DOCTOR OF PHILOSOPHY

The coulometric determination of total inorganic carbon in seawater and the study of the inter-relationship between the planktonic metabolism of carbon dioxide and oxygen.

Robertson, Jane Isabella

Award date:
1989

Awarding institution:
Bangor University

THE COULOMETRIC DETERMINATION OF TOTAL INORGANIC CARBON IN SEAWATER AND THE STUDY OF THE INTER-RELATIONSHIP BETWEEN THE PLANKTONIC METABOLISM OF CARBON DIOXIDE AND OXYGEN.

Thesis submitted in accordance with the requirements of the University of Wales for the degree of Doctor in Philosophy.

by

JANE ISABELLA ROBERTSON

School of Ocean Sciences,
University College of North Wales,
Bangor, Gwynedd.

July 1989

THE COULOMETRIC DETERMINATION OF TOTAL INORGANIC CARBON IN SEAWATER AND THE STUDY OF THE INTER-RELATIONSHIP BETWEEN THE PLANKTONIC METABOLISM OF CARBON DIOXIDE AND OXYGEN.

ABSTRACT Jane Isabella Robertson

A microprocessor- controlled coulometric system for measuring total inorganic carbon in seawater samples was refined. A precision of 0.5 micromoles/kg (one standard error) from a single sample was routinely achieved in the laboratory. This was reduced to 1.0 micromoles/kg at sea due to an increase in the instrument blank. The system has proved to be a robust and reliable method, well suited for routine plankton productivity measurements and oceanic mapping.

The coulometric technique was used in conjunction with an automated Winkler oxygen method to make *in vitro* and *in situ* observations of planktonic photosynthetic and respiratory quotients. In common with earlier published observations, a wide range of quotients were obtained. A detailed consideration of analytical and sampling errors led to the conclusion that the quotients could mostly be explained by the stoichiometry of conventional biochemical products and reactants.

In situ observations were carried out within mesocosms. In one field study, particular attention was paid to the correction of data for physical mixing within the mesocosm and exchange with the atmosphere. A dye diffusion study coupled with continuous temperature profiles led to the the conclusion that the circulation within these bags is complex and cannot be described by use of a one-dimensional vertical diffusion model.

The total inorganic carbon measurements determined from vertical CTD profiles during the 1987 RV Challenger cruise were compared to similar stations sampled during the Transient Tracers in the Ocean Programme (1981). Although the TTO measurements were calculated from a potentiometric titration there was no evidence for major errors of accuracy.

ACKNOWLEDGEMENTS

I am both grateful and indebted to my supervisor Professor P.J. LeB. Williams, School of Ocean Science, University College of North Wales, Bangor, Gwynedd. Peter provided considerable guidance throughout the studentship and practical help with arduous fieldwork. Most of the measurements made during the mesocosm experiments could not been completed without his willing help in sampling and analysis, especially during those innumerous early morning starts.

My appreciation to the National Environmental Research Council for the post-graduate research studentship.

I wish to acknowledge the assistance of Mr. O. Calvario-Martinez, Dr. P. Tett and Dr. D. Mills (U.C.N.W.), Mr. B. Turrell (D.A.F.S., Aberdeen, Scotland), Dr. K. Koop (University of Stockholm), Ms. M. Larsson (University of Goteborg) during fieldwork. Thanks must also go to the members of the plankton group at D.A.F.S for their patience and help during the fieldwork at Loch Ewe.

Special thanks to Mr. O. Calvario-Martinez, Mr. J. Sharples, Dr. P. Tett, Dr. C. Whittaker, Dr. A. Elliott, Mr. P. R. Intriago-Legarda and the late Mr. G. Gwynne for their respective help, guidance and fruitful discussions.

I would like to acknowledge the considerable impressive and highly skilled technical support from Mr R. Wilton and Mr. N. Suddaby, School of Ocean Sciences, during the rebuilding and interfacing of the coulometric system.

Finally, and not least, I am grateful to Mr. D. C. Boon, Chief Technical Engineer, School of Ocean Sciences, U.C.N.W. for practical help and moral guidance above and beyond the call of duty.

I have yet to see any problem, however complicated, which, when you look at it in the right way, did not become still more complicated.

Poul Anderson

CONTENTS

LIST OF TABLES

Chapter Seven : Mesocosm, Asko, Sweden

Chapter Eight : Mesocosm, Loch Ewe, Scotland

LIST OF FIGURES

Chapter Six : Method

Chapter Seven : Mesocosm experiment, Asko, Sweden

Chapter Eight : Mesocosm, Loch Ewe, Scotland

8.11 Dye profile 4.
8.12 Dye profile 5.
8.13 Temperature profiles (one to six m) taken whilst dye in the bag.
8.14 Observed *in situ* oxygen (1, 3, 4 and 5m depths) (12/8/87 1800 h to 14/8/87 1745 h).
8.15 Observed *in situ* TCO_2 (1, 3, 4 and 5m depths) (12/8/87 1800 h to 14/8/87 1745 h).
8.16 Percentage saturation of oxygen before and after mixing the bag (surface to nine metres).
8.17 Observed *in situ* oxygen (one to six metres) (18/8/87 1700 h to 20/8/87 0615 h).
8.18 Observed *in situ* TCO_2 (one to six metres) (18/8/87 1700 h to 20/8/87 0615 h).
8.19 Observed *in situ* oxygen (one to six metres) (21/8/87 1800 h to 24/8/87 0600 h).
8.20 Observed *in situ* TCO_2 (one to six metres) (21/8/87 1800 h to 24/8/87 0600 h).
8.21 Observed *in situ* TCO_2 (four to six metres) (21/8/87 1800 h to 24/8/87 0600 h).
8.22 Observed and corrected *in situ* oxygen 3 m depth (21/8/87 1800 h to 24/8/87 0600 h).
8.23 Observed and corrected *in situ* TCO_2 3 m depth (21/8/87 1800 h to 24/8/87 0600 h).
8.24 Observed and corrected *in situ* TCO_2 5 m depth (21/8/87 1800 h to 24/8/87 0600 h).

