      AVGT=S9/8.0
C
C        AVERAGE  Yi...,  Y.j..,  Y..k.
C        -----------------------------
C
      AVI(1)=(AVG(1)+AVG(3)+AVG(5)+AVG(7))/4.0
      AVI(2)=(AVG(2)+AVG(4)+AVG(6)+AVG(8))/4.0
C
      AVJ(1)=(AVG(1)+AVG(2)+AVG(5)+AVG(6))/4.0
      AVJ(2)=(AVG(3)+AVG(4)+AVG(7)+AVG(8))/4.0
C
      AVK(1)=(AVG(1)+AVG(2)+AVG(3)+AVG(4))/4.0
      AVK(2)=(AVG(5)+AVG(6)+AVG(7)+AVG(8))/4.0
C
C        AVERAGE  Yij..,  Yi.k.,  Y.jk.
C        -----------------------------
C
      AVIJ(1)=(AVG(1)+AVG(5))/2.0
      AVIJ(2)=(AVG(3)+AVG(7))/2.0
      AVIJ(3)=(AVG(2)+AVG(6))/2.0
      AVIJ(4)=(AVG(4)+AVG(8))/2.0
C
      AVIK(1)=(AVG(1)+AVG(3))/2.0
      AVIK(2)=(AVG(5)+AVG(7))/2.0
      AVIK(3)=(AVG(2)+AVG(4))/2.0
      AVIK(4)=(AVG(6)+AVG(8))/2.0
C
      AVJK(1)=(AVG(1)+AVG(2))/2.0
      AVJK(2)=(AVG(5)+AVG(6))/2.0
      AVJK(3)=(AVG(3)+AVG(4))/2.0
      AVJK(4)=(AVG(7)+AVG(8))/2.0
C
C        ALPHA, BETA AND GAMA
C        --------------------
C
      ALPHA(1)=AVI(1)-AVGT
      ALPHA(2)=AVI(2)-AVGT
      ALPHAT=ALPHA(1)+ALPHA(2)
C
      BETA(1)=AVJ(1)-AVGT
      BETA(2)=AVJ(2)-AVGT
      BETAT=BETA(1)+BETA(2)
C
      GAMA(1)=AVK(1)-AVGT
      GAMA(2)=AVK(2)-AVGT
      GAMAT=GAMA(1)+GAMA(2)
C
C        ALPHA x BETA,  ALPHA x GAMA,  BETA x GAMA
C        -----------------------------------------
C
      AB(1)=AVIJ(1)-AVI(1)-AVJ(1)+AVGT
      AB(2)=AVIJ(2)-AVI(1)-AVJ(2)+AVGT
      AB(3)=AVIJ(3)-AVI(2)-AVJ(1)+AVGT
      AB(4)=AVIJ(4)-AVI(2)-AVJ(2)+AVGT
```

```
      ABT=AB(1)+AB(2)+AB(3)+AB(4)
C
      AG(1)=AVIK(1)-AVI(1)-AVK(1)+AVGT
      AG(2)=AVIK(2)-AVI(1)-AVK(2)+AVGT
      AG(3)=AVIK(3)-AVI(2)-AVK(1)+AVGT
      AG(4)=AVIK(4)-AVI(2)-AVK(2)+AVGT
      AGT=AG(1)+AG(2)+AG(3)+AG(4)
C
      BG(1)=AVJK(1)-AVJ(1)-AVK(1)+AVGT
      BG(2)=AVJK(2)-AVJ(1)-AVK(2)+AVGT
      BG(3)=AVJK(3)-AVJ(2)-AVK(1)+AVGT
      BG(4)=AVJK(4)-AVJ(2)-AVK(2)+AVGT
      BGT=BG(1)+BG(2)+BG(3)+BG(4)
C
C       ALPHA x BETA x GAMA
C       -------------------
C
      ABG(1)=AVG(1)-AVIJ(1)-AVIK(1)-AVJK(1)+AVI(1)+AVJ(1)+AVK(1)-AVGT
      ABG(2)=AVG(2)-AVIJ(3)-AVIK(3)-AVJK(1)+AVI(2)+AVJ(1)+AVK(1)-AVGT
      ABG(3)=AVG(3)-AVIJ(2)-AVIK(1)-AVJK(3)+AVI(1)+AVJ(2)+AVK(1)-AVGT
      ABG(4)=AVG(4)-AVIJ(4)-AVIK(3)-AVJK(3)+AVI(2)+AVJ(2)+AVK(1)-AVGT
      ABG(5)=AVG(5)-AVIJ(1)-AVIK(2)-AVJK(2)+AVI(1)+AVJ(1)+AVK(2)-AVGT
      ABG(6)=AVG(6)-AVIJ(3)-AVIK(4)-AVJK(2)+AVI(2)+AVJ(1)+AVK(2)-AVGT
      ABG(7)=AVG(7)-AVIJ(2)-AVIK(2)-AVJK(4)+AVI(1)+AVJ(2)+AVK(2)-AVGT
      ABG(8)=AVG(8)-AVIJ(4)-AVIK(4)-AVJK(4)+AVI(2)+AVJ(2)+AVK(2)-AVGT
      ABGT=ABG(1)+ABG(2)+ABG(3)+ABG(4)+ABG(5)+ABG(6)+ABG(7)+ABG(8)
C
C       PREDICTED  Yijkl
C       ----------------
C
      PRED(1)=AVGT+ALPHA(1)+BETA(1)+GAMA(1)+AB(1)+AG(1)+BG(1)+ABG(1)
      PRED(2)=AVGT+ALPHA(2)+BETA(1)+GAMA(1)+AB(3)+AG(3)+BG(1)+ABG(2)
      PRED(3)=AVGT+ALPHA(1)+BETA(2)+GAMA(1)+AB(2)+AG(1)+BG(3)+ABG(3)
      PRED(4)=AVGT+ALPHA(2)+BETA(2)+GAMA(1)+AB(4)+AG(3)+BG(3)+ABG(4)
      PRED(5)=AVGT+ALPHA(1)+BETA(1)+GAMA(2)+AB(1)+AG(2)+BG(2)+ABG(5)
      PRED(6)=AVGT+ALPHA(2)+BETA(1)+GAMA(2)+AB(3)+AG(4)+BG(2)+ABG(6)
      PRED(7)=AVGT+ALPHA(1)+BETA(2)+GAMA(2)+AB(2)+AG(2)+BG(4)+ABG(7)
      PRED(8)=AVGT+ALPHA(2)+BETA(2)+GAMA(2)+AB(4)+AG(4)+BG(4)+ABG(8)
C
C       RESIDUALS
C       ---------
C
      DO 140 I=1,8
       DO 150 J=1,3
        RES(I,J)=A(I,J)-PRED(I)
 150   CONTINUE
 140  CONTINUE
C
C     ===============================================================
C       THE 2**3 FACTORIAL DESIGN
C     ===============================================================
C
C       MAIN CONTRASTS
C       --------------
C
      CR=Y1(5)+Y1(7)+Y1(6)+Y1(8)-Y1(1)-Y1(3)-Y1(2)-Y1(4)
```

```
      CD=Y1(3)+Y1(7)+Y1(4)+Y1(8)-Y1(1)-Y1(5)-Y1(2)-Y1(6)
      CV=Y1(2)+Y1(6)+Y1(4)+Y1(8)-Y1(1)-Y1(5)-Y1(3)-Y1(7)
C
C        TWO-FACTOR INTERACTION CONTRASTS
C        ------------------------------
C
      CRD=Y1(1)+Y1(2)+Y1(7)+Y1(8)-Y1(5)-Y1(6)-Y1(3)-Y1(4)
      CRV=Y1(1)+Y1(6)+Y1(3)+Y1(8)-Y1(5)-Y1(2)-Y1(7)-Y1(4)
      CDV=Y1(1)+Y1(5)+Y1(4)+Y1(8)-Y1(2)-Y1(6)-Y1(3)-Y1(7)
C
C        THREE-FACTOR INTERACTION CONTRAST
C        --------------------------------
C
      CRDV=Y1(5)+Y1(2)+Y1(3)+Y1(8)-Y1(1)-Y1(6)-Y1(7)-Y1(4)
C
C        MAIN AND INTERACTION EFFECTS
C        --------------------------
C
      ER=CR/(4.0*REPL)
      ED=CD/(4.0*REPL)
      EV=CV/(4.0*REPL)
      ERD=CRD/(4.0*REPL)
      ERV=CRV/(4.0*REPL)
      EDV=CDV/(4.0*REPL)
      ERDV=CRDV/(4.0*REPL)
C
C        SUM OF SQUARES FOR THE EFFECTS
C        ----------------------------
C
      ESSR=((ABS(CR))**2.0)/(8.0*REPL)
      ESSD=((ABS(CD))**2.0)/(8.0*REPL)
      ESSV=((ABS(CV))**2.0)/(8.0*REPL)
      ESRD=((ABS(CRD))**2.0)/(8.0*REPL)
      ESRV=((ABS(CRV))**2.0)/(8.0*REPL)
      ESDV=((ABS(CDV))**2.0)/(8.0*REPL)
      ES3F=((ABS(CRDV))**2.0)/(8.0*REPL)
C
C        VARIANCE OF EFFECTS
C        ------------------
C
      VEF=(4.0*SQE)/24.0
      STDE=SQRT(VEF)
C
C     ================================================================
C         PRINTING OF RESULTS
C     ================================================================
C
      WRITE(8,2000)
 2000 FORMAT(///2X,65('=')/8X,'REPL1',7X,'REPL2',7X,'REPL3',7X,'MEAN',
     @8X,'Yijk.'/2X,65('='))
      DO 160 I=1,8
       WRITE(8,2100) A(I,1),A(I,2),A(I,3),AVG(I),Y1(I)
 160  CONTINUE
 2100 FORMAT(2X,5F12.6)
      WRITE(8,2200)
 2200 FORMAT(2X,65('='))
```

```
       WRITE(8,2300)
  2300 FORMAT(/2X,50('=')/8X,'Yij..',7X,'Yi.k.',7X,'Y.jk.'/2X,50('='))
       DO 170 I=1,4
        WRITE(8,2400) Y2(I),Y3(I),Y4(I)
  170  CONTINUE
  2400 FORMAT(3X,3F12.6)
       WRITE(8,2500)
  2500 FORMAT(2X,50('='))
C
       WRITE(8,2600)
  2600 FORMAT(/2X,50('=')/8X,'Yi...',7X,'Y.j..',7X,'Y..k.'/2X,50('='))
       DO 180 I=1,2
        WRITE(8,2700) Y5(I),Y6(I),Y7(I)
  180  CONTINUE
  2700 FORMAT(3X,3F12.6)
       WRITE(8,2800)
  2800 FORMAT(2X,50('='))

       WRITE(8,2900)  Y8(1)
  2900 FORMAT(/2X,'Y.... = ',F13.6)
C
C        ANOVA TABLE
C
       DO 190 I=1,9
        READ(6,3000) NAME(I)
  190  CONTINUE
  3000 FORMAT(A15)
       WRITE(8,3100)
  3100 FORMAT(/2X,70('=')/3X,'SOURCE OF',9X,'SUM OF ',5X,'DEGREES OF',5X,
      @'MEAN',9X,'F RATIO'/3X,'VARIATION',9X,'SQUARES',5X,'FREEDOM',8X,'S
      @QUARES'/2X,70('='))
       WRITE(8,3200) NAME(1),SSR,DFR,SQR,FR
       WRITE(8,3200) NAME(2),SSD,DFD,SQD,FD
       WRITE(8,3200) NAME(3),SSV,DFV,SQV,FV
       WRITE(8,3200) NAME(4),SSRD,DFRD,SQRD,FRD
       WRITE(8,3200) NAME(5),SSRV,DFRV,SQRV,FRV
       WRITE(8,3200) NAME(6),SSDV,DFDV,SQDV,FDV
       WRITE(8,3200) NAME(7),SS3F,DF3F,SQ3F,F3F
       WRITE(8,3300) NAME(8),SSE,DFE,SQE
       WRITE(8,3400) NAME(9),SST,DFT
  3200 FORMAT(2X,A15,E12.3,6X,F3.1,5X,E12.3,5X,F8.3)
  3300 FORMAT(2X,A15,E12.3,6X,F4.1,4X,E12.3)
  3400 FORMAT(2X,A15,E12.3,6X,F4.1)
       WRITE(8,3500)
  3500 FORMAT(/2X,70('='))
C
C        ALPHA,BETA AND GAMA VALUES AND INTERACTIONS
C
       WRITE(8,3600)
  3600 FORMAT(/2X,50('=')/7X,'ALPHAi',7X,'BETAj',8X,'GAMAk'/2X,50('='))
       DO 200 I=1,2
        WRITE(8,3700) ALPHA(I),BETA(I),GAMA(I)
  200  CONTINUE
  3700 FORMAT(3X,3F12.6)
       WRITE(8,3800) ALPHAT,BETAT,GAMAT
```

```
 3800 FORMAT(2X,50('-')/3X,3F12.6)
      WRITE(8,3900)
 3900 FORMAT(2X,50('='))
C
      WRITE(8,4000)
 4000 FORMAT(/2X,50('=')/8X,'(AB)ij',6X,'(AG)ik',5X,'(BG)jk'/2X,50('='))
      DO 210 I=1,4
       WRITE(8,4100) AB(I),AG(I),BG(I)
 210  CONTINUE
 4100 FORMAT(3X,3F12.6)
      WRITE(8,4200) ABT,AGT,BGT
 4200 FORMAT(2X,50('-')/3X,3F12.6)
      WRITE(8,4300)
 4300 FORMAT(2X,50('='))
C
      WRITE(8,4400)
 4400 FORMAT(/2X,15('=')/5X,'(ABG)ijk'/2X,15('='))
      DO 220 I=1,8
       WRITE(8,4500) ABG(I)
 220  CONTINUE
 4500 FORMAT(3X,F10.6)
      WRITE(8,4600) ABGT
 4600 FORMAT(2X,15('-')/3X,F10.6)
      WRITE(8,4700)
 4700 FORMAT(2X,15('='))
C
C        OBSERVED,PREDICTED AND RESIDUAL VALUES
C
      WRITE(8,4800)
 4800 FORMAT(/2X,50('=')/7X,'OBSERVED',4X,'PREDICTED',4X,'RESIDUAL'/2X,5
     @0('='))
      DO 230 I=1,8
       DO 240 J=1,3
        WRITE(8,4900) A(I,J),PRED(I),RES(I,J)
 240   CONTINUE
 230  CONTINUE
 4900 FORMAT(3X,3F12.6)
      WRITE(8,5000)
 5000 FORMAT(2X,50('='))
C
C        2**3 FACTORIAL DESIGN RESULTS
C
      WRITE(8,5100)
 5100 FORMAT(/2X,60('=')/10X,'2**3 FACTORIAL DESIGN'/2X,60('=')/3X,'EFFE
     @CT',18X,'ESTIMATE',11X,'SUM OF SQUARES'/2X,60('='))
      DO 250 I=1,10
       READ(7,5200) FACTOR(I)
 250  CONTINUE
 5200 FORMAT(A22)
      WRITE(8,5300) FACTOR(1)
      WRITE(8,5400) FACTOR(2),ER,ESSR
      WRITE(8,5400) FACTOR(3),ED,ESSD
      WRITE(8,5400) FACTOR(4),EV,ESSV
      WRITE(8,5300) FACTOR(5)
      WRITE(8,5400) FACTOR(6),ERD,ESRD
      WRITE(8,5400) FACTOR(7),ERV,ESRV
```

```
      WRITE(8,5400) FACTOR(8),EDV,ESDV
      WRITE(8,5300) FACTOR(9)
      WRITE(8,5400) FACTOR(10),ERDV,ES3F
 5300 FORMAT(A22)
 5400 FORMAT(2X,A22,E12.3,10X,E12.3)
      WRITE(8,5500)
 5500 FORMAT(2X,60('='))
C
      WRITE(8,5600) VEF
 5600 FORMAT(/2X,'VARIANCE OF EFFECTS= ',E12.3)
      WRITE(8,5700) STDE
 5700 FORMAT(/2X,'STD.ERROR OF EFFECTS= ',F12.6)
      WRITE(8,5800)
 5800 FORMAT(//2X,60('='))
C
      CLOSE(5)
      CLOSE(6)
      CLOSE(7)
      CLOSE(8)
C
C
      STOP
      END
```

APPENDICES C.2

MULTIVARIATE ANALYSIS OF VARIANCE PROGRAM OUTPUT FOR THE REAERATION RATE COEFFICIENT

```
=====================================================================
      REPL1        REPL2        REPL3        MEAN         Yijk.
=====================================================================
    0.008587     0.008238     0.006882     0.007902     0.023707
    0.030452     0.025029     0.025269     0.026917     0.080750
    0.006303     0.006298     0.007673     0.006758     0.020274
    0.016734     0.015108     0.015361     0.015734     0.047203
    0.008271     0.009138     0.010019     0.009143     0.027428
    0.034594     0.029933     0.031485     0.032004     0.096012
    0.007935     0.007337     0.007156     0.007476     0.022428
    0.017618     0.014951     0.016611     0.016393     0.049180
=====================================================================

=====================================================
      Yij..        Yi.k.        Y.jk.
=====================================================
     0.104457     0.043981     0.051135
     0.067477     0.127953     0.176762
     0.123440     0.049856     0.042702
     0.071608     0.145192     0.096383
=====================================================

=====================================================
      Yi...        Y.j..        Y..k.
=====================================================
     0.171934     0.227897     0.093837
     0.195048     0.139085     0.273145
=====================================================

Y.... =       0.366982

===========================================================================
 SOURCE OF          SUM OF      DEGREES OF      MEAN          F RATIO
 VARIATION          SQUARES     FREEDOM         SQUARES
===========================================================================
 ROUGHNESS(R)      0.223E-04       1.0        0.223E-04          8.917
 DEPTH(D)          0.329E-03       1.0        0.329E-03        131.682
 VELOCITY(V)       0.134E-02       1.0        0.134E-02        536.775
 RD                0.919E-05       1.0        0.919E-05          3.684
 RV                0.538E-05       1.0        0.538E-05          2.157
 DV                0.216E-03       1.0        0.216E-03         86.420
 RDV               0.572E-05       1.0        0.572E-05          2.293
 ERROR             0.399E-04      16.0        0.250E-05
 TOTAL             0.197E-02      23.0
===========================================================================
```

```
=================================================
     ALPHAi        BETAj         GAMAk
=================================================
    -0.007471     0.003700    -0.000963
     0.007471    -0.003700     0.000963
-------------------------------------------------
     0.000000     0.000000     0.000000
=================================================

=================================================
      (AB)ij       (AG)ik      (BG)jk
=================================================
    -0.002998     0.000473    -0.000619
     0.002998    -0.000474     0.000619
     0.002998    -0.000473     0.000619
    -0.002998     0.000474    -0.000619
-------------------------------------------------
     0.000000    -0.000000    -0.000000
=================================================

==============
   (ABG)ijk
==============
   0.000488
  -0.000488
  -0.000488
   0.000488
  -0.000488
   0.000488
   0.000488
  -0.000488
--------------
  -0.000000
==============

=================================================
     OBSERVED     PREDICTED     RESIDUAL
=================================================
     0.008587     0.007902     0.000685
     0.008238     0.007902     0.000336
     0.006882     0.007902    -0.001020
     0.030452     0.026917     0.003535
     0.025029     0.026917    -0.001888
     0.025269     0.026917    -0.001648
     0.006303     0.006758    -0.000455
     0.006298     0.006758    -0.000460
     0.007673     0.006758     0.000915
     0.016734     0.015734     0.001000
     0.015108     0.015734    -0.000626
     0.015361     0.015734    -0.000373
     0.008271     0.009143    -0.000872
     0.009138     0.009143    -0.000005
     0.010019     0.009143     0.000876
     0.034594     0.032004     0.002590
     0.029933     0.032004    -0.002071
     0.031485     0.032004    -0.000519
```

```
      0.007935    0.007476    0.000459
      0.007337    0.007476   -0.000139
      0.007156    0.007476   -0.000320
      0.017618    0.016393    0.001225
      0.014951    0.016393   -0.001442
      0.016611    0.016393    0.000218
 ==================================================

 ============================================================
        2**3 FACTORIAL DESIGN
 ============================================================
  EFFECT                    ESTIMATE            SUM OF SQUARES
 ============================================================
MAIN EFFECTS
   ROUGHNESS(R)              0.193E-02              0.223E-04
   DEPTH(D)                 -0.740E-02              0.329E-03
   VELOCITY(V)               0.149E-01              0.134E-02
2-FACTOR INTERACTION
     RD                     -0.124E-02              0.919E-05
     RV                      0.947E-03              0.538E-05
     DV                     -0.600E-02              0.216E-03
3-FACTOR INTERACTION
     RDV                    -0.977E-03              0.572E-05
 ============================================================

 VARIANCE OF EFFECTS=     0.416E-06

 STD.ERROR OF EFFECTS=      0.000645


 ============================================================
```

APPENDICES C.3

MULTIVARIATE ANALYSIS OF VARIANCE PROGRAM OUTPUT FOR THE OXYGEN TRANSFER COEFFICIENT

```
=================================================================
      REPL1       REPL2       REPL3       MEAN        Yijk.
=================================================================
    0.085870    0.082380    0.068820    0.079023    0.237070
    0.304520    0.250290    0.252690    0.269167    0.807500
    0.100848    0.100768    0.122768    0.108128    0.324384
    0.267744    0.241728    0.245776    0.251749    0.755248
    0.082710    0.091380    0.100190    0.091427    0.274280
    0.345940    0.299330    0.314850    0.320040    0.960120
    0.126960    0.117392    0.114496    0.119616    0.358848
    0.281888    0.239216    0.265776    0.262293    0.786880
=================================================================

==================================================
      Yij..       Yi.k.       Y.jk.
==================================================
     1.044570    0.561454    0.511350
     1.079632    1.562748    1.767619
     1.234400    0.633128    0.683232
     1.145727    1.747000    1.542128
==================================================

==================================================
      Yi...       Y.j..       Y..k.
==================================================
     2.124201    2.278969    1.194582
     2.380127    2.225359    3.309747
==================================================

Y.... =      4.504329

=======================================================================
 SOURCE OF         SUM OF      DEGREES OF     MEAN           F RATIO
 VARIATION         SQUARES     FREEDOM        SQUARES
=======================================================================
 ROUGHNESS(R)     0.273E-02      1.0        0.273E-02          8.651
 DEPTH(D)         0.120E-03      1.0        0.120E-03          0.381
 VELOCITY(V)      0.186E+00      1.0        0.186E+00        590.875
 RD               0.638E-03      1.0        0.638E-03          2.023
 RV               0.528E-03      1.0        0.528E-03          1.675
 DV               0.658E-02      1.0        0.658E-02         20.855
 RDV              0.582E-03      1.0        0.582E-03          1.844
 ERROR            0.505E-02     16.0        0.315E-03
 TOTAL            0.203E+00     23.0
=======================================================================
```

```
==================================================
    ALPHAi        BETAj        GAMAk
==================================================
   -0.088132    0.002234   -0.010663
    0.088132   -0.002234    0.010664
--------------------------------------------------
    0.000000    0.000000    0.000000
==================================================

==================================================
     (AB)ij       (AG)ik      (BG)jk
==================================================
   -0.016557    0.004691   -0.005156
    0.016557   -0.004691    0.005155
    0.016557   -0.004691    0.005156
   -0.016557    0.004691   -0.005156
--------------------------------------------------
   -0.000000   -0.000000   -0.000000
==================================================

===============
  (ABG)ijk
===============
   0.004927
  -0.004927
  -0.004927
   0.004927
  -0.004927
   0.004927
   0.004927
  -0.004927
---------------
   0.000000
===============

==================================================
    OBSERVED    PREDICTED    RESIDUAL
==================================================
     0.085870    0.079023    0.006847
     0.082380    0.079023    0.003357
     0.068820    0.079023   -0.010203
     0.304520    0.269167    0.035353
     0.250290    0.269167   -0.018877
     0.252690    0.269167   -0.016477
     0.100848    0.108128   -0.007280
     0.100768    0.108128   -0.007360
     0.122768    0.108128    0.014640
     0.267744    0.251749    0.015995
     0.241728    0.251749   -0.010021
     0.245776    0.251749   -0.005973
     0.082710    0.091427   -0.008717
     0.091380    0.091427   -0.000047
     0.100190    0.091427    0.008763
     0.345940    0.320040    0.025900
     0.299330    0.320040   -0.020710
     0.314850    0.320040   -0.005190
```

```
      0.126960    0.119616    0.007344
      0.117392    0.119616   -0.002224
      0.114496    0.119616   -0.005120
      0.281888    0.262293    0.019595
      0.239216    0.262293   -0.023077
      0.265776    0.262293    0.003483
 ==================================================

 ============================================================
         2**3 FACTORIAL DESIGN
 ============================================================
  EFFECT                   ESTIMATE             SUM OF SQUARES
 ============================================================
MAIN EFFECTS
   ROUGHNESS(R)             0.213E-01              0.273E-02
   DEPTH(D)                -0.447E-02              0.120E-03
   VELOCITY(V)              0.176E+00              0.186E+00
2-FACTOR INTERACTION
     RD                    -0.103E-01              0.638E-03
     RV                     0.938E-02              0.528E-03
     DV                    -0.331E-01              0.658E-02
3-FACTOR INTERACTION
     RDV                   -0.985E-02              0.583E-03
 ============================================================

 VARIANCE OF EFFECTS=    0.526E-04

 STD.ERROR OF EFFECTS=     0.007251


 ============================================================
```

APPENDICES C.4

MULTIVARIATE ANALYSIS OF VARIANCE PROGRAM OUTPUT FOR THE PROPANE GAS DESORPTION RATE COEFFICIENT

```
======================================================================
     REPL1        REPL2        REPL3        MEAN         Yijk.
======================================================================
   0.006106     0.006040     0.005257     0.005801     0.017403
   0.021703     0.018026     0.019210     0.019646     0.058939
   0.004252     0.004056     0.005860     0.004723     0.014168
   0.013364     0.010936     0.011035     0.011778     0.035335
   0.005861     0.006088     0.007219     0.006389     0.019168
   0.029815     0.022721     0.027534     0.026690     0.080070
   0.005568     0.004547     0.005320     0.005145     0.015435
   0.013036     0.010681     0.013848     0.012522     0.037565
======================================================================

======================================================
     Yij..        Yi.k.        Y.jk.
======================================================
   0.076342     0.031571     0.036571
   0.049503     0.094274     0.139009
   0.099238     0.034603     0.029603
   0.053000     0.117635     0.072900
======================================================

======================================================
     Yi...        Y.j..        Y..k.
======================================================
   0.125845     0.175580     0.066174
   0.152238     0.102503     0.211909
======================================================

Y.... =      0.278083

============================================================================
 SOURCE OF          SUM OF        DEGREES OF      MEAN          F RATIO
 VARIATION          SQUARES       FREEDOM         SQUARES
============================================================================
 ROUGHNESS(R)      0.290E-04        1.0          0.290E-04        9.987
 DEPTH(D)          0.223E-03        1.0          0.223E-03       76.577
 VELOCITY(V)       0.885E-03        1.0          0.885E-03      304.551
 RD                0.157E-04        1.0          0.157E-04        5.397
 RV                0.172E-04        1.0          0.172E-04        5.929
 DV                0.146E-03        1.0          0.146E-03       50.154
 RDV               0.141E-04        1.0          0.141E-04        4.854
 ERROR             0.465E-04       16.0          0.291E-05
 TOTAL             0.138E-02       23.0
============================================================================
```

```
==================================================
     ALPHAi       BETAj        GAMAk
==================================================
    -0.006072    0.003045    -0.001100
     0.006072   -0.003045     0.001100
--------------------------------------------------
     0.000000    0.000000     0.000000
==================================================

==================================================
      (AB)ij      (AG)ik      (BG)jk
==================================================
    -0.002464    0.000847    -0.000808
     0.002464   -0.000847     0.000808
     0.002464   -0.000847     0.000808
    -0.002464    0.000847    -0.000808
--------------------------------------------------
    -0.000000   -0.000000    -0.000000
==================================================

===============
   (ABG)ijk
===============
   0.000767
  -0.000767
  -0.000767
   0.000767
  -0.000767
   0.000767
   0.000767
  -0.000767
---------------
   0.000000
===============

==================================================
     OBSERVED    PREDICTED    RESIDUAL
==================================================
     0.006106    0.005801     0.000305
     0.006040    0.005801     0.000239
     0.005257    0.005801    -0.000544
     0.021703    0.019646     0.002057
     0.018026    0.019646    -0.001620
     0.019210    0.019646    -0.000436
     0.004252    0.004723    -0.000471
     0.004056    0.004723    -0.000667
     0.005860    0.004723     0.001137
     0.013364    0.011778     0.001586
     0.010936    0.011778    -0.000842
     0.011035    0.011778    -0.000743
     0.005861    0.006389    -0.000528
     0.006088    0.006389    -0.000301
     0.007219    0.006389     0.000830
     0.029815    0.026690     0.003125
     0.022721    0.026690    -0.003969
     0.027534    0.026690     0.000844
```

```
      0.005568    0.005145    0.000423
      0.004547    0.005145   -0.000598
      0.005320    0.005145    0.000175
      0.013036    0.012522    0.000514
      0.010681    0.012522   -0.001841
      0.013848    0.012522    0.001326
 ==================================================

 ============================================================
        2**3 FACTORIAL DESIGN
 ============================================================
 EFFECT                    ESTIMATE           SUM OF SQUARES
 ============================================================
MAIN EFFECTS
   ROUGHNESS(R)             0.220E-02            0.290E-04
   DEPTH(D)                -0.609E-02            0.223E-03
   VELOCITY(V)              0.121E-01            0.885E-03
2-FACTOR INTERACTION
     RD                    -0.162E-02            0.157E-04
     RV                     0.169E-02            0.172E-04
     DV                    -0.493E-02            0.146E-03
3-FACTOR INTERACTION
     RDV                   -0.153E-02            0.141E-04
 ============================================================