Chapter Nine : Challenger cruise 16/87

9.1 CTD Station 1 (O_2, TCO_2, Temp., Salinity).
9.2 CTD Station 4 (O_2, TCO_2, Chlorophyll, Temp., Salinity).
9.3 CTD Station 5 (O_2, TCO_2, Chlorophyll, Temp., Salinity).
9.4 CTD Station 6 (O_2, TCO_2, Chlorophyll, Temp., Salinity).
9.5 CTD Station 8 (O_2, TCO_2, Chlorophyll, Temp., Salinity).
9.6 CTD Station 9 (O_2, TCO_2, Chlorophyll, Temp., Salinity).
9.7 CTD Station 11 (O_2, TCO_2, Chlorophyll, Temp., Salinity).

Chapter Ten : Laboratory experiments

10.1 Examination of the system blank.
10.2 Examination of the system blank.
10.3 Examination of the system blank, five samples titrated.
10.4 Examination of the system blank, ten samples titrated.
10.5 Examination of the system blank, fifteen samples titrated.
10.6 Examination of the system blank, twenty samples titrated.

REFERENCES

APPENDICES

Appendix 1 : Calculation of Eddy Diffusivity Coefficents
Appendix 2 : Correction of Observed Gas Flux
Appendix 3 : Calculation of Standard Error for a Quotient
Appendix 4 : Calculation of Gas Transfer across Air-Sea Interface
Appendix 5 : Two-Tailed T-Tests for Fixing Experiments

Data Appendix : Sweden Mesocosm
LochEwe Mesocosm
Challenger Cruise

Williams, P.J.LeB. & Robertson, J.I. (1988). A serious inhibition problem from Niskin sampler encountered during plankton productivity studies.
Accepted Limnology and Oceanography.

CHAPTER 1

GENERAL INTRODUCTION AND GOALS OF THE STUDY

1.1 General Introduction

In the oceans as on land, the fundamental biological process is photosynthetic fixation of carbon.

A general relationship exists between primary production of phytoplankton and the abundance of zooplankton and organisms higher up the food-chain. Assessment and prediction of this association has grown in importance as man increasingly looks to the oceans for future exploitation. In addition, a thorough understanding of primary production is necessary for comprehension of the major biogeochemical cycles of the oceans (GOFS 1984).

Despite the obvious importance of an assessment of primary production, the magnitude of estimates for oceanic production is still disputed (Sorokin 1971, Joiris 1977, Sieburth 1977, Gieskes et al 1979, Eppley 1980, Weichart 1980, Shulenberger and Reid 1981, Jenkins 1982, Jenkins and Goldman 1984).

Early attempts did not take into account differences between different oceanic regions. Riley (1944) made one of the first attempts based on a small data set of oxygen determinations but failed to take oligotrophic regions into account, hence his estimate was certainly far too high.

Steemann Neilsen and Jensen (1957), using the radiocarbon technique for the first time on the Galathea Expedition, moderated the estimate considerably. However the Galathea cruise was mainly in tropical and subtropical waters and the estimate probably too low.

More recent estimates have taken into account regional differences and the scale of the estimates have tended to increase over the decades (Table 2, p 291, in Whittaker and Likens 1973).

Current estimates are derived almost entirely from a single method: the 14C-$NaHCO_3$ technique (Steemann Neilsen 1952). Discrepancies between the most recent primary productivity estimates have mainly centred on the supposed limitations of this technique (Verduin 1975, Gieskes et al 1979, Tijssen 1979, Postma and Rommets 1979, Shulenberger and Reid 1981, Jenkins 1982).

Despite these criticisms, there is considerable work suggesting the technique can provide reasonable estimates of primary production (Williams et al 1979, Davies and Williams 1984, Gieskes and Kraay 1984, Laws et al 1984, 1987, Bowers et al 1987, Bender et al 1987).

Limitations of the 14C-$NaHCO_3$ technique (interpretation and respiration measurements) rather than accuracy is providing the current impetus to develop an alternative, unambiguous approach to carbon flow measurements.

A significant part of the controversy surrounding the 14C-$NaHCO_3$ technique has been that of containment (Berman and Eppley 1974, Carpenter and Lively 1980). Although overlooked until relatively recently, an implicit requirement of in vitro techniques is sample collection and manipulation in addition to containment. It is now realised that sample handling may give rise to errors far and above those associated with physiological uncertainties (Chavez and Barber 1987, Williams and Robertson in press, Grande et al in press).

Due to uncertainties in recent production estimates, the aim of this study is to introduce a novel and unambiguous approach to the measurement of carbon flux (Johnson et al 1985,1987), in association with traditional O_2 measurements (Williams et al 1979).

Measurements are to be undertaken both *in situ* and *in vitro* and under a variety of environmental conditions. This is not an exercise in comparative techniques rather an attempt to elucidate some aspects of current practise and assumptions concerning algal metabolism.