 VARIANCE OF EFFECTS=     0.484E-06

 STD.ERROR OF EFFECTS=      0.000696


 ============================================================
```

APPENDICES C.5

MULTIVARIATE ANALYSIS OF VARIANCE PROGRAM OUTPUT FOR THE VELOCITY OF BENZOIC ACID DISSOLUTION COEFFICIENT

```
=================================================================
      REPL1        REPL2        REPL3        MEAN         Yijk.
=================================================================
    0.000107     0.000117     0.000117     0.000114     0.000341
    0.000190     0.000178     0.000179     0.000182     0.000547
    0.000119     0.000116     0.000133     0.000123     0.000368
    0.000188     0.000191     0.000195     0.000191     0.000574
    0.000119     0.000132     0.000126     0.000126     0.000377
    0.000187     0.000173     0.000166     0.000175     0.000526
    0.000140     0.000133     0.000132     0.000135     0.000405
    0.000164     0.000145     0.000144     0.000151     0.000453
=================================================================

==================================================
      Yij..        Yi.k.        Y.jk.
==================================================
     0.000888     0.000709     0.000718
     0.000942     0.001121     0.001073
     0.000903     0.000782     0.000773
     0.000858     0.000979     0.001027
==================================================

==================================================
      Yi...        Y.j..        Y..k.
==================================================
     0.001830     0.001791     0.001491
     0.001761     0.001800     0.002100
==================================================

Y.... =      0.003591

=====================================================================
 SOURCE OF        SUM OF       DEGREES OF    MEAN          F RATIO
 VARIATION        SQUARES      FREEDOM       SQUARES
=====================================================================
 ROUGHNESS(R)    0.198E-09       1.0        0.198E-09        3.321
 DEPTH(D)        0.318E-11       1.0        0.318E-11        0.053
 VELOCITY(V)     0.155E-07       1.0        0.155E-07      259.218
 RD              0.409E-09       1.0        0.409E-09        6.853
 RV              0.193E-08       1.0        0.193E-08       32.312
 DV              0.425E-09       1.0        0.425E-09        7.126
 RDV             0.425E-09       1.0        0.425E-09        7.131
 ERROR           0.954E-09      16.0        0.596E-10
 TOTAL           0.198E-07      23.0
=====================================================================
```

```
==================================================
     ALPHAi        BETAj        GAMAk
==================================================
   -0.000025   -0.000000    0.000003
    0.000025    0.000000   -0.000003
--------------------------------------------------
    0.0         0.0         0.000000
==================================================

==================================================
      (AB)ij       (AG)ik      (BG)jk
==================================================
   -0.000004   -0.000009   -0.000004
    0.000004    0.000009    0.000004
    0.000004    0.000009    0.000004
   -0.000004   -0.000009   -0.000004
--------------------------------------------------
    0.000000    0.000000    0.0
==================================================

===============
   (ABG)ijk
===============
   0.000004
  -0.000004
  -0.000004
   0.000004
  -0.000004
   0.000004
   0.000004
  -0.000004
---------------
   0.000000
===============

==================================================
     OBSERVED     PREDICTED     RESIDUAL
==================================================
     0.000107     0.000114    -0.000007
     0.000117     0.000114     0.000003
     0.000117     0.000114     0.000003
     0.000190     0.000182     0.000008
     0.000178     0.000182    -0.000004
     0.000179     0.000182    -0.000003
     0.000119     0.000123    -0.000004
     0.000116     0.000123    -0.000007
     0.000133     0.000123     0.000010
     0.000188     0.000191    -0.000003
     0.000191     0.000191    -0.000000
     0.000195     0.000191     0.000004
     0.000119     0.000126    -0.000007
     0.000132     0.000126     0.000006
     0.000126     0.000126     0.000000
     0.000187     0.000175     0.000012
     0.000173     0.000175    -0.000002
     0.000166     0.000175    -0.000009
```

```
     0.000140    0.000135    0.000005
     0.000133    0.000135   -0.000002
     0.000132    0.000135   -0.000003
     0.000164    0.000151    0.000013
     0.000145    0.000151   -0.000006
     0.000144    0.000151   -0.000007
 ==================================================

 ============================================================
        2**3 FACTORIAL DESIGN
 ============================================================
  EFFECT                     ESTIMATE             SUM OF SQUARES
 ============================================================
MAIN EFFECTS
   ROUGHNESS(R)             -0.575E-05               0.198E-09
   DEPTH(D)                  0.750E-06               0.337E-11
   VELOCITY(V)               0.508E-04               0.155E-07
2-FACTOR INTERACTION
     RD                     -0.825E-05               0.408E-09
     RV                     -0.179E-04               0.193E-08
     DV                     -0.842E-05               0.425E-09
3-FACTOR INTERACTION
     RDV                    -0.842E-05               0.425E-09
 ============================================================

 VARIANCE OF EFFECTS=    0.994E-11

 STD.ERROR OF EFFECTS=     0.000003


 ============================================================
```

APPENDICES C.6

ANALYSIS OF RESIDUALS FOR THE FOUR RESPONSE VARIABLES FROM THE MULTIVARIATE ANALYSIS OF VARIANCE RESULTS

```
MTB > READ 'OBS.PRED1K2' C1-C3
     24 ROWS READ

MTB > PRINT C1-C3


 ROW       OBS         PRED        RESID


   1   0.008587   0.007902   0.000685
   2   0.008238   0.007902   0.000336
   3   0.006882   0.007902  -0.001020
   4   0.030452   0.026917   0.003535
   5   0.025029   0.026917  -0.001888
   6   0.025269   0.026917  -0.001648
   7   0.006303   0.006758  -0.000455
   8   0.006298   0.006758  -0.000460
   9   0.007673   0.006758   0.000915
  10   0.016734   0.015734   0.001000
  11   0.015108   0.015734  -0.000626
  12   0.015361   0.015734  -0.000373
  13   0.008271   0.009143  -0.000872
  14   0.009138   0.009143  -0.000005
  15   0.010019   0.009143   0.000876
  16   0.034594   0.032004   0.002590
  17   0.029933   0.032004  -0.002071
  18   0.031485   0.032004  -0.000519
  19   0.007935   0.007476   0.000459
  20   0.007337   0.007476  -0.000139
  21   0.007156   0.007476  -0.000320
  22   0.017618   0.016393   0.001225
  23   0.014951   0.016393  -0.001442
  24   0.016611   0.016393   0.000218

MTB > DOTPLOT C3

                   .
       .. . .  . .::  .. ...  ..: .           .      .
   -+---------+---------+---------+---------+---------+------RESID
-0.0024   -0.0012    0.0000    0.0012    0.0024    0.0036
```

```
MTB > PLOT C3 C2

        -                                             *
  0.0032+
        -
RESID   -                                                       *
        -
        -
  0.0016+
        -                        *
        -     *   *            *
        -       *
        -      **                *
  0.0000+      *  *
        -     2*               *
        -                      *                                *
        -       * *
        -
 -0.0016+                        *                    *
        -                                             *         *
        -
          +---------+---------+---------+---------+---------+------PRED
     0.0050    0.0100    0.0150    0.0200    0.0250    0.0300

MTB > NSCORES C3 C4
MTB > PLOT C3 C4

        -                                                         *
  0.0032+
        -
RESID   -                                                  *
        -
        -
  0.0016+
        -                                               *
        -                                       *  *  *
        -                                      *
        -                                 **  *
  0.0000+                              **
        -                        ** **
        -                    * *
        -                 * *
        -
 -0.0016+           *  *
        - *      *
        -
          --------+---------+---------+---------+---------+--------NSCORES
              -1.40     -0.70      0.00      0.70      1.40

MTB > READ 'OBS.PRED1KL' C1-C3
     24 ROWS READ

MTB > PRINT C1-C3
 ROW       OBS        PRED       RESID

   1  0.085870    0.079023    0.006847
```

```
  2   0.082380   0.079023   0.003357
  3   0.068820   0.079023  -0.010203
  4   0.304520   0.269167   0.035353
  5   0.250290   0.269167  -0.018877
  6   0.252690   0.269167  -0.016477
  7   0.100848   0.108128  -0.007280
  8   0.100768   0.108128  -0.007360
  9   0.122768   0.108128   0.014640
 10   0.267744   0.251749   0.015995
 11   0.241728   0.251749  -0.010021
 12   0.245776   0.251749  -0.005973
 13   0.082710   0.091427  -0.008717
 14   0.091380   0.091427  -0.000047
 15   0.100190   0.091427   0.008763
 16   0.345940   0.320040   0.025960
 17   0.299330   0.320040  -0.020710
 18   0.314850   0.320040  -0.005190
 19   0.126960   0.119616   0.007344
 20   0.117392   0.119616  -0.002224
 21   0.114496   0.119616  -0.005120
 22   0.281888   0.262293   0.019595
 23   0.239216   0.262293  -0.023077
 24   0.265776   0.262293   0.003483

MTB > DOTPLOT C3

              . .. .    ...:.: . .  :  :.     ..  .     .      .
          ---+---------+---------+---------+---------+---------+---RESID
          -0.024    -0.012     0.000     0.012     0.024     0.036

MTB > PLOT C3 C2

   0.040+
        -                                             *
RESID   -
        -
        -                                                       *
   0.020+                                           *
        -             *                           *
        -
        -       * *     *
        -       *                                   *
   0.000+         *
        -               2                         *             *
        -         *   2
        -       *                                 *
        -                                             *
  -0.020+                                             *         *
        -                                           *
        -
        -
          +---------+---------+---------+---------+---------+------PRED
      0.050     0.100     0.150     0.200     0.250     0.300

MTB > NSCORES C3 C4
MTB > PLOT C3 C4
```

```
   0.040+
        -                                                         *
RESID   -
        -
        -                                                  *
   0.020+                                               *
        -                                         *  *
        -
        -                                    * **
        -                                 **
   0.000+                               *
        -                         * ** *
        -                    * * *
        -                 * *
        -              *
  -0.020+        *  *
        - *
        -
        -
          --------+---------+---------+---------+---------+--------NSCORES
              -1.40     -0.70      0.00      0.70      1.40

MTB > READ 'OBS.PRED1KP' C1-C3
     24 ROWS READ


MTB > PRINT C1-C3

 ROW        OBS       PRED      RESID

   1   0.006106   0.005801   0.000305
   2   0.006040   0.005801   0.000239
   3   0.005257   0.005801  -0.000544
   4   0.021703   0.019646   0.002057
   5   0.018026   0.019646  -0.001620
   6   0.019210   0.019646  -0.000436
   7   0.004252   0.004723  -0.000471
   8   0.004056   0.004723  -0.000667
   9   0.005860   0.004723   0.001137
  10   0.013364   0.011778   0.001586
  11   0.010936   0.011778  -0.000842
  12   0.011035   0.011778  -0.000743
  13   0.005861   0.006389  -0.000528
  14   0.006088   0.006389  -0.000301
  15   0.007219   0.006389   0.000830
  16   0.029815   0.026690   0.003125
  17   0.022721   0.026690  -0.003969
  18   0.027534   0.026690   0.000844
  19   0.005568   0.005145   0.000423
  20   0.004547   0.005145  -0.000598
  21   0.005320   0.005145   0.000175
  22   0.013036   0.012522   0.000514
  23   0.010681   0.012522  -0.001841
  24   0.013848   0.012522   0.001326
```

```
MTB > DOTPLOT C3


                                     :
               .             ..    ..::.  .::  : .. .  .      .
          -+---------+---------+---------+---------+---------+-----RESID
       -0.0045   -0.0030   -0.0015    0.0000    0.0015    0.0030

MTB > PLOT C3 C2

RESID   -                                                    *
        -
        -
  0.0020+                                      *
        -                       *
        -        *               *
        -            *                                       *
        -         * 2            *
  0.0000+         *
        -        ** *2                         *
        -        *              2
        -
        -                                      *
 -0.0020+                        *
        -
        -
        -
        -
 -0.0040+                                                    *
          --------+---------+---------+---------+---------+--------PRED
             0.0050    0.0100    0.0150    0.0200    0.0250

MTB > NSCORES C3 C4
MTB > PLOT C3 C4

RESID   -                                                         *
        -
        -
  0.0020+                                                  *
        -                                               *
        -                                         *  *
        -                                      **
        -                               * ** *
  0.0000+                              *
        -                    * * ** **
        -              *  * *
        -
        -           *
 -0.0020+        *
        -
        -
        -
        -
 -0.0040+ *
          --------+---------+---------+---------+---------+--------NSCORES
              -1.40     -0.70      0.00      0.70      1.40
```

```
MTB > READ 'OBS.PRED1KS' C1-C3

     24 ROWS READ


MTB > PRINT C1-C3

 ROW       OBS        PRED       RESID

   1  0.000107  0.000114  -0.000007
   2  0.000117  0.000114   0.000003
   3  0.000117  0.000114   0.000003
   4  0.000190  0.000182   0.000008
   5  0.000178  0.000182  -0.000004
   6  0.000179  0.000182  -0.000003
   7  0.000119  0.000123  -0.000004
   8  0.000116  0.000123  -0.000007
   9  0.000133  0.000123   0.000010
  10  0.000188  0.000191  -0.000003
  11  0.000191  0.000191   0.000000
  12  0.000195  0.000191   0.000004
  13  0.000119  0.000126  -0.000007
  14  0.000132  0.000126   0.000006
  15  0.000126  0.000126   0.000000
  16  0.000187  0.000175   0.000012
  17  0.000173  0.000175  -0.000002
  18  0.000166  0.000175  -0.000009
  19  0.000140  0.000135   0.000005
  20  0.000133  0.000135  -0.000002
  21  0.000132  0.000135  -0.000003
  22  0.000164  0.000151   0.000013
  23  0.000145  0.000151  -0.000006
  24  0.000144  0.000151  -0.000007


MTB > DOTPLOT C3

            :       .
        .   : .   : : :   :     : . . .   .   .   . .
   ---+---------+---------+---------+---------+---------+---RESID
-1.00E-05 -5.00E-06 0.0000000 0.0000050 0.0000100 0.0000150


MTB > PLOT C3 C2
```

```
1.40E-05+
        -                            *               *
RESID   -
        -         *
        -                                                *
7.00E-06+           *     *
        -                                                      *
        -   2
        -
0.00E+00+           *                                          *
        -                 *                          *
        -                 *                              *     *
        -         *                                      *
        -                            *
-7.0E-06+   *     * *                *
        -                                            *
        -
        -
          ------+---------+---------+---------+---------+---------+PRED
         0.000120  0.000135  0.000150  0.000165  0.000180  0.000195

MTB > NSCORES C3 C4
MTB > PLOT C3 C4

1.40E-05+
        -                                                  *      *
RESID   -
        -                                               *
        -                                            *
7.00E-06+
        -                                       *  *
        -                                      *
        -                                   2
        -
0.00E+00+                                2
        -                             2
        -                         3
        -                     2
        -                   *
-7.0E-06+             4
        - *
        -
        -
          --------+---------+---------+---------+---------+--------NSCORES
              -1.40     -0.70      0.00      0.70      1.40

MTB > OUTFILE
```

APPENDICES C.7

VARIANCE STABILIZING TRANSFORMATIONS

REGRESSION ANALYSIS FOR THE EMPIRICAL DETERMINATION OF AN APPROPRIATE DATA TRANSFORMATION

```
MTB > READ 'AVG.STD1' C1-C8

      8 ROWS READ


MTB > PRINT C1-C4

 ROW      AVG.K2      STD.K2      AVG.KL     STD.KL

   1    0.007902    0.000901    0.07902    0.00901
   2    0.026917    0.003064    0.26917    0.03064
   3    0.006758    0.000792    0.10813    0.01268
   4    0.015734    0.000875    0.25175    0.01400
   5    0.009143    0.000874    0.09143    0.00874
   6    0.032004    0.002373    0.32004    0.02373
   7    0.007476    0.000408    0.11962    0.00652
   8    0.016393    0.001347    0.26229    0.02155


MTB > PRINT C5-C8

 ROW      AVG.KP      STD.KP      AVG.KS        STD.KS

   1    0.005801    0.000472    0.000114    0.0000058
   2    0.019646    0.001877    0.000182    0.0000067
   3    0.004726    0.000986    0.000123    0.0000091
   4    0.011778    0.001374    0.000191    0.0000035
   5    0.006389    0.000727    0.000126    0.0000065
   6    0.026690    0.003622    0.000175    0.0000107
   7    0.005145    0.000533    0.000135    0.0000044
   8    0.012522    0.001645    0.000151    0.0000113

MTB > LET C10=LOGE(C1)
MTB > LET C11=LOGE(C2)
MTB > LET C12=LOGE(C3)
MTB > LET C13=LOGE(C4)
MTB > LET C14=LOGE(C5)
MTB > LET C15=LOGE(C6)
MTB > LET C16=LOGE(C7)
MTB > LET C17=LOGE(C8)


MTB > NAME C10 'LN.AVGK2',C11 'LN.STDK2',C12 'LN.AVGKL',C13 'LN.STDKL'
```

```
MTB > NAME C14 'LN.AVGKP',C15 'LN.STDKP',C16 'LN.AVGKS',C17 'LN.STDKS'


MTB > PLOT C11 C10


        -                                                   *
        -
   -6.00+                                                        *
        -
LN.STDK2-
        -
        -
   -6.60+                                  *
        -
        -
        -          *
        -               *                 *
   -7.20+    *
        -
        -
        -
        -
   -7.80+        *
        -
          +---------+---------+---------+---------+---------+------LN.AVGK2
      -5.10     -4.80     -4.50     -4.20     -3.90     -3.60

MTB > REGRESS C11 1 C10


The regression equation is
LN.STDK2 = - 2.73 + 0.940 LN.AVGK2


Predictor       Coef          Stdev     t-ratio
Constant     -2.7268         0.9226       -2.96
LN.AVGK2      0.9401         0.2106        4.46

s = 0.3355      R-sq = 76.9%     R-sq(adj) = 73.0%

Analysis of Variance

SOURCE       DF          SS          MS
Regression    1      2.2427      2.2427
Error         6      0.6755      0.1126
Total         7      2.9182
```

Regression analysis suggets log-transformation of data since the slope of the regression line is 0.940 (refer to Box et al., 1978, for details).

```
MTB > PLOT C13 C12

        -
   -3.50+                                               *
        -
LN.STDKL-                                                     *
        -                                              *
        -
   -4.00+
        -
        -
        -                                             *
        -                 *
   -4.50+
        -
        -      *    *
        -
        -
   -5.00+                    *
        -
        -
          +---------+---------+---------+---------+---------+------LN.AVGKL
        -2.70     -2.40     -2.10     -1.80     -1.50     -1.20

MTB > REGRESS C13 1 C12


The regression equation is
LN.STDKL = - 2.81 + 0.812 LN.AVGKL


Predictor       Coef         Stdev     t-ratio
Constant     -2.8059        0.3996       -7.02
LN.AVGKL      0.8123        0.2123        3.83

s = 0.3181      R-sq = 70.9%     R-sq(adj) = 66.1%


Analysis of Variance


SOURCE        DF          SS          MS
Regression     1      1.4807      1.4807
Error          6      0.6071      0.1012
Total          7      2.0878
```

Regression analysis suggests log-transformation of data since the slope of the straight line is 0.812 (refer to Box et al., 1978, for details).

```
MTB > PLOT C15 C14

        -
LN.STDKP-                                                     *
        -
        -
   -6.00+
        -
        -                                             *
        -                                *
        -
   -6.60+                              *
        -
        -
        -    *
        -
   -7.20+             *
        -
        -
        -      *
        -          *
          ------+---------+---------+---------+---------+---------+LN.AVGKP
            -5.25     -4.90     -4.55     -4.20     -3.85     -3.50

MTB > REGRESS C15 1 C14


The regression equation is
LN.STDKP = - 2.29 + 0.966 LN.AVGKP

Predictor        Coef         Stdev     t-ratio
Constant      -2.2898        0.8247       -2.78
LN.AVGKP       0.9656        0.1758        5.49

s = 0.3036      R-sq = 83.4%     R-sq(adj) = 80.6%

Analysis of Variance

SOURCE       DF          SS          MS
Regression    1      2.7801      2.7801
Error         6      0.5531      0.0922
Total         7      3.3332

Unusual Observations
Obs.LN.AVGKP  LN.STDKP       Fit Stdev.Fit  Residual   St.Resid
  3    -5.35    -6.922    -7.461     0.164     0.539      2.11R

R denotes an obs. with a large st. resid.
```

Regression analysis suggests log-transformation of data since the slope of the straight line is 0.966 (refer to Box et al., 1978, for details).

```
MTB > PLOT C17 C16

LN.STDKS-
        -                               *
        -                                              *
  -11.55+
        -           *
        -
        -
        -
  -11.90+                                                  *
        -             *
        -   *
        -
        -
  -12.25+
        -                    *
        -
        -
        -                                                       *
  -12.60+
          +---------+---------+---------+---------+---------+------LN.AVGKS
      -9.10     -9.00     -8.90     -8.80     -8.70     -8.60

MTB > REGRESS C17 1 C16


The regression equation is
LN.STDKS = - 13.5 - 0.183 LN.AVGKS

Predictor       Coef          Stdev     t-ratio
Constant     -13.524          7.560       -1.79
LN.AVGKS     -0.1830         0.8566       -0.21

s = 0.4473      R-sq = 0.8%      R-sq(adj) = 0.0%

Analysis of Variance

SOURCE       DF          SS          MS
Regression    1      0.0091      0.0091
Error         6      1.2006      0.2001
Total         7      1.2097
```

No apparent data transformation is needed since no correlation has been verified between the standard error and mean of the velocity of solids dissolution data set (refer to Box et al., 1978, for details).

APPENDICES C.8

MULTIVARIATE ANALYSIS OF VARIANCE PROGRAM OUTPUT FOR THE LOG-TRANSFORMED DATA OF THE REAERATION RATE COEFFICIENT

```
=================================================================
    REPL1       REPL2       REPL3       MEAN        Yijk.
=================================================================
  -4.757506   -4.798998   -4.978846   -4.845117  -14.535350
  -3.491604   -3.687720   -3.678177   -3.619166  -10.857501
  -5.066730   -5.067523   -4.870048   -5.001433  -15.004300
  -4.090313   -4.192531   -4.175923   -4.152922  -12.458767
  -4.795000   -4.695313   -4.603271   -4.697861  -14.093584
  -3.364075   -3.508794   -3.458244   -3.443704  -10.331113
  -4.836473   -4.914825   -4.939804   -4.897034  -14.691103
  -4.038834   -4.202977   -4.097691   -4.113167  -12.339501
=================================================================

==================================================
    Yij..       Yi.k.       Y.jk.
==================================================
  -25.392838  -29.539642  -28.628922
  -27.463058  -23.316254  -21.188614
  -24.424683  -28.784683  -29.695389
  -27.030594  -22.670609  -24.798264
==================================================

==================================================
    Yi...       Y.j..       Y..k.
==================================================
  -52.855881  -49.817535  -58.324310
  -51.455276  -54.493652  -45.986877
==================================================

Y.... =   -104.311188

======================================================================
 SOURCE OF        SUM OF     DEGREES OF     MEAN          F RATIO
 VARIATION        SQUARES    FREEDOM        SQUARES
======================================================================
 ROUGHNESS(R)    0.808E-01      1.0        0.808E-01        9.807
 DEPTH(D)        0.911E+00      1.0        0.911E+00      110.519
 VELOCITY(V)     0.634E+01      1.0        0.634E+01      769.629
 RD              0.125E-01      1.0        0.125E-01        1.511
 RV              0.122E-02      1.0        0.122E-02        0.148
 DV              0.270E+00      1.0        0.270E+00       32.741
 RDV             0.293E-02      1.0        0.293E-02        0.356
 ERROR           0.132E+00     16.0        0.824E-02
 TOTAL           0.775E+01     23.0
======================================================================
```

```
==================================================
     ALPHAi        BETAj        GAMAk
==================================================
    -0.514061    0.194839   -0.058361
     0.514059   -0.194839    0.058357
--------------------------------------------------
    -0.000002    0.0        -0.000004
==================================================

==================================================
      (AB)ij      (AG)ik      (BG)jk
==================================================
    -0.105968   -0.004555   -0.022322
     0.105966    0.004555    0.022320
     0.105965    0.004557    0.022322
    -0.105966   -0.004553   -0.022320
--------------------------------------------------
    -0.000004    0.000004    0.0
==================================================

===============
   (ABG)ijk
===============
   0.011609
  -0.011605
  -0.011606
   0.011605
  -0.011604
   0.011607
   0.011607
  -0.011607
---------------
   0.000006
===============

==================================================
     OBSERVED    PREDICTED    RESIDUAL
==================================================
    -4.757506   -4.845117    0.087610
    -4.798998   -4.845117    0.046119
    -4.978846   -4.845117   -0.133729
    -3.491604   -3.619166    0.127563
    -3.687720   -3.619166   -0.068554
    -3.678177   -3.619166   -0.059011
    -5.066730   -5.001433   -0.065296
    -5.067523   -5.001433   -0.066090
    -4.870048   -5.001433    0.131386
    -4.090313   -4.152922    0.062609
    -4.192531   -4.152922   -0.039609
    -4.175923   -4.152922   -0.023002
    -4.795000   -4.697861   -0.097139
    -4.695313   -4.697861    0.002547
    -4.603271   -4.697861    0.094590
    -3.364075   -3.443704    0.079629
    -3.508794   -3.443704   -0.065090
    -3.458244   -3.443704   -0.014541
```

```
    -4.836473   -4.897034    0.060560
    -4.914825   -4.897034   -0.017792
    -4.939804   -4.897034   -0.042770
    -4.038834   -4.113167    0.074333
    -4.202977   -4.113167   -0.089810
    -4.097691   -4.113167    0.015476
 ==================================================

 ==============================================================
        2**3 FACTORIAL DESIGN
 ==============================================================
  EFFECT                  ESTIMATE             SUM OF SQUARES
 ==============================================================
MAIN EFFECTS
   ROUGHNESS(R)            0.117E+00             0.817E-01
   DEPTH(D)               -0.390E+00             0.911E+00
   VELOCITY(V)             0.103E+01             0.634E+01
2-FACTOR INTERACTION
     RD                   -0.446E-01             0.120E-01
     RV                   -0.910E-02             0.497E-03
     DV                   -0.212E+00             0.269E+00
3-FACTOR INTERACTION
     RDV                  -0.232E-01             0.323E-02
 ==============================================================

  VARIANCE OF EFFECTS=    0.137E-02

  STD.ERROR OF EFFECTS=     0.037058


 ==============================================================
```

APPENDICES C.9

MULTIVARIATE ANALYSIS OF VARIANCE PROGRAM OUTPUT FOR THE LOG-TRANSFORMATION OF THE OXYGEN TRANSFER COEFFICIENT

```
=================================================================
      REPL1        REPL2        REPL3        MEAN        Yijk.
=================================================================
   -2.454920   -2.496412   -2.676261   -2.542531   -7.627593
   -1.189018   -1.385135   -1.375591   -1.316581   -3.949744
   -2.294141   -2.294934   -2.097459   -2.228845   -6.686534
   -1.317723   -1.419942   -1.403335   -1.380333   -4.141000
   -2.492414   -2.392729   -2.300687   -2.395276   -7.185830
   -1.061489   -1.206208   -1.155659   -1.141118   -3.423356
   -2.063883   -2.142236   -2.167215   -2.124444   -6.373334
   -1.266245   -1.430387   -1.325101   -1.340577   -4.021732
=================================================================

==================================================
      Yij..        Yi.k.        Y.jk.
==================================================
   -11.577337  -14.314127  -14.813423
   -10.827534   -8.090744   -7.373100
   -10.609186  -13.559164  -13.059868
   -10.395066   -7.445088   -8.162732
==================================================

==================================================
      Yi...        Y.j..        Y..k.
==================================================
   -22.404861  -22.186523  -27.873291
   -21.004242  -21.222595  -15.535832
==================================================

Y.... =    -43.409119

=======================================================================
 SOURCE OF         SUM OF      DEGREES OF     MEAN          F RATIO
 VARIATION         SQUARES     FREEDOM        SQUARES
=======================================================================
 ROUGHNESS(R)     0.817E-01       1.0       0.817E-01         9.843
 DEPTH(D)         0.387E-01       1.0       0.387E-01         4.661
 VELOCITY(V)      0.634E+01       1.0       0.634E+01       763.711
 RD               0.120E-01       1.0       0.120E-01         1.448
 RV               0.381E-03       1.0       0.381E-03         0.046
 DV               0.269E+00       1.0       0.269E+00        32.446
 RDV              0.317E-02       1.0       0.317E-02         0.382
 ERROR            0.133E+00      16.0       0.830E-02
 TOTAL            0.688E+01      23.0
=======================================================================
```

```
==================================================
     ALPHAi        BETAj          GAMAk
==================================================
    -0.514061   -0.040163    -0.058359
     0.514061    0.040164     0.058359
--------------------------------------------------
     0.0         0.000001     0.0
==================================================

==================================================
      (AB)ij       (AG)ik       (BG)jk
==================================================
    -0.105967   -0.004555    -0.022321
     0.105966    0.004555     0.022320
     0.105966    0.004555     0.022320
    -0.105967   -0.004555    -0.022321
--------------------------------------------------
    -0.000002    0.0         -0.000002
==================================================

===============
   (ABG)ijk
===============
   0.011607
  -0.011606
  -0.011606
   0.011606
  -0.011606
   0.011607
   0.011607
  -0.011606
---------------
   0.000003
===============

==================================================
     OBSERVED     PREDICTED     RESIDUAL
==================================================
    -2.454920   -2.542531     0.087611
    -2.496412   -2.542531     0.046119
    -2.676261   -2.542531    -0.133730
    -1.189018   -1.316581     0.127563
    -1.385135   -1.316581    -0.068554
    -1.375591   -1.316581    -0.059011
    -2.294141   -2.228845    -0.065296
    -2.294934   -2.228845    -0.066090
    -2.097459   -2.228845     0.131386
    -1.317723   -1.380333     0.062610
    -1.419942   -1.380333    -0.039609
    -1.403335   -1.380333    -0.023002
    -2.492414   -2.395276    -0.097138
    -2.392729   -2.395276     0.002547
    -2.300687   -2.395276     0.094589
    -1.061489   -1.141118     0.079629
    -1.206208   -1.141118    -0.065090
    -1.155659   -1.141118    -0.014541
```