1.2 Goals of the Study

1) Evaluation, refinement and testing of the TIC coulometric system for routine productivity measurements and sea-going survey measurements of the carbonate system.

2) Exploration of the stoichiometry of O_2 and CO_2 flux pertinent to community metabolism.

3) Examination of the use of mesocosms to provide *in situ* estimates of apparent net community activity in comparison to traditionally used *in vitro* incubations - an assessment of containment and manipulation effects.

CHAPTER 2

PROCESSES AND DEFINITIONS

2.1 Algal Processes

It is necessary to start by discussing some aspects of the algal processes that are measured in this study, and others not directly evaluated but important in algal metabolism.

2.1.2 Photosynthesis

The photosynthetic process can be divided into two parts, the light reactions and the dark reactions.

Light Reactions

These reactions take place in the thylakoid membrane system. It is believed that there are two photochemical reactions occurring in series (Mathis and Paillotin 1981).

Light reaction 1 is associated with the withdrawal of hydrogen from water and its passage along a series of hydrogen carriers to NADP (nicotinamide adenine dinucleotide phosphate) so that $NADPH_2$ is formed. Associated with this hydrogen (or electron) transport there is a conversion of ADP (adenosine di-phosphate) to ATP (adenosine tri-phosphate). These chemical changes are dependent on the light energy absorbed by the chloroplasts (Kirk 1983). Light reaction 2 is the liberation of oxygen from water.

Dark Reactions

These reactions take place in the stroma of the chloroplast. The $NADPH_2$ produced in the light reactions is used to reduce CO_2 to the level of carbohydrate, the energy for which is supplied by the breakdown of ATP to ADP as produced in the light reactions (Kirk 1983). The pathway by which $NADPH_2$ and ATP convert CO_2 to carbohydrate is called the Calvin-Benson cycle.

In bright sunlight, photosynthesis produces carbohydrate faster than they can be used in respiration and growth. Therefore the algae store the carbon for use later, most commonly as a polysaccharide (Craigie 1974).

Background to the measurement of photosynthesis

Photosynthesis may be measured by following chemically or isotopically the assimilation of CO_2, or the production of oxygen. There have been several reviews concerning both the theoretical and practical aspects of measuring photosynthesis (Morris 1980, Peterson 1980, Carpenter and Lively 1980, Harris 1978, Harris 1984, Talling 1984 and Harris 1986). Specific details of the radiochemical 14C-$NaHCO_3$ and chemical O_2 techniques will be discussed in greater depth later in the chapter. The chemical measurement of CO_2 is discussed in chapter five and the methods section in chapter six.

Measurements can be made either <u>in situ</u> or through a process of sampling and containment; <u>in vitro</u>.

2.1.3 Respiration

There are a number of processes that procede in opposition to photosynthesis. These involve the uptake of oxygen, associated with the oxidation of reduced compounds, and frequently the evolution of CO_2.

For convenience, it is possible to divide respiration into two main categories.

First, "mitochondrial" or dark respiration, which occurs in both the light and dark. Second, "photorespiration" which is primarily associated with the light.

Dark Respiration

Dark respiration reactions supply NADPH, ATP and carbon skeletons required for growth and maintenance within the algae. Several reviews have been published concerning the biochemical nature of the pathways involved in dark respiration (Raven 1972a, Burris 1980, Raven and Beardall 1981).

The central part of carbohydrate metabolism is the glycolytic pathway. In association with the glycolytic pathway is the oxidative pentose phosphate pathway (PPP), while the TCA (tricarboxylic acid cycle) cycle is in series with glycolysis (Raven and Beardall 1981).

The ratio of dark respiration to photosynthesis (P/R ratio) varies from species to species, environment to environment (Ryther 1954, Humphrey 1975 and Burris 1977). Healthy populations in exponential growth have the highest P/R ratios (Ryther 1956, Laws and Caperon 1976). Hence a single percentage or P/R ratio cannot be assumed to be an estimate of dark respiration. Respiration must be estimated experimentally if required.

Background to the measurement of dark respiration

A number of approaches to the estimation of the capacity of dark respiratory processes in algae have been employed. Essentially three main approaches may be recognised (Williams 1984).

1) Measurement of the change in concentration of a reactant (O_2) or product (CO_2) of the respiration process.
2) Measurement of a biochemical parameter associated with respiration : the activity of the electron transport system (ETS).
3) Calculations from biomass change using established or presumed size-specific relationships.

Most data currently available is based on just two methods; measurement of oxygen consumption (Table 1, p 360,361 in Williams 1984) and ETS measurements (Table 7, p 376 in Williams 1984).

Williams (1984) commented on the paucity of direct measurements of planktonic respiration. The data that does exist is primarily based on oxygen measurements, suprisingly few observations are based on CO_2 production rates. This contrasts sharply with the wealth of observations that exist on photosynthetic CO_2 fixation. The need to remedy this imbalance is both urgent and perhaps self evident.

2.1.4 Photorespiration

Photorespiration is the oxidation of glycolate, a recent product of photosynthesis, with consumption of oxygen and release of carbon dioxide in the light. Algae can excrete or photorespire glycolate.

Ecologically, the significance of photorespiration for estimates of carbon flow is difficult to assess as carbon would not be available to consumers if once fixed it is immediately respired.

Photorespiration differs from dark respiration in that it occurs mainly in the light, does not conserve energy as ATP and does not utilise subtrates of the TCA cycle (Burris 1981).