```
     -2.063883   -2.124444    0.060561
     -2.142236   -2.124444   -0.017792
     -2.167215   -2.124444   -0.042771
     -1.266245   -1.340577    0.074332
     -1.430387   -1.340577   -0.089809
     -1.325101   -1.340577    0.015476
 ==================================================

 ============================================================
         2**3 FACTORIAL DESIGN
 ============================================================
  EFFECT                   ESTIMATE            SUM OF SQUARES
 ============================================================
MAIN EFFECTS
   ROUGHNESS(R)            0.117E+00             0.817E-01
   DEPTH(D)                0.803E-01             0.387E-01
   VELOCITY(V)             0.103E+01             0.634E+01
2-FACTOR INTERACTION
     RD                   -0.446E-01             0.120E-01
     RV                   -0.911E-02             0.498E-03
     DV                   -0.212E+00             0.269E+00
3-FACTOR INTERACTION
     RDV                  -0.232E-01             0.323E-02
 ============================================================

 VARIANCE OF EFFECTS=     0.138E-02

 STD.ERROR OF EFFECTS=      0.037203


 ============================================================
```

APPENDICES C.10

MULTIVARIATE ANALYISIS OF VARIANCE PROGRAM OUTPUT FOR THE LOG-TRANSFORMATION OF THE PROPANE GAS DESORPTION RATE COEFFICIENT

```
=================================================================
      REPL1        REPL2        REPL3        MEAN        Yijk.
=================================================================
   -5.098483   -5.109351   -5.248195   -5.152009  -15.456029
   -3.830304   -4.015940   -3.952324   -3.932856  -11.798568
   -5.460365   -5.507558   -5.139606   -5.369176  -16.107529
   -4.315191   -4.515696   -4.506683   -4.445856  -13.337570
   -5.139435   -5.101436   -4.931039   -5.057302  -15.171909
   -3.512744   -3.784466   -3.592334   -3.629848  -10.889544
   -5.190719   -5.393288   -5.236281   -5.273429  -15.820288
   -4.340040   -4.539289   -4.279614   -4.386314  -13.158944
=================================================================

==================================================
      Yij..        Yi.k.        Y.jk.
==================================================
   -27.254593  -31.563553  -30.627930
   -29.445099  -25.136124  -22.688110
   -26.061447  -30.992188  -31.927811
   -28.979218  -24.048477  -26.496506
==================================================

==================================================
      Yi...        Y.j..        Y..k.
==================================================
   -56.699692  -53.316040  -62.555740
   -55.040665  -58.424316  -49.184616
==================================================

Y.... =   -111.740356

======================================================================
 SOURCE OF         SUM OF       DEGREES OF      MEAN          F RATIO
 VARIATION         SQUARES      FREEDOM         SQUARES
======================================================================
 ROUGHNESS(R)     0.114E+00       1.0         0.114E+00          7.036
 DEPTH(D)         0.109E+01       1.0         0.109E+01         67.073
 VELOCITY(V)      0.745E+01       1.0         0.745E+01        459.676
 RD               0.227E-01       1.0         0.227E-01          1.401
 RV               0.117E-01       1.0         0.117E-01          0.723
 DV               0.263E+00       1.0         0.263E+00         16.211
 RDV              0.217E-01       1.0         0.217E-01          1.341
 ERROR            0.259E+00      16.0         0.162E-01
 TOTAL            0.923E+01      23.0
======================================================================
```

```
==================================================
     ALPHAi        BETAj         GAMAk
==================================================
    -0.557135    0.212843   -0.069128
     0.557127   -0.212847    0.069120
--------------------------------------------------
    -0.000008   -0.000004   -0.000008
==================================================


==================================================
      (AB)ij       (AG)ik      (BG)jk
==================================================
    -0.104520    0.021514   -0.030303
     0.104523   -0.021507    0.030306
     0.104523   -0.021511    0.030303
    -0.104522    0.021516   -0.030301
--------------------------------------------------
     0.000004    0.000011    0.000005
==================================================


===============
   (ABG)ijk
===============
   0.030563
  -0.030562
  -0.030562
   0.030565
  -0.030566
   0.030561
   0.030561
  -0.030564
---------------
  -0.000004
===============


==================================================
     OBSERVED     PREDICTED    RESIDUAL
==================================================
    -5.098483    -5.152009    0.053526
    -5.109351    -5.152009    0.042658
    -5.248195    -5.152009   -0.096186
    -3.830304    -3.932856    0.102551
    -4.015940    -3.932856   -0.083084
    -3.952324    -3.932856   -0.019468
    -5.460365    -5.369176   -0.091189
    -5.507558    -5.369176   -0.138382
    -5.139606    -5.369176    0.229569
    -4.315191    -4.445856    0.130665
    -4.515696    -4.445856   -0.069839
    -4.506683    -4.445856   -0.060827
    -5.139435    -5.057302   -0.082132
    -5.101436    -5.057302   -0.044133
    -4.931039    -5.057302    0.126264
    -3.512744    -3.629848    0.117104
    -3.784466    -3.629848   -0.154618
    -3.592334    -3.629848    0.037514
```

```
    -5.190719   -5.273429    0.082710
    -5.393288   -5.273429   -0.119859
    -5.236281   -5.273429    0.037148
    -4.340040   -4.386314    0.046274
    -4.539289   -4.386314   -0.152975
    -4.279614   -4.386314    0.106700
 ==================================================

 ============================================================
        2**3 FACTORIAL DESIGN
 ============================================================
 EFFECT                    ESTIMATE           SUM OF SQUARES
 ============================================================
MAIN EFFECTS
   ROUGHNESS(R)             0.138E+00            0.115E+00
   DEPTH(D)                -0.426E+00            0.109E+01
   VELOCITY(V)              0.111E+01            0.745E+01
2-FACTOR INTERACTION
     RD                    -0.606E-01            0.220E-01
     RV                     0.430E-01            0.111E-01
     DV                    -0.209E+00            0.262E+00
3-FACTOR INTERACTION
     RDV                   -0.611E-01            0.224E-01
 ============================================================

 VARIANCE OF EFFECTS=    0.270E-02

 STD.ERROR OF EFFECTS=     0.051969


 ============================================================
```

APPENDICES C.11

ANALYSIS OF RESIDUALS OF THREE LOG-TRANSFORMED RESPONSE VARIABLES FROM THE MULTIVARIATE ANALYSIS OF VARIANCE RESULTS

```
MTB > READ 'OBS.PRED2K2' C1-C3
     24 ROWS READ

MTB > PRINT C1-C3


 ROW       OBS       PRED       RESID

   1  -4.75751  -4.84512   0.087610
   2  -4.79900  -4.84512   0.046119
   3  -4.97885  -4.84512  -0.133729
   4  -3.49160  -3.61917   0.127563
   5  -3.68772  -3.61917  -0.068554
   6  -3.67818  -3.61917  -0.059011
   7  -5.06673  -5.00143  -0.065296
   8  -5.06752  -5.00143  -0.066090
   9  -4.87005  -5.00143   0.131386
  10  -4.09031  -4.15292   0.062609
  11  -4.19253  -4.15292  -0.039609
  12  -4.17592  -4.15292  -0.023002
  13  -4.79500  -4.69786  -0.097139
  14  -4.69531  -4.69786   0.002547
  15  -4.60327  -4.69786   0.094590
  16  -3.36407  -3.44370   0.079629
  17  -3.50879  -3.44370  -0.065090
  18  -3.45824  -3.44370  -0.014541
  19  -4.83647  -4.89703   0.060560
  20  -4.91482  -4.89703  -0.017792
  21  -4.93980  -4.89703  -0.042770
  22  -4.03883  -4.11317   0.074333
  23  -4.20298  -4.11317  -0.089810
  24  -4.09769  -4.11317   0.015476

MTB > DOTPLOT C3


                        .
          .       ..   .:.  ..  ...   . .     .  .. .. ..      :
          -------+---------+---------+---------+---------+---------RESID
              -0.100    -0.050     0.000     0.050     0.100     0.150

MTB > PLOT C3 C2
```

```
        -
RESID   -    *                                              *
        -
        -              *
   0.080+         *                         *                     *
        -        *                         *
        -         *
        -
        -                                   *
   0.000+              *
        -        *                         *                      *
        -                                  *
        -        *
        -    2                                              2     *
  -0.080+
        -              *                    *
        -
        -         *
        -
          +---------+---------+---------+---------+---------+---------+-------PRED
      -5.10     -4.80     -4.50     -4.20     -3.90     -3.60
```

```
MTB > NSCORES C3 C4

MTB > PLOT C3 C4
```

```
        -
RESID   -                                                   *       *
        -
        -                                                *
   0.080+                                        * *  *
        -                                     * *
        -                                   *
        -
        -                                  *
   0.000+                                *
        -                            **  *
        -                          *
        -                         *
        -               *  * ** *
  -0.080+
        -         *  *
        -
        - *
        -
          ---------+---------+---------+---------+---------+--------NSCORES
               -1.40     -0.70      0.00      0.70      1.40
```

```
MTB > READ 'OBS.PRED2KL' C1-C3
     24 ROWS READ

MTB > PRINT C1-C3
 ROW       OBS       PRED      RESID

   1  -2.45492  -2.54253   0.087611
   2  -2.49641  -2.54253   0.046119
```

```
  3  -2.67626  -2.54253  -0.133730
  4  -1.18902  -1.31658   0.127563
  5  -1.38513  -1.31658  -0.068554
  6  -1.37559  -1.31658  -0.059011
  7  -2.29414  -2.22884  -0.065296
  8  -2.29493  -2.22884  -0.066090
  9  -2.09746  -2.22884   0.131386
 10  -1.31772  -1.38033   0.062610
 11  -1.41994  -1.38033  -0.039609
 12  -1.40333  -1.38033  -0.023002
 13  -2.49241  -2.39528  -0.097138
 14  -2.39273  -2.39528   0.002547
 15  -2.30069  -2.39528   0.094589
 16  -1.06149  -1.14112   0.079629
 17  -1.20621  -1.14112  -0.065090
 18  -1.15566  -1.14112  -0.014541
 19  -2.06388  -2.12444   0.060561
 20  -2.14224  -2.12444  -0.017792
 21  -2.16721  -2.12444  -0.042771
 22  -1.26624  -1.34058   0.074332
 23  -1.43039  -1.34058  -0.089809
 24  -1.32510  -1.34058   0.015476

MTB > DOTPLOT C3

                        .
          .       ..   .:.  ..  ...   . .     .  .. ..  ..      :
          -------+---------+---------+---------+---------+---------RESID
              -0.100    -0.050     0.000     0.050     0.100     0.150

MTB > PLOT C3 C2

        -
RESID   -                 *                             *
        -
        -           *
   0.080+      *                                       *      *
        -                    *                        *
        -      *
        -
        -                                              *
   0.000+           *
        -                    *                        *       *
        -                                             *
        -                    *
        -                 2                             2     *
  -0.080+
        -           *                                  *
        -
        -      *
        -
          +---------+---------+---------+---------+---------+------PRED
      -2.70     -2.40     -2.10     -1.80     -1.50     -1.20

MTB > NSCORES C3 C4
MTB > PLOT C3 C4
```

```
        -
RESID   -                                                  *      *
        -
        -                                               *
   0.080+                                       * *  *
        -                                    * *
        -                                  *
        -
        -                                 *
   0.000+                               *
        -                           ** *
        -                         *
        -                        *
        -             *  * ** *
  -0.080+
        -        *  *
        -
        - *
        -

          --------+---------+---------+---------+---------+---------NSCORES
              -1.40     -0.70      0.00      0.70      1.40

MTB > READ 'OBS.PRED2KP' C1-C3
     24 ROWS READ


MTB > PRINT C1-C3

 ROW       OBS       PRED      RESID

   1  -5.09848  -5.15201   0.053526
   2  -5.10935  -5.15201   0.042658
   3  -5.24819  -5.15201  -0.096186
   4  -3.83030  -3.93286   0.102551
   5  -4.01594  -3.93286  -0.083084
   6  -3.95232  -3.93286  -0.019468
   7  -5.46036  -5.36918  -0.091189
   8  -5.50756  -5.36918  -0.138382
   9  -5.13961  -5.36918   0.229569
  10  -4.31519  -4.44586   0.130665
  11  -4.51570  -4.44586  -0.069839
  12  -4.50668  -4.44586  -0.060827
  13  -5.13943  -5.05730  -0.082132
  14  -5.10144  -5.05730  -0.044133
  15  -4.93104  -5.05730   0.126264
  16  -3.51274  -3.62985   0.117104
  17  -3.78447  -3.62985  -0.154618
  18  -3.59233  -3.62985   0.037514
  19  -5.19072  -5.27343   0.082710
  20  -5.39329  -5.27343  -0.119859
  21  -5.23628  -5.27343   0.037148
  22  -4.34004  -4.38631   0.046274
  23  -4.53929  -4.38631  -0.152975
  24  -4.27961  -4.38631   0.106700
```

```
MTB > DOTPLOT C3

          :.  .  ..: ..  .  .       :...   .  : ...             .
          -+---------+---------+---------+---------+---------+-----RESID
        -0.140    -0.070    0.000     0.070     0.140     0.210

MTB > PLOT C3 C2

    0.24+    *
        -
RESID   -
        -
        -
    0.12+             *                *                      *
        -                                *            *
        -      *
        -      *   2                     *                    *
        -
    0.00+
        -                                             *
        -             *
        -             *                2              *
        -    *     *
   -0.12+      *
        -    *                           *                    *
        -
        -

          ------+---------+---------+---------+---------+---------+PRED
            -5.25     -4.90     -4.55     -4.20     -3.85     -3.50

MTB > NSCORES C3 C4
MTB > PLOT C3 C4

    0.24+                                                         *
        -
RESID   -
        -
        -
    0.12+                                            *  *  *
        -                                       *  *
        -                                      *
        -                              ** ** *
        -
    0.00+
        -                            *
        -                           *
        -                    * * **
        -                 * *
   -0.12+              *
        - *      *  *
        -
        -

          --------+---------+---------+---------+---------+--------NSCORES
              -1.40     -0.70      0.00      0.70      1.40
```

APPENDICES C.12

ONE-WAY ANALYSIS OF VARIANCE FOR THE FACTORIAL EXPERIMENTAL DESIGN DATA SET

```
MTB > read 'labjul87.k2' c1-c8
      3 ROWS READ

MTB > print c1-c4
 ROW      h1v1s      h1v2s      h2v1s      h2v2s

   1   0.008587   0.030452   0.006303   0.016734
   2   0.008238   0.025029   0.006298   0.015108
   3   0.006882   0.025269   0.007673   0.015361

MTB > print c5-c8
 ROW      h1v1r      h1v2r      h2v1r      h2v2r

   1   0.008271   0.034594   0.007935   0.017618
   2   0.009138   0.029933   0.007337   0.014951
   3   0.010019   0.031485   0.007156   0.016611