The role of photorespiration in algae has been much considered (Jackson and Volk 1970, Zelitch 1971, Raven 1972b, Tolbert 1974, Lloyd et al 1977, Burris 1981, Raven and Beardall 1981), however, the occurrence and importance of the process is still in dispute (Burris 1981). To a certain extent, the uncertainty is due to the difficulty in quantifying the process.

Measurement of Photorespiration

Photorespiration was first described by Decker (1955), and most research has been based on terrestrial plants (Jackson and Volk 1970). During photorespiration CO_2 is produced and O_2 consumed in the light, also dark respiration occurring will produce CO_2 and consume O_2. In addition, photosynthesis will consume CO_2 and produce O_2. These three simultaneous sets of reactions prevent direct determination of photorespiration by gas or isotope exchange measurements. Hence the reasons for photorespiration being an extremely evasive process to measure. As a consequence a wide variety of approaches have been evolved, all of which are indirect :

1) Burris (1977) exposed marine macro-algae to 14C-$NaHCO_3$ under varying levels of oxygen, following the accumulation of the 14C label in glycine and serine, intermediates of the photorespiratory pathway. Burris (1977) showed greatest accumulation of the label under highest oxygen concentrations. This appears to indicate a greater flow of carbon through the glycolate or photorespiratory pathway under those conditions favourable to photorespiration. This approach does not however enable a quantitative determination of photorespiration.

2) The activity of glycolate pathway enzymes has been measured (Paul et al 1975, Paul and Volcani 1976), however this is not a conclusive demonstration that photorespiration is therefore also occurring. (Burris 1980)

3) Another indirect approach involves measurement of the post-illumination burst of CO_2 production and O_2 uptake. This acceleration is assumed to be a measure of photorespiration.

The photorespiratory subtrate pools are rapidly exhausted and then the rate of O_2 consumption and CO_2 production drops to a steady rate associated with respiration. The difference between the two rates is considered to be due photorespiration (Burris 1981).

Burris (1977) observed the 'burst' in some algal species, but not in others. Brown and Weiss (1959) failed to observe the 'burst'. Brown and Whittington (1955) observed opposite behaviour with a CO_2 'burst' at the start of illumination. Objections to the validity of this approach are that the intra-cellular reassimilation of CO_2 is not accounted for and it is possible that part of the post-illumination burst is caused by oxidation of carbon compounds other than those associated with the photorespiratory pathway (Burris 1981).

4) Glycollic acid has been shown to be excreted under conditions favourable to photorespiration. Excretion has been used an indicator of glycolate pathway activity and hence photorespiration (Tolbert 1974). Algal excretion is a notoriously difficult and much contested area of research and with the current state of techniques (Fogg, 1977 and Sharp 1977) it is probably an unsound base from which to predict photorespiration. (Burris 1980).

5) Low photosynthetic quotients could be taken as an indication of photorespiration. O_2 uptake is not necessarily matched by CO_2 production, glycolate may be excreted or not metabolised further than glycine (Tolbert 1974). However other factors have been shown to influence the photosynthetic quotient (Williams et al 1979, Megard et al 1985) and cannot be currently separated from an observed drop in the quotient in order to quantify photorespiration.

6) Bender et al (1987) used an isotopic oxygen method in order to provide unambiguous estimates of gross photosynthesis.

Used in conjunction with Winkler light dark bottle incubations the rate of respiration in the light can be calculated from the difference between ^{18}O gross production and O_2 net production. Bender et al (1987) found differences in the rates of light and dark respiration in some of the samples and concluded the effect could be due to either photorespiration or light enhancement of mitochondrial respiration. The ^{18}O technique can show whether a difference exists between light and dark respiration rates however it cannot conclusively ascribe it to photorespiration.

7) Another approach has been the measurement of CO_2 release during photorespiration. This has involved the measurement of CO_2 loss into CO_2-free air by either infra-red gas analysis or radioactively labelled $^{14}CO_2$ (Tolbert 1974). This is not necessarily a true measure of photorespiration due to the possibility of reassimilation by the algae and interference from dark respiration. Refixation of CO_2 by photosynthetic activity can be important (Raven 1972a,b).

In conclusion, evidence of photorespiration in algae is ambiguous. Burris (1977) demonstrated photorespiration in eight species of algae by following the accumulation of the 14C-label in glycine and serine. By contrast, Lloyd et al (1977) concluded that green algae do not possess a conventional photorespiratory system and so may not photorespire at all. Bidwell (1977) showed, by contrast, that in Chlamydomonas, light respiration is a continuation of respiration in the dark, by use of an artificial leaf technique and measurement of 14C-12C exchange.

In terrestrial plants, it has been shown to increase under conditions of high light, high oxygen and low CO_2 concentration (Goldsworthy 1970) however this has yet to be demonstrated in algae.

In addition, these conditions would not be commonly found in marine systems, so the importance of photorespiration both quantitatively and ecologically is probably not significant.

2.2 Definitions and assumptions

As with most fields of scientific research, precise definitions are critical in order to avoid misunderstanding and aid interpretation. Before continuing with further details of the methods to be used in this study it is essential to consider the definitions of the processes under examination.

In the present work, the following terms will be used; photosynthesis (gross and net), production (gross, net primary and net community), respiration and photorespiration.

Traditionally and conveniently, the term photosynthesis is restricted to the physiological process and production to the operational measurement of the process (Strickland 1960).

2.2.1 Photosynthesis

Photosynthesis may be defined as the conversion of light to chemical energy. Closely associated with the biochemical process is the release of oxygen and less closely the fixation of inorganic carbon and the reduction of nitrate.

Gross photosynthesis will be defined as the rate of conversion of light into potential chemical energy and net photosynthesis as the net change in chemical energy, both logically measured in the light.

2.2.2 Production

Primary production may be defined as the input of chemical energy into the ecosystem, hence photoheterotrophy, bacterial photosynthesis and chemosynthesis should be taken into account (Fogg 1975, 1980). As with the physiological process of photosynthesis, production is by definition a flux of potential energy. In practise however, this measurement is rarely achieved and more commonly in most marine, oxygenated environments, phytoplankton photosynthesis is regarded as being predominant and the following overall equation taken to represent community production.

$$nCO_2 + 2nH_2O \rightarrow [\ CH_2O\ ]_n + nO_2$$

Where $[\ CH_2O\ ]_n$ represents an empirical formula for organic products.

Traditionally, changes in either CO_2 or O_2 have been followed in order to characterise the above process. This approach gives rise to a set of operational definitions.

Gross photosynthetic production

Gross production is the rate of conversion of light energy to chemical energy, it is rarely measured as such, the usual procedure being to derive it as a sum of chemical changes seen both in the light and in the dark.

Operationally therefore gross production (GP) is the observed (net) measurement of production in the light plus all losses as represented by respiration measured in the dark. This definition is necessary as otherwise it is very difficult to measure.

GP has no true ecological value, however, it is frequently used to compare communities and taken as an indication of their ability to store potential energy.

If plankton photosynthesis is the only biochemical light-storing process occuring then gross photosynthetic production is equivalent to gross primary production and in turn gross photosynthesis.

Net primary and net community production

In the marine literature the term net production has been loosely used to refer to two quite distinct processes. Whilst most measurements were made with the 14C-$NaHCO_3$ method this was acceptable, however with the common introduction of chemical techniques it is necessary to distinguish between the two.

Net primary production (NPP) is equivalent to the physiological term of net photosynthesis and implies solely plankton photosynthesis. This term is difficult to measure with chemical observations in natural systems due to a mixture of autotrophic and heterotrophic processes. This term is important however, when discussing the interpretation of the 14C-NaHCO3 technique (Peterson 1980).

Net community production (NCP), is equivalent to the traditional net production term and is the balance between the rate of formation and utilisation within a community. It is currently the only term that can be measured unambiguously in the planktonic environment, by chemical or radiochemical means. If the process is positive, the rate will be expressed as an increase in O_2 concentration and a decrease in CO_2 with time.

Net community production (NCP) is a key ecological property, for at any one point in time it represents the balance between production and consumption of organic matter available for exportation (ie sedimentation) and harvesting.

NCP is by definition the difference between gross production and respiration.

2.2.3 Respiration

A number of different processes may be grouped together under the general term of respiration, which occur in both the light and dark. Hence the definition of respiration may be best left as an operational definition of a process which results in the consumption of oxygen and production of CO_2 in the dark.

In the present operational definition used when discussing respiration, it will be assumed that light respiration processes are equivalent to that measured in the dark.

Given an accurate measurement of respiration then gross production can be estimated using NCP.

2.2.4 Photorespiration

Photorespiration, as discussed already, is the oxidation of glycolate, a recent product of photosynthesis, with consumption of O_2 and release of CO_2 in the light. This process is very difficult to measure and the magnitude of the process in relation to dark respiration is usually taken to be neglible.

2.2.5 Operational definitions

The following are operational definitions of the above as calculated following fluxes in O_2 and CO_2 respectively.

Oxygen

Gross production	= Net community production plus respiration
Net community production	= Oxygen increase in the light
Respiration	= Oxygen decrease in the dark

Carbon dioxide

Gross production	= Net community production plus respiration
Net community production	= TCO_2 decrease in the light
Respiration	= TCO_2 increase in the dark

Given the technical difficulties and uncertainties associated with ecological work, it is possible to produce a definition of NCP which permits direct evaluation. This is not true for GP, indirectly it is obtained as the sum of NCP and respiration. These quantities are measured under varying environmental conditions (ie separately in the light and in the dark). The major problem with this approach is that respiration measured in the dark is that it is assumed to be equivalent to that occurring in the light.

The uncertainty which this assumption can be divided into two problems, first photorespiration and second, dark respiration rates in the light.

1) The scale of photorespiration in the light.

Photorespiration may occur in the light, however, there is uncertainty over the prominence of algal photorespiration in the literature (see previous section).

2) Dark respiration rates are not necessarily equivalent to that occurring in the light

- Respiration may be greater in the heavily oxygenated water surrounding a cell during photosynthesis than in oxygen depleted water in the dark. (Ryther and Vaccaro 1954, Gessner and Pannier 1958).

- Dark bottle respiration measured on the initial crop might not be applicable to a light bottle in which biomass could have increased.(Edmondson and Edmondson 1947).

- Strickland (1960) questioned whether algae produce a chemical bactericidal agent in the light. Alternatively whether dead and dying cells in the dark bottle promote the growth of significantly more bacteria.

Recently, Lancelot and Mathot (1985) reviewed that the general concensus is that dark respiration rates appear to be mainly unaffected in the light or in some instances slightly depressed depending on the circumstances (Glidewell and Raven 1975, Raven and Glidewell 1975, Bidwell 1977, Harris and Piccunin 1977).

In conclusion, for the operational definitions to be used a number of assumptions are made. These assumptions though undesirable are currently the only means by which the processes can be defined.