MTB > aovoneway c1-c8

ANALYSIS OF VARIANCE
SOURCE     DF        SS        MS        F
FACTOR      7 0.0019265 0.0002752   110.25
ERROR      16 0.0000399 0.0000025
TOTAL      23 0.0019665
                                   INDIVIDUAL 95 PCT CI'S FOR MEAN
                                   BASED ON POOLED STDEV
LEVEL       N      MEAN     STDEV  ----+---------+---------+---------+--
h1v1s       3  0.007902  0.000901   (--*-)
h1v2s       3  0.026917  0.003064                           (--*-)
h2v1s       3  0.006758  0.000792  (-*--)
h2v2s       3  0.015734  0.000875             (--*-)
h1v1r       3  0.009143  0.000874     (-*--)
h1v2r       3  0.032004  0.002373                                  (-*-)
h2v1r       3  0.007476  0.000408   (-*--)
h2v2r       3  0.016393  0.001347              (-*--)
                                   ----+---------+---------+---------+--
POOLED STDEV = 0.001580              0.0080    0.0160    0.0240    0.0320
```

The above diagram indicates that: (for reaeration)

(i) there is no significant effect of either depth or roughness at low velocity levels;

(ii) there is no significant effect of roughness at deep and rapid flow conditions;

(iii) there is a slight effect of roughness at shallow and rapid flow conditions;

```
MTB > read 'labjul87.kl' c1-c8
      3 ROWS READ

MTB > print c1-c4
 ROW     h1v1s     h1v2s      h2v1s      h2v2s

   1   0.08587   0.30452   0.100848   0.267744
   2   0.08238   0.25029   0.100768   0.241728
   3   0.06882   0.25269   0.122768   0.245776

MTB > print c5-c8
 ROW     h1v1r     h1v2r      h2v1r      h2v2r

   1   0.08271   0.34594   0.126960   0.281888
   2   0.09138   0.29933   0.117392   0.239216
   3   0.10019   0.31485   0.114496   0.265776

MTB > aovoneway c1-c8

ANALYSIS OF VARIANCE
SOURCE     DF        SS        MS        F
FACTOR      7  0.197590  0.028227    89.49
ERROR      16  0.005047  0.000315
TOTAL      23  0.202637
                                   INDIVIDUAL 95 PCT CI'S FOR MEAN
                                   BASED ON POOLED STDEV
LEVEL       N      MEAN     STDEV  ---+---------+---------+---------+---
h1v1s       3   0.07902   0.00901  (--*--)
h1v2s       3   0.26917   0.03064                           (--*-)
h2v1s       3   0.10813   0.01268      (--*-)
h2v2s       3   0.25175   0.01400                         (-*--)
h1v1r       3   0.09143   0.00874    (-*--)
h1v2r       3   0.32004   0.02373                                 (--*--)
h2v1r       3   0.11962   0.00652       (--*--)
h2v2r       3   0.26229   0.02155                          (--*--)
                                   ---+---------+---------+---------+---
POOLED STDEV =  0.01776             0.080     0.160     0.240     0.320
```

The above diagram indicates that: (for oxygen transfer coeff.)

(i) there is no significant effect of either depth or roughness at low velocities;

(ii) there is no significant effect of either depthor roughness at high velocities;

```
MTB > read 'labjul87.kp' c1-c8
      3 ROWS READ
```

```
MTB > print c1-c4
 ROW      h1v1s      h1v2s      h2v1s      h2v2s

   1   0.006106   0.021703   0.004252   0.013364
   2   0.006040   0.018026   0.004066   0.010936
   3   0.005257   0.019210   0.005860   0.011035

MTB > print c5-c8
 ROW      h1v1r      h1v2r      h2v1r      h2v2r

   1   0.005861   0.029815   0.005568   0.013036
   2   0.006088   0.022721   0.004547   0.010681
   3   0.007219   0.027534   0.005320   0.013848

MTB > aovoneway c1-c8

ANALYSIS OF VARIANCE
SOURCE     DF        SS        MS        F
FACTOR      7 0.0013291 0.0001899    65.36
ERROR      16 0.0000465 0.0000029
TOTAL      23 0.0013756
                                   INDIVIDUAL 95 PCT CI'S FOR MEAN
                                   BASED ON POOLED STDEV
LEVEL       N      MEAN     STDEV  -------+---------+---------+---------
h1v1s       3  0.005801  0.000472    (-*--)
h1v2s       3  0.019646  0.001877                      (--*-)
h2v1s       3  0.004726  0.000986  (--*--)
h2v2s       3  0.011778  0.001374           (--*-)
h1v1r       3  0.006389  0.000727    (--*--)
h1v2r       3  0.026690  0.003622                               (-*--)
h2v1r       3  0.005145  0.000533   (-*--)
h2v2r       3  0.012522  0.001645            (--*-)
                                   -------+---------+---------+---------
POOLED STDEV = 0.001704                 0.0080    0.0160     0.0240
```

The above diagram indicates that: (propane gas desorption)

(i) there is no significant effect of either depth or roughness at low velocity levels;

(ii) there is no significant effect of roughness at deep and rapid flow conditions;

(iii) there is a slight effect of roughness at shallow and rapid flow conditions;

```
MTB > read 'labjul87.ks' c1-c8
      3 ROWS READ

MTB > print c1-c4
 ROW      h1v1s      h1v2s      h2v1s      h2v2s

   1   0.000107   0.000190   0.000119   0.000188
   2   0.000117   0.000178   0.000116   0.000191
   3   0.000117   0.000179   0.000133   0.000195
```

```
MTB > print c5-c8
 ROW      h1v1r      h1v2r      h2v1r      h2v2r

   1   0.000119   0.000187   0.000140   0.000164
   2   0.000132   0.000173   0.000133   0.000145
   3   0.000126   0.000166   0.000132   0.000144