CHAPTER 3

REVIEW OF PHOTOSYNTHETIC MEASUREMENTS

3.1 ^{14}C-$NaHCO_3$ Assimilation

The most commonly used procedure for assessing primary production in the marine system involves the measurement of the rate of assimilation of radioactively labelled bicarbonate ions, during an *in vitro* incubation in the light.

The carbon taken up during photosynthesis either remains in the algae as particulate organic carbon (POC) or is excreted into the water as dissolved organic carbon (DOC) (Steemann Neilsen 1975).

The method was first introduced by Steemann Neilsen (1952) and represents one of the most basic tools of aquatic ecology. The original technique has been subsequently revised (Parsons *et al* 1984).

Although this method is not to be used in the following study, most current measurements of production and photosynthetic quotients involve rates of oxygen flux and radioactively-labelled carbon uptake and therefore it would seem that a consideration of the method is relevant.

3.1.1 Details of Methodology

A known amount of ^{14}C-$NaHCO_3$ (as dissolved $NaHCO_3$) is added to a series of replicated bottles containing the water sample. One set of replicates are incubated in the light, a second in the dark, and the remainder provide a time zero control.

After incubation for a determined period, the organic carbon associated with the algae is separated from the remaining inorganic label by a process of filtration. Any radioactively-labelled dissolved organic carbon (DOC) remaining in the filtrate can be determined by driving off the remaining inorganic carbon by a process of acidification and bubbling.

If the total inorganic carbon (TCO_2) is known in the initial water sample, and the amount of radioactive label added, then the rate of uptake of carbon can be determined (Peterson 1980, Parsons et al 1984).

There are a series of technical problems associated with the method (Sournia 1971, Peterson 1980, Leftley et al 1983), alongside a general lack of standardization in methodology between workers (Falkowski 1980).

However, the main shortcomings associated with the method are in that it does not provide a ready estimate of respiration, and tracer compartmentalism problems make the interpretation of results difficult, if not impossible.

3.1.2 Respiration measurements

Steemann Neilsen and Hanssen (1959) introduced a radio-chemical approach in order to estimate algal respiration in cultures. Algae were labelled during a light period and then respiration measured as the decrease in radioactivity associated with a following dark period. Subsequently, the method has been used with natural populations (Eppley and Sharp 1975, Smith 1977).

3.1.3 Interpretation

Dark fixation

To a certain extent the importance of the role of dark fixation of 14C-$NaHCO_3$ during an incubation has been ignored. Opinions differ over whether dark fixation should be ignored or subtracted from measurements in the light. This uncertainty has reduced the sensitivity of the technique considerably. The 14C-$NaHCO_3$ method has been championed as the only method sensitive enough to provide productivity rates in oligotrophic regions. These areas have long been known to possess high dark fixation rates and it is not uncommon to find dark fixation equal to light fixation (Morris et al 1971).

Tracer compartmentalism

Carbon fixation rates are often interpreted as being close to net production, however, recent reviewers have noted that it is still uncertain as to what the results represent (Yentsch 1974, Fogg 1975, Peterson 1980).

At the start of an incubation no 14C is present in the cells and initially the internal CO_2 pool must reach equilibrium with the external concentrations. Immediately following this equilibrium the initial rate of uptake will be an estimate of gross primary photosynthesis (GPP). As 14C accumulates in the cells and enters the respiratory pools, the rate of 14C uptake shifts from gross towards measuring net photosynthesis. When the specific activity of the 14C inside the cells becomes equal to that of the external medium, any further uptake will estimate net photosynthesis (Dring and Jewson 1982). Exactly what the rate of 14C-$NaHCO_3$ uptake does measure will depend on the length of the incubation and the time taken for the various intracellular pools to achieve equilibrium (Dring and Jewson 1982).

Photorespiratory substrates are probably saturated with 14C within a few minutes under favourable light conditions, but more slowly at low light intensities, especially in the presence of extensive reassimilation (Raven 1972). Dark respiratory substrates are saturated more slowly, but some mixing of the two substrate pools, photorespiratory and dark respiration, evidently occurs during several hours of light incubation (Raven 1972).

In the absence of respiratory release of 14C in the light, 14C fixation will measure net photosynthesis if there is 100% internal reassimilation of respired $12CO_2$ and initially gross photosynthesis if no reassimilation occurs. Reassimilation in unicellular algae is variable and depends on the experimental situation, age and culture condition (Raven 1972).

In conclusion, most workers assume that long incubations (ie greater than 24 h) provide an estimate of net photosynthesis, providing excretion is minimal and reassimilation complete (Dring and Jewson 1982, Hobson et al 1976). Short incubations (ie less than 3 hours) are assumed to provide an estimate between gross and net photosynthesis depending on the environmental conditions (Hobson et al 1976, Harris and Piccunin 1977, Peterson 1978).

In the light of these major problems associated with the 14C method it is perhaps difficult to reconcile the widespread use of the technique. When first introduced, the method was widely welcomed and enthusiastically promoted as the one sensitive technique that would provide fundamental information regarding the incorporation of carbon into the phytoplankton specifically, and hence marine ecosystems generally.

The exact nature of the complicated physiological processes under examination were not well understood consequently marine scientists became experts at measuring uptake of 14C-labelled ions but failed to understand what the results actually meant.

Strickland and Parsons (1972) issued a plea for a critical re-examination and independent check on the method. To a great extent this was hampered by the lack of an independent check, especially in areas of low light intensities or oligotrophic regions. Recent developments in the classical Winkler titrimetric method (Bryan et al 1976, Williams and Jenkinson 1982) provided the first real opportunity for comparison.

Another more recent development has been the introduction of an automated, coulometric, end-point detection system for total inorganic carbon (TIC) in seawater (Johnson et al 1985, 1987)

These two approaches now permit an assessment of the 14C-$NaHCO_3$ method, both in terms of oxygen and carbon flux.

3.2 Photosynthetic oxygen flux measurements

Most of the existing oxygen data has been obtained by either the classical Winkler titrimetric method (1888) for measuring dissolved oxygen in aqueous solutions or one of the numerous modifications.

Other methods that have been used - the microgasometric determination (Scholander et al 1955), the mass spectrometric method (Benson and Parker 1961, Parsons et al 1984), the gas chromatographic procedure (Swinnerton et al 1962,1964 and Weiss and Craig 1973), the amperometric determination (Carritt and Kanwisher 1959, Grasshoff 1962,1963).

The polarographic method with a rapid dropping mercury electrode and the dead-stop titration method (Grasshoff 1962) are used for mainly for special purposes or for a continuous record of oxygen consumption.

A thorough discussion of electrochemical methods for the determination of dissolved oxygen in both seawater and freshwater in given by Grasshoff (1981). However, the standardisation or calibration of many of these methods is ultimately achieved by reference to Winkler analyses or to 'saturation' tables prepared from data obtained largely by using the Winkler method.

The Winkler method is well documented and deceptively simple, however, the highest precision can only be obtained by careful attention to detail. A detailed discussion of method and errors can be found in Grasshoff (1962), Carpenter (1965,1966), Carritt and Carpenter (1966).

3.2.1 Details of Methodology

Chemically the Winkler method is based on the following principle:

The dissolved oxygen in a measured amount of water is chemically bound by $Mn_{(II)}$ hydroxide in a strong alkaline medium. At the high pH the divalent form is rapidly and quantitatively oxidized to $Mn_{(III)}$ (and not to $Mn_{(IV)}$ as commonly stated because of the large surplus of $Mn_{(II)}$ hydroxide present, Grasshoff 1983).

Subsequent to the reaction, the oxygen and precipitate of mixed $Mn_{(II)}$ and $Mn_{(III)}$ hydroxides, are dissolved by acidification to a pH less than 2.5 (Grasshoff 1983). The precipitated hydroxides dissolve and $Mn_{(III)}$ ions are liberated. $Mn_{(III)}$ is a strong oxidizing agent in acidic media and reacts with iodide ions (added to the water sample along with the potassium hydroxide).

The iodide ions are oxidised to iodine, which in turn forms a tri-iodide ion complex with the surplus iodide. This complex formation is essential to the accuracy of the method because dissolved iodine has a relatively high vapour pressure and tends to escape during the subsequent steps of the analysis (Grasshoff 1983). The tri-iodide complex has a low vapour pressure but will decompose readily if iodine is removed from the system.

In the third step of the analysis the iodine is titrated with thiosulphate. The iodine is reduced to iodide and the thiosulphate is in turn oxidized to the tetrathionate ion.

The classical end-point of the redox titration is indicated usually by a starch indicator.

The basic method as described above has a precision of 0.5% (Parsons et al 1984) which is only sufficiently sensitive for it to used under highly productive conditions and consequently alternative approaches have been attempted.

The two main sources of error in the basic Winkler method are (Carritt and Carpenter 1966) :

a) The loss of iodine by volatilization which occurs mainly during the transferance of the acidified solution to the titration vessel.

b) Lack of definition and subjectivity in the starch-iodine end-point.

Volatilisation may be avoided by use of a whole bottle titration, first suggested by Green and Carritt (1966). Error associated with the starch indicator has been avoided by use of a number of alternative end-point procedures.

Electrochemical techniques (amperometric or potentiometric) have been used (Grasshoff 1981) as have photometric techniques based on the unusually high extinction coefficient of the tri-iodide ion in the near ultra-violet absorption band.

According to Carpenter (1966) this approach increases the sensitivity of the end-point detection attainable twenty-fold upon the starch end-point.

Amperometric devices have the great merit of using dissolved oxygen directly as a reactant, but due to limitations of stability, sensitivity to temperature and stirring, do not yield the high precision attainable with the classical Winkler method (Talling 1973).

The conventional Winkler has been attributed a C.V. of 0.5%. With use of a photometric end-point detection and whole bottle technique it is possible to achieve a C.V. of 0.1% or better (Bryan et al 1976). Automation of the whole titration has been achieved by microprocessor control (Hartwig and Michael 1978, Williams and Jenkinson 1982), this has made sample processing rapid (3-4 mins) and in normal use been attributed a C.V. of 0.03 - 0.1%.

The application of a sensitive end-point detection system (Bryan et al 1976), opened a new chapter in the history of productivity with quick, accurate and reproducible measurements. An independent check for the 14C-$NaHCO_3$ method was now available for use in less productive regions and environments.

3.2.2 Interpretation

A number of the problems associated with the 14C-$NaHCO_3$ technique are not shared by the oxygen light and dark bottle method. First, respiration measurements are in principal possible, second, in situ measurements can be undertaken and finally the conceptual nature of the measurement appears to be simplified. Oxygen measurements can provide an estimate of net community productivity.

Following the system devised by Bryan et al (1976) and Williams and Jenkinson (1982) it became possible to undertake a series of comparisons in order to provide a check on the 14C-$NaHCO_3$ method.

CHAPTER 4

ASPECTS OF INTER-METHOD COMPARISONS

4.1 History of comparison experiments

Williams et al (1979) concluded that there was no significant difference between the two techniques of oxygen and 14C-$NaHCO_3$, in coastal waters using in vitro incubations, provided the effect of the nitrogen source on the PQ was taken into account.