MTB > aovoneway c1-c8

ANALYSIS OF VARIANCE
SOURCE     DF        SS        MS        F
FACTOR      7 0.0000000 0.0000000    45.33
ERROR      16 0.0000000 0.0000000
TOTAL      23 0.0000000
                                   INDIVIDUAL 95 PCT CI'S FOR MEAN
                                   BASED ON POOLED STDEV
LEVEL       N      MEAN     STDEV  ------+---------+---------+---------+
h1v1s       3  1.14E-04  5.77E-06   (--*--)
h1v2s       3  1.82E-04  6.66E-06                           (--*--)
h2v1s       3  1.23E-04  9.07E-06      (--*--)
h2v2s       3  1.91E-04  3.51E-06                              (--*--)
h1v1r       3  1.26E-04  6.51E-06       (--*--)
h1v2r       3  1.75E-04  1.07E-05                        (--*---)
h2v1r       3  1.35E-04  4.36E-06          (--*--)
h2v2r       3  1.51E-04  1.13E-05               (--*--)
                                   ------+---------+---------+---------+
POOLED STDEV = 7.71E-06                0.000120  0.000150  0.000180  0.000210
```

The above diagram indicate that: (solids dissolution)

(i) there is no significant effect of either depth or roughness at low velocity levels;

(ii) slight effect of depth at situations of rough bed and fast velocities;

(iii) less significant effect of depth at situations of smooth bed and fast velocities;

(iv) the slight depth effects might be generated by noise;

APPENDICES D.1

RESPONSE SURFACE METHODOLOGY

FIRST ORDER MODEL FITTING FOR THE REAERATION COEFFICIENT

NATURAL VARIABLES		CODED VARIABLES		RESPONSE
VELOC.(V)	DEPTH(D)	X_1	X_2	K_2
0.25	10.0	-1	-1	0.008021
0.25	16.0	-1	+1	0.006715
0.50	10.0	+1	-1	0.027718
0.50	16.0	+1	+1	0.015187
0.375	13.0	0	0	0.016301
0.375	13.0	0	0	0.018428
0.375	13.0	0	0	0.017695
0.375	13.0	0	0	0.016763

*velocity values are in m/s and depth in cm;

The coded variables are:

$X_1 = (V - 0.375)/0.125$ and $X_2 = (D - 13.0)/3.0$

The first order model fitted to the above data by least squares is given by:

$$K_2 = 0.0159 + 0.00704\, X_1 - 0.00346\, X_2$$

The following ANOVA table could then be obtained:

Source of Variation	SS ($\times10^{-5}$)	Degrees of Freedom	MS ($\times10^{-5}$)	F-ratio
Regression	24.624	2	12.312	12.094
Residual	5.088	5	1.018	
interaction	3.150	1	3.150	34.80
pure quadractic	1.666	1	1.666	18.41
pure error	0.271	3	0.091	
Total	29.712	7		

from where it is seen that interaction and quadractic effects are highly significant;

APPENDICES D.2

RESPONSE SURFACE METHODOLOGY

FIRST ORDER MODEL FITTING FOR THE OXYGEN TRANSFER COEFFICIENT

NATURAL VARIABLES		CODED VARIABLES		RESPONSE
VELOC.(V)	DEPTH(D)	X_1	X_2	K_L
0.25	10.0	-1	-1	0.080209
0.25	16.0	-1	+1	0.107437
0.50	10.0	+1	-1	0.277188
0.50	16.0	+1	+1	0.243007
0.375	13.0	0	0	0.217919
0.375	13.0	0	0	0.230035
0.375	13.0	0	0	0.239564
0.375	13.0	0	0	0.211913

*velocity values are in m/s and depth in cm;

The coded variables are:

$X_1 = (V - 0.375)/0.125$ and $X_2 = (D - 13.0)/3.0$

The first order model fitted to the above data by least squares is given by:

$$K_L = 0.201 + 0.0831\ X_1 - 0.0017\ X_2$$

The following ANOVA table could then be obtained:

Source of Variation	SS $(\times 10^{-3})$	Degrees of Freedom	MS $(\times 10^{-3})$	F-ratio
Regression	27.659	2	13.830	11.54
Residual	5.990	5	1.198	
interaction	0.943	1	0.943	6.16
pure quadractic	4.589	1	4.589	30.01
pure error	0.458	3	0.015	
Total	33.646	7		

from where it is seen that quadractic effects are highly significant; interaction effects only slightly significant;

APPENDICES D.3

RESPONSE SURFACE METHODOLOGY

FIRST ORDER MODEL FITTING FOR THE PROPANE DESORPTION RATE COEFFICIENT

NATURAL VARIABLES		CODED VARIABLES		RESPONSE
VELOC.(V)	DEPTH(D)	X_1	X_2	K_p
0.25	10.0	-1	-1	0.005709
0.25	16.0	-1	+1	0.004597
0.50	10.0	+1	-1	0.021442
0.50	16.0	+1	+1	0.011366
0.375	13.0	0	0	0.012357
0.375	13.0	0	0	0.012346
0.375	13.0	0	0	0.012742
0.375	13.0	0	0	0.011694

*velocity values are in m/s and depth in cm;

The coded variables are:

$X_1 = (V - 0.375)/0.125$ and $X_2 = (D - 13.0)/3.0$

The first order model fitted to the above data by least squares is given by:

$$K_p = 0.0115 + 0.00563\ X_1 - 0.00280\ X_2$$

The following ANOVA table could then be obtained:

Source of Variation	SS ($\times10^{-5}$)	Degrees of Freedom	MS ($\times10^{-5}$)	F-ratio
Regression	15.788	2	7.894	15.66
Residual	2.519	5	0.504	
interaction	2.009	1	2.009	106.29
pure quadractic	0.454	1	0.454	24.02
pure error	0.057	3	0.019	
Total	18.307	7		

from where it is seen that interaction and quadractic effects are highly significant;

APPENDICES D.4

RESPONSE SURFACE METHODOLOGY

FIRST ORDER MODEL FITTING FOR THE VELOCITY OF BENZOIC ACID DISSOLUTION

NATURAL VARIABLES		CODED VARIABLES		RESPONSE
VELOC.(V)	DEPTH(D)	X_1	X_2	K_s
0.25	10.0	-1	-1	0.000114
0.25	16.0	-1	+1	0.000123
0.50	10.0	+1	-1	0.000182
0.50	16.0	+1	+1	0.000191
0.375	13.0	0	0	0.000146
0.375	13.0	0	0	0.000145
0.375	13.0	0	0	0.000159
0.375	13.0	0	0	0.000139

*velocity values are in m/s and depth in cm;

The coded variables are:

$X_1 = (V - 0.375)/0.125$ and $X_2 = (D - 13.0)/3.0$

The first order model fitted to the above data by least squares is given by:

$$K_s = 0.000150 + 0.000034\ X_1 + 0.0000045\ X_2$$

The following ANOVA table could then be obtained:

Source of Variation	SS $(\times 10^{-10})$	Degrees of Freedom	MS $(\times 10^{-10})$	F-ratio
Regression	47.000	2	23.500	39.17
Residual	3.000	5	0.600	
interaction	0.000	1	0.000	0.00
pure quadractic	0.720	1	0.720	1.02
pure error	2.280	3	0.709	
Total	50.000	7		

from where it is seen that neither quadractic nor interaction effects are significant and the model appears to be adequate;

APPENDICES D.5

RESPONSE SURFACE METHODOLOGY

SECOND ORDER MODEL FITTING FOR THE REAERATION RATE COEFFICIENT

NATURAL VARIABLES		CODED VARIABLES		RESPONSE
VELOC.(V)	DEPTH(D)	X_1	X_2	K_2
0.25	10.0	-1	-1	0.008021
0.25	16.0	-1	+1	0.006715
0.50	10.0	+1	-1	0.027718
0.50	16.0	+1	+1	0.015187
0.375	13.0	0	0	0.016301
0.375	13.0	0	0	0.018428
0.375	13.0	0	0	0.017695
0.375	13.0	0	0	0.016763
0.550	13.0	+1.4	0	0.027411
0.200	13.0	-1.4	0	0.005671
0.375	17.2	0	+1.4	0.008606
0.375	8.8	0	-1.4	0.026464

*velocity values are in m/s and depth in cm;

The coded variables are:

$X_1 = (V - 0.375)/0.125$ and $X_2 = (D - 13.0)/3.0$

The second-order model fitted to the above data is given by:

$$K_2 = 0.0173 + 0.00740\ X_1 - 0.00490\ X_2 - 0.00107\ X_1^2 - $$
$$- 0.000561\ X_2^2 - 0.00281\ X_1X_2$$

The following ANOVA table could then be obtained:

Source of Variation	SS $(\times 10^{-5})$	Degrees of Freedom	MS $(\times 10^{-6})$	F-ratio
Regression	66.353	5	132.71	23.36
Residual	3.409	6	5.68	
lack of fit	0.694	3	2.31	2.56
pure error	0.272	3	0.091	
Total	69.761	11		

From where it can be seen that the second-order model fitted to the data seems to adequately represent the phenomenon.

The canonical form of the model is given by:

$$K_2' = 0.00290 - 0.002243\ w_1^2 + 0.000612\ w_2^2$$

which is used to further characterise the stationary point.

The variables X are related to the canonical variables w by the following equations:

$$w_1 = 0.7675\ (X_1 + 4.0167) + 0.6410\ (X_2 - 5.6924)$$

$$w_2 = -0.641\ (X_1 + 4.0167) + 0.7675\ (X_2 - 5.6924)$$

APPENDICES D.6

RESPONSE SURFACE METHODOLOGY

SECOND ORDER MODEL FITTING FOR THE OXYGEN TRANSFER COEFFICIENT

NATURAL VARIABLES		CODED VARIABLES		RESPONSE
VELOC.(V)	DEPTH(D)	X_1	X_2	K_L
0.25	10.0	-1	-1	0.080209
0.25	16.0	-1	+1	0.107437
0.50	10.0	+1	-1	0.277188
0.50	16.0	+1	+1	0.243007
0.375	13.0	0	0	0.217919
0.375	13.0	0	0	0.230035
0.375	13.0	0	0	0.239564
0.375	13.0	0	0	0.211913
0.550	13.0	+1.4	0	0.356343
0.200	13.0	-1.4	0	0.064293
0.375	17.2	0	+1.4	0.148015
0.375	8.8	0	-1.4	0.232879

*velocity values are in m/s and depth in cm;

The coded variables are:

$X_1 = (V - 0.375)/0.125$ and $X_2 = (D - 13.0)/3.0$

The second-order model fitted to the above data is given by:

$$K_L = 0.2250 + 0.09360\, X_1 - 0.01590\, X_2 - 0.01340\, X_1^2 - $$
$$- 0.02350\, X_2^2 - 0.01540\, X_1X_2$$

The following ANOVA table could then be obtained:

Source of Variation	SS ($\times 10^{-3}$)	Degrees of Freedom	MS ($\times 10^{-3}$)	F-ratio
Regression	76.301	5	15.26	22.94
Residual	3.991	6	0.67	
lack of fit	3.530	3	1.18	7.71
pure error	0.459	3	0.153	
Total	80.292	11		

From where it can be seen that the second-order model fitted to the data seems to adequately represent the phenomenon.

The canonical form of the model is given by:

$$K_L' = 0.450 - 0.009241\ w_1^2 + 0.027658\ w_2^2$$

which is used to further characterise the stationary point.

The variables X are related to the canonical variables w by the following equations:

$$w_1 = 0.8799\ (X_1 - 4.5421) - 0.4752\ (X_2 + 1.8266)$$

$$w_2 = 0.4752\ (X_1 - 4.5421) + 0.8799\ (X_2 + 1.8266)$$

APPENDICES D.7

RESPONSE SURFACE METHODOLOGY

SECOND ORDER MODEL FITTING FOR THE PROPANE GAS DESORPTION RATE COEFFICIENT

NATURAL VARIABLES		CODED VARIABLES		RESPONSE
VELOC.(V)	DEPTH(D)	X_1	X_2	K_p
0.25	10.0	-1	-1	0.080209
0.25	16.0	-1	+1	0.107437
0.50	10.0	+1	-1	0.277188
0.50	16.0	+1	+1	0.243007
0.375	13.0	0	0	0.217919
0.375	13.0	0	0	0.230035
0.375	13.0	0	0	0.239564
0.375	13.0	0	0	0.211913
0.550	13.0	+1.4	0	0.356343
0.200	13.0	-1.4	0	0.064293
0.375	17.2	0	+1.4	0.148015
0.375	8.8	0	-1.4	0.232879

*velocity values are in m/s and depth in cm;

The coded variables are:

$$X_1 = (V - 0.375)/0.125 \quad \text{and} \quad X_2 = (D - 13.0)/3.0$$

The second-order model fitted to the above data is given by:

$$K_p = 0.0123 + 0.00561\,X_1 - 0.00369\,X_2 - 0.000394\,X_1^2 - \\ - 0.000247\,X_2^2 - 0.00224\,X_1X_2$$

The following ANOVA table could then be obtained:

Source of Variation	SS ($\times 10^{-5}$)	Degrees of Freedom	MS ($\times 10^{-6}$)	F-ratio
Regression	37.866	5	75.73	34.96
Residual	1.336	6	2.23	
lack of fit	1.279	3	4.26	22.54
pure error	0.057	3	0.189	
Total	39.201	11		

From where it can be seen that the second-order model fitted to the data seems to adequately represent the phenomenon. However, it also seems that the error variability is not constant, and for some reason it is rather small when one considers the four replicates in the middle. Logarithmic transformation does not lead to any improvement to the model and the cubic model is not either adequate. In any case, what is demonstrated is that the quadractic model appears to approximate reasonably well the true response surface, but there is some evidence that the fit could be improved.

The canonical form of the model is given by:

$$K_p' = - 0.0129 - 0.001443\ w_1^2 + 0.000802\ w_2^2$$

which is used to further characterise the stationary point.

The variables X are related to the canonical variables w by the following equations:

$$w_1 = 0.7299\ (X_1 + 2.3846) + 0.6839\ (X_2 - 3.3434)$$

$$w_2 = -0.684\ (X_1 + 2.3846) + 0.7299\ (X_2 - 3.3434)$$

APPENDICES E.1

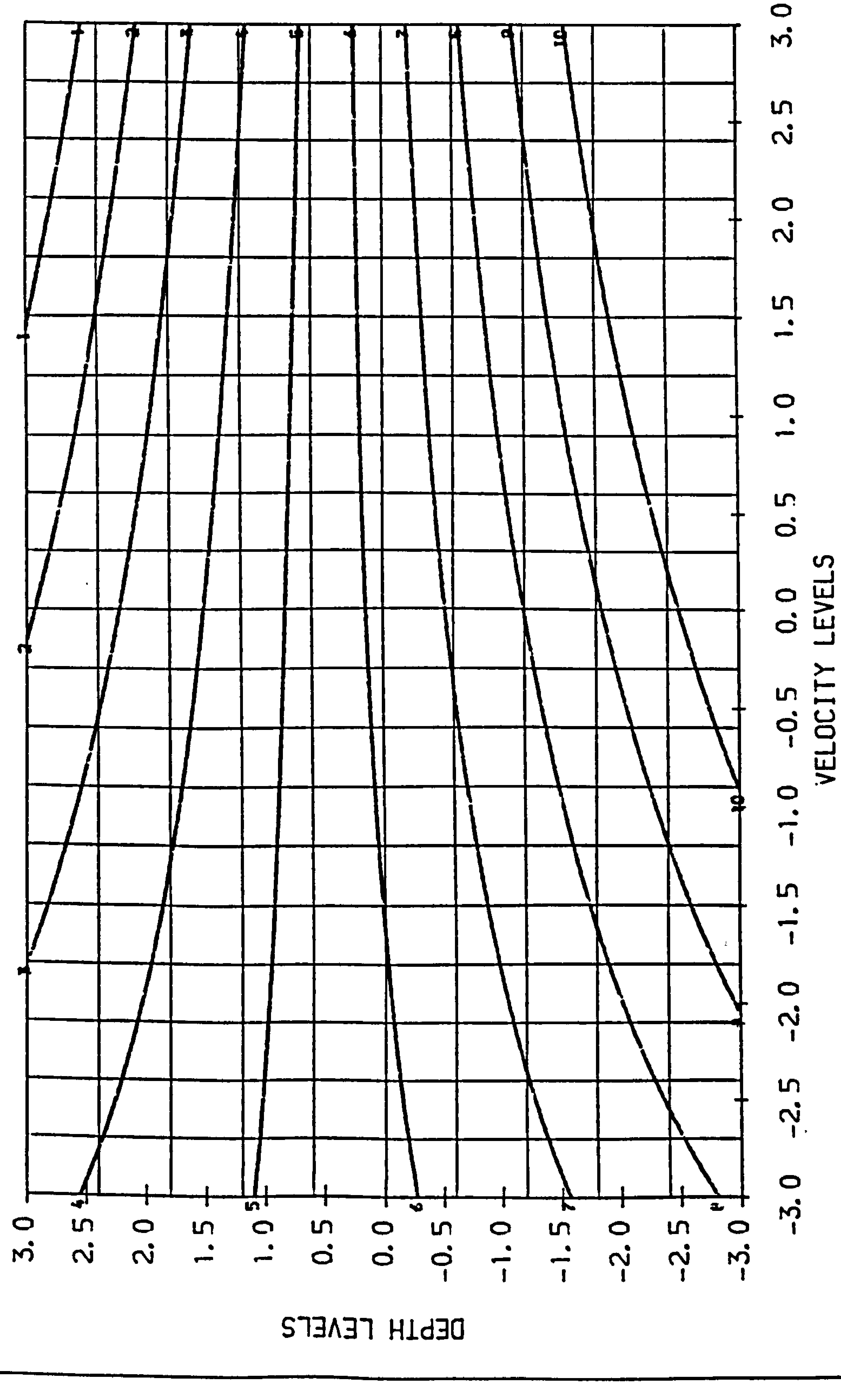
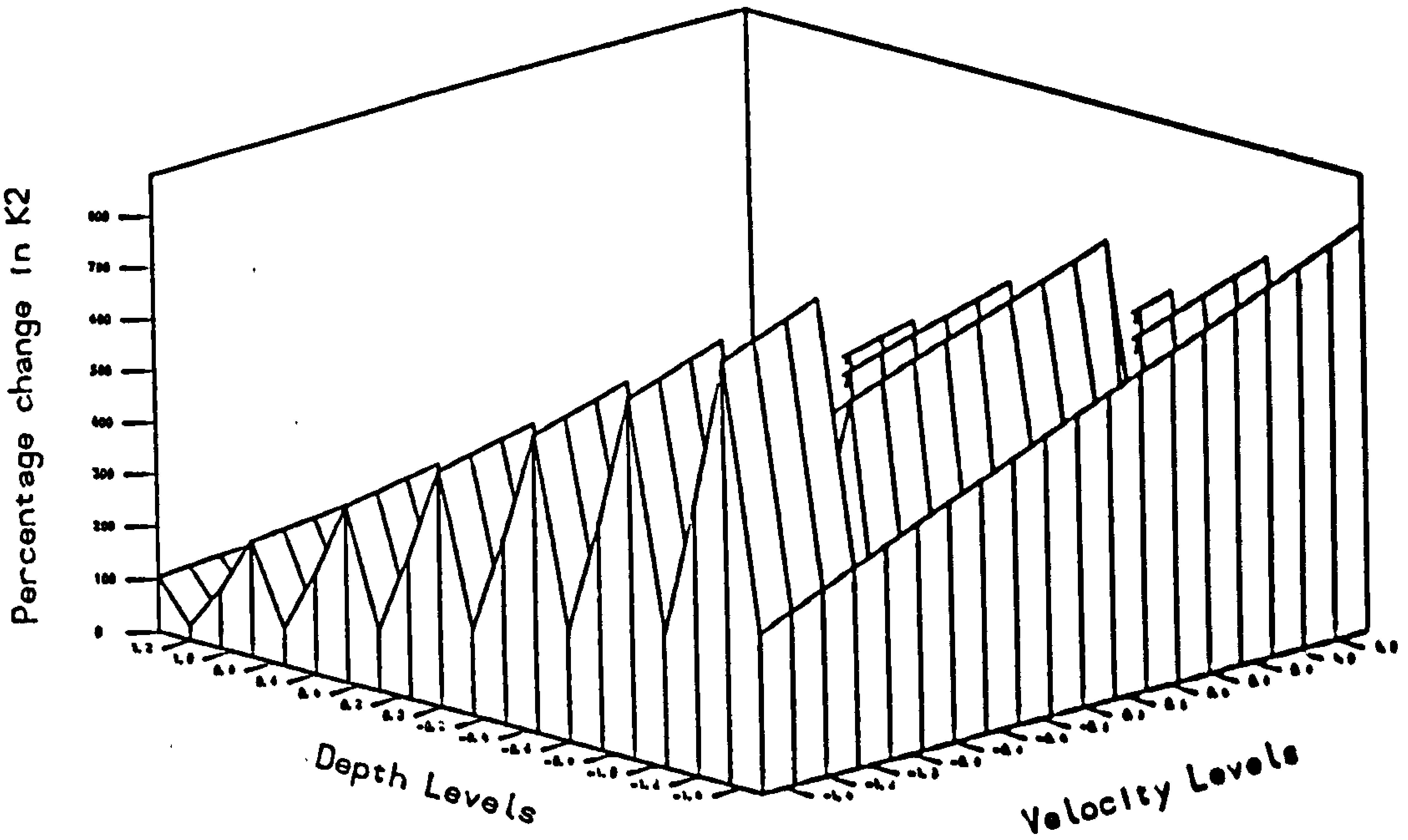


FIGURE E.1 - SURFACE CONTOURS FOR K2 (RIVER DATA)

APPENDICES E.2



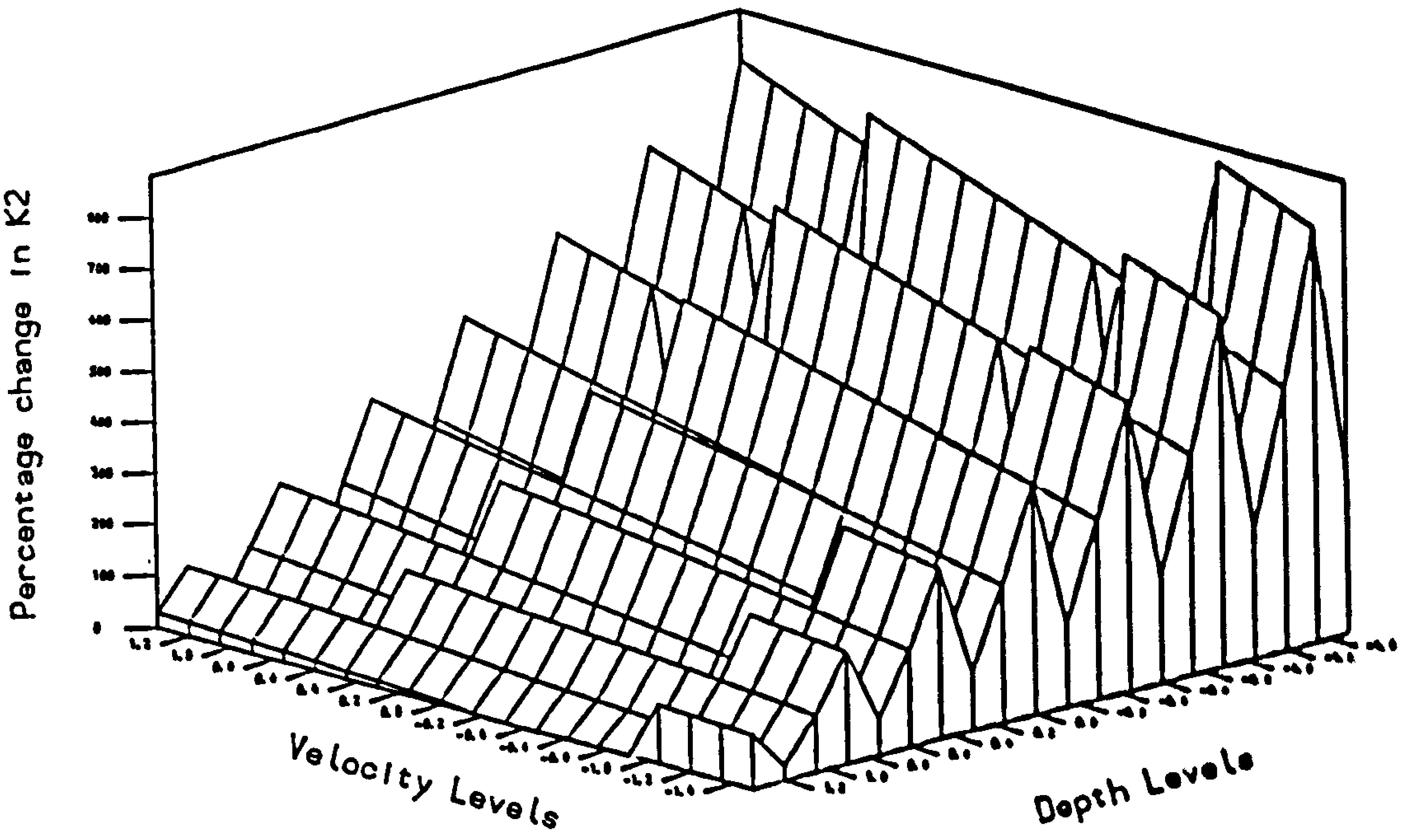
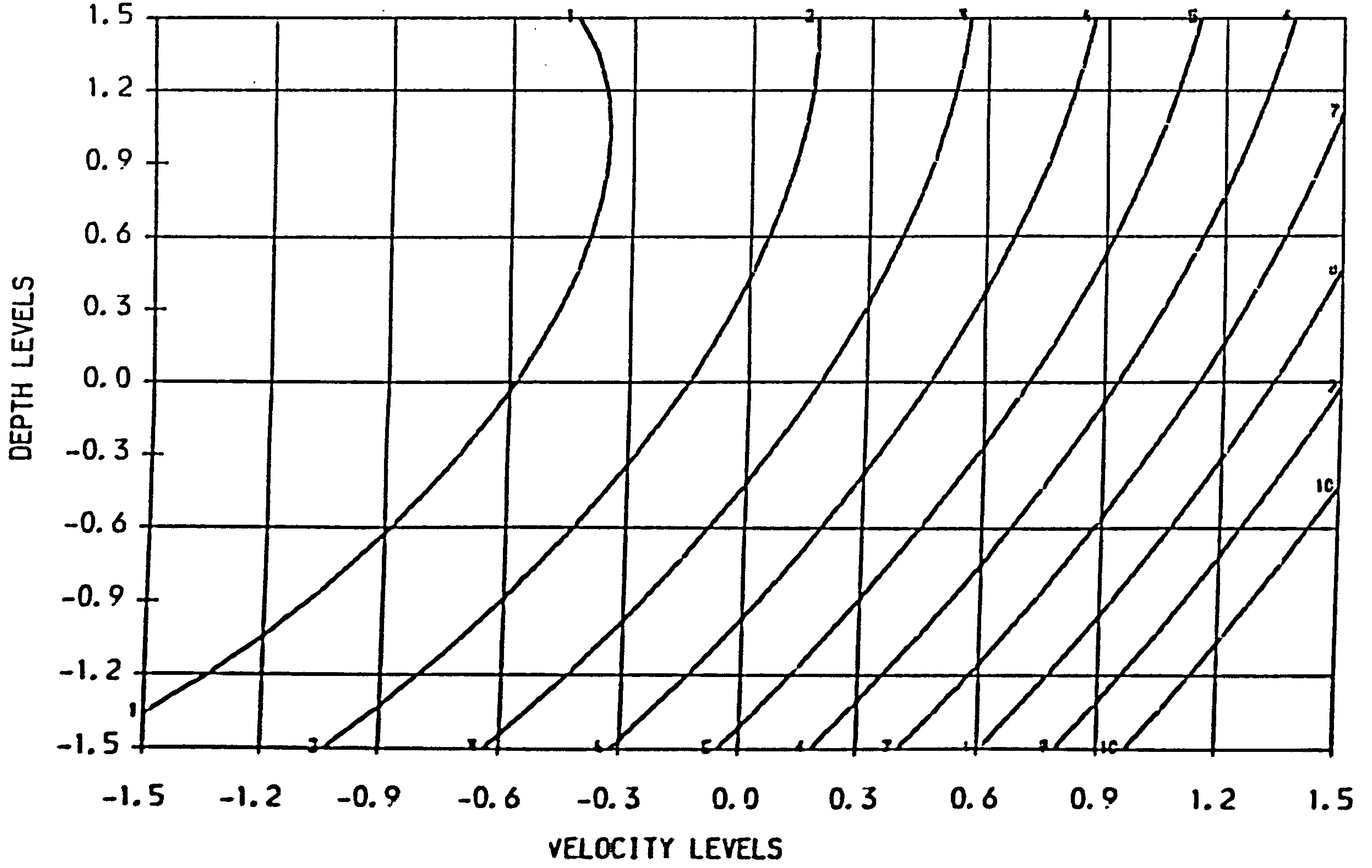


FIGURE E.2 - 3D RESPONSE SURFACE FOR K2 (RIVER DATA)

APPENDICES F.1

FIGURE F.1 - SURFACE CONTOURS FOR SPEC. ENERGY DISIP. RATE



APPENDICES F.2

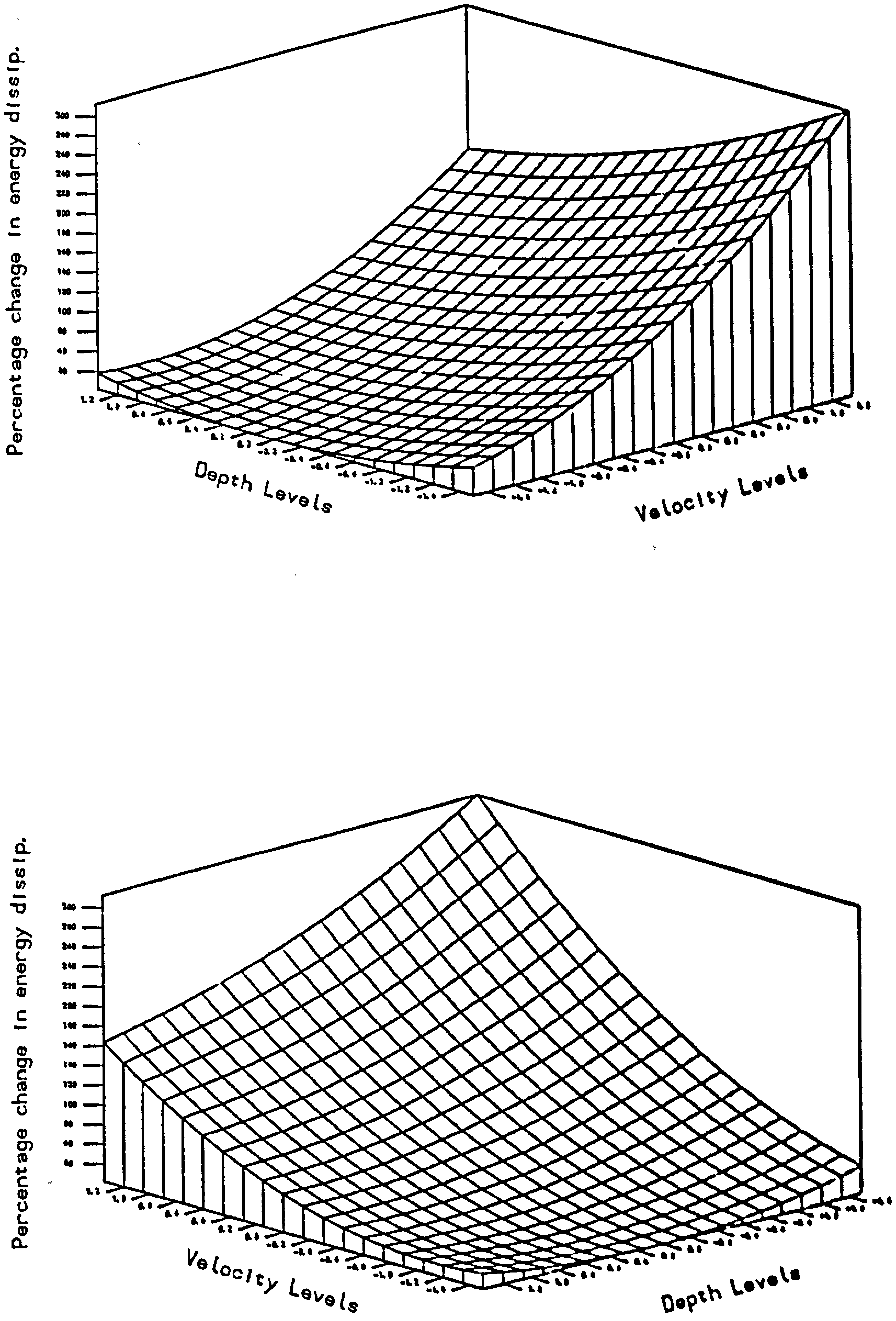
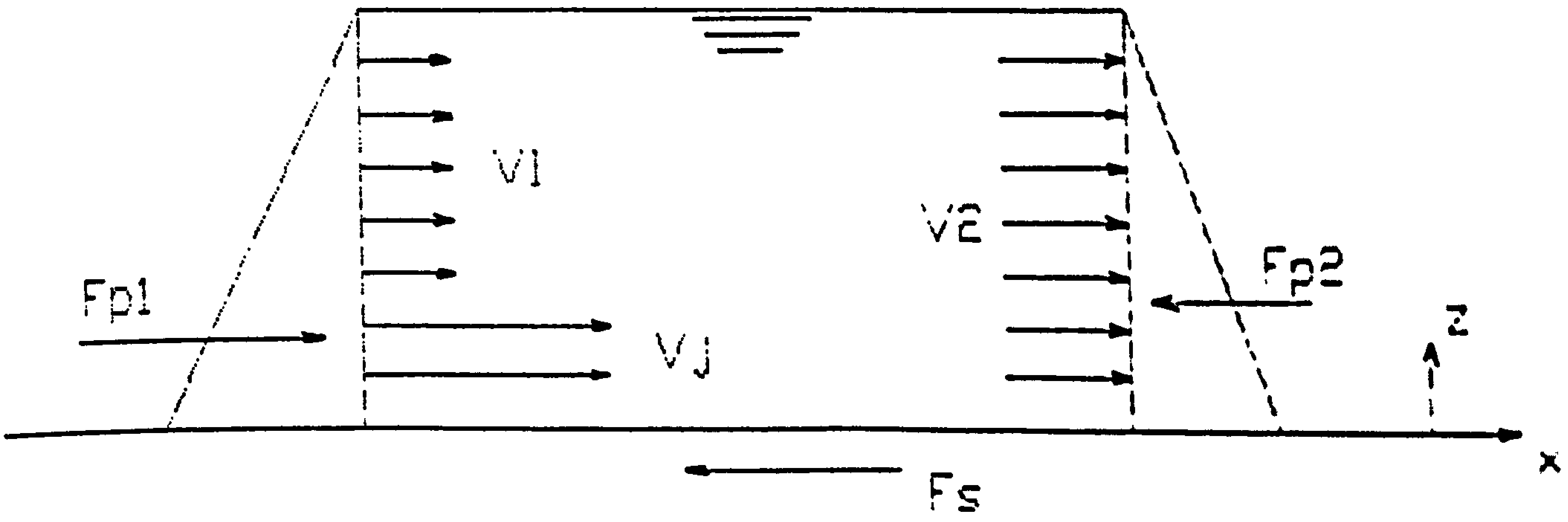


FIGURE F.2 - 3D RESPONSE SURFACE FOR SPEC. ENERGY DISSIP. RATE

APPENDICES F.3

THE CALCULATION OF THE ENERGY DISSIPATION RATE

Assuming the following control section for the annular channel:



The energy equation, when applied to the above control section is given by:

$$\dot{Q} - \dot{W}_s = \int_{cs} VdA \left(\frac{V^2}{2} + gz + \frac{p}{\rho} + u\right) \qquad (1)$$

where $\dot{Q}$ is the heat load (dQ/dt), $\dot{W}_s$ is the heat produced by mechanical power (dW_s/dt), V is the fluid average velocity, A is the cross-sectional area, g is the acceleration due to gravity, z is the elevation or potential energy per unit weight of fluid with respect to an arbitrary datum, p is the pressure energy per unit weight of fluid, ρ is the specific weight of the fluid and u is the specific internal energy.

Integration of equation (1) within the limits of the above control section gives:

$$\dot{Q} - \dot{W}_s = [\rho.V_j.\frac{V_j^2}{2} + \rho.V_j.g.z_{cj} + \rho.V_j.\rho.g.\frac{(h_1 - z_{cj})}{\rho}].A_j + \quad (2)$$

$$+ [\rho.V_1.\frac{V_1^2}{2} + \rho.V_1.g.h_1 + \rho.V_1.\frac{gh_1}{\rho}].A_1 \quad (3)$$

$$- [\rho.V_2.\frac{V_2^2}{2} + \rho.V_2.g.h_2 + \rho.V_2.\frac{gh_2}{\rho}].A_2 \quad (4)$$

$$+ [u_j.\rho.V_j.A_j + u_1.\rho.V_1.A_1 - u_2.\rho.V_2.A_2] \quad (5)$$

If the energy dissipated by the system is expressed by the sum of equations (2), (3) and (4), then:

$$\phi = (Q - W_s) - [u_j.\rho.V_j.A_j + u_1.\rho.V_1.A_1 - u_2.\rho.V_2.A_2] \quad (6)$$

The specific energy dissipation rate is obtained by a simplification of equation (1), so that the kinetic and pressure enrgy terms are assumed to be the same at sections (1) and (2). Its final form is therefore given by:

$$\Phi = \frac{\phi}{\rho ALg} = \frac{\phi}{\rho hBLg} = S.V \quad (7)$$

where ϕ is the total energy being dissipated, Φ is the specific energy dissipation rate [L/T], A is the cross-sectional area, L is a linear dimension in the x-direction, B is the width of the channel, h is the depth of flow, g is the acceleration due to gravity, S is the slope of the channel and V is the average velocity of flow.

The average velocity at section 1 (V_1) is computed from the continuity equation given by:

$$V_jA_j + V_1A_1 = V_2A_2 \quad (8)$$

The following average values were then obtained in the annular channel for the computation of the energy dissipation response surface:

CODED VELOC	CODED DEPTH	V_j (m/s)	SPECIFIC ENERGY DISSIP. (cm/min)
-1	-1	2.30	0.002903
-1	+1	2.35	0.001485
+1	-1	3.55	0.013261
+1	+1	3.60	0.007995
0	0	2.85	0.004548
+1.4	0	3.80	0.012264
-1.4	0	2.20	0.001567
0	+1.4	2.95	0.003579
0	-1.4	2.80	0.007829

The following quadractic model was then fitted to the data:

$$\Phi = 0.00455 + 0.00402.V - 0.00160.H + 0.00123.V^2 + + 0.000608.H^2 - 0.000962.V.H \qquad (9)$$

Statistical analysis performed (analysis of variance) indicated that the above model is a reasonable approximation of the true response surface.