Andersen and Sand-Jensen (1980) observed that the 14C-$NaHCO_3$ technique underestimated gross photosynthesis at low light levels as estimated by the oxygen technique. They concluded that the underestimation, was due to increased reassimilation of respired CO_2 at low light intensities.

Shulenberger and Reid (1981) compared a long term seasonal accumulation of oxygen to that estimated using discrete 14C-$NaHCO_3$ in vitro incubations in an oligotrophic region. They concluded that the 14C-$NaHCO_3$ method, either uniquely, or due to extrapolation for long time scales, seriously underestimated production. A lively debate ensued regarding the calculations of Shulenberger and Reid (1981). Platt (1984), Platt et al (1984), Platt and Harrison (1985,1986) claimed that too many assumptions invalidated the essence of the theory. In addition, Platt (1984) felt it was an unfair comparison of the 14C-$NaHCO_3$ technique, in that it is misleading to compare a few discrete measurements with one embracing large scales of both time and space.

Discrepancies noted by Shulenberger and Reid (1981) may have been due to the containment effect inherent with bottle incubations or contamination during sampling (Williams and Robertson, in press) rather than the technique itself under examination.

Williams et al (1983) in a comparison of in vitro 14C-$NaHCO_3$ and O_2 techniques in oligotrophic waters again found no serious underestimation on behalf of the 14C-$NaHCO_3$ technique.

Sakamoto et al (1984) reinforced this with further in vitro comparisons and found no significant difference provided the nitrogen source is taken into account.

Davies and Williams (1984) compared 14C-$NaHCO_3$ and O_2 in vitro but also in situ O_2 and in vitro O_2 values. No significant differences could be demonstrated in the case of the O_2 technique due to containment or between the 14C-$NaHCO_3$ and O_2 technique, providing the effect of the nitrogen source on the PQ is taken into account.

Jenkins and Goldman (1984) following a similiar approach to Shulenberger and Reid (1981) also concluded that long term assessment of production embracing large spatial and seasonal time scales did not agree with use of discrete 14C-$NaHCO_3$ data.

Raine (1985) in another in vitro comparison found no significant difference between the techniques provided the effect of the nitrogen source on the PQ is taken into account. Megard et al (1985) found that the 14C-$NaHCO_3$ technique underestimated the oxygen method at low light levels and concluded it was due to the light-dependent reduction of nitrate, which competes with CO_2 for oxygenic photoreductant. Oviatt et al (1986) found that the 14C-$NaHCO_3$ technique underestimated oxygen based production estimates. Bender et al (1987) did not find any gross differences between the 14C-$NaHCO_3$ technique and either the oxygen, TCO_2 or ^{18}O techniques.

Fahnenstiel and Carrick (1988) compared 14C-$NaHCO_3$ and O_2 *in vitro*, also the O_2 method *in vitro* and *in situ*. They conclude that the two techniques provided similar estimates of production *in vitro*, however that *in vitro* oxygen measurements in this instance, underestimate *in situ* measurements. They imply that the difference is due to containment effects.

4.2 Major drawbacks to such comparisons

It is apparent that use of the oxygen technique in order to provide a check on the validity of the 14C-$NaHCO_3$ method suffers from two major drawbacks.

First, the nature of the 14C-$NaHCO_3$ technique necessitates *in vitro* incubations whereas *in situ* measurements are preferable due to sampling and manipulation effects. A comparison based on *in vitro* measurements suffers from inherent problems that may obscure the comparison itself.

4.2.1 In situ measurements

The measurement and observation of an *in situ* diurnal rhythmn for either O_2 or/and CO_2 is a difficult process.

However, this approach does avoid sampling, manipulation and containment errors. In addition, the timescales involved are more realistic when attempting to quantify a daily process.

A variety of factors can interfere with curve interpretation; turbulence of water masses, air-sea exchange and most significantly horizontal advection.

Until recently *in situ* work in marine systems has been mainly restricted to the interpretation of deep, dissolved oxygen distributions (Riley 1951) and seasonal or annual O_2 and CO_2 changes (Ben-Yaakov 1972, Shulenberger and Reid 1981, Jenkins and Goldman 1984). The potential for diel studies, *in situ*, has only recently been realised (Tijssen 1979, Tijssen and Eijgenraam 1982, Johnson *et al* 1981, Davies and Williams 1984, Fahnenstiel and Carrick 1988).

Where data for diurnal *in situ* changes does exist, calculated rates in comparison to *in vitro* measurements are sometimes observed to be higher (Tijssen 1979, Johnson *et al* 1981) and sometimes not (Williams *et al* 1983, Davies and Williams 1984, Fahnenstiel and Carrick 1988).

There are in general, two main approaches to measurements made *in situ*. First is the recording of "freewater" changes, as provided by the use of drogued stations to follow the sampled water mass. Details of the drifter design and ability to accurately track a water mass are described in Tijssen and Wetsteyn (1984), McCormick *et al* (1985) and Scavia and Fahnenstiel (1987). Freewater measurements are subject to considerable correction for interfering processes and logistically are difficult to execute.

The second approach to *in situ* data collection is to make measurements in a large contained ecosystem or mesocosm. In the mesocosm, horizontal advection is presumed to be largely eliminated and vertical processes considerably reduced (Davies and Williams 1984). A controlled experimental ecosystem is clearly more amenable to mass balancing and budgeting than an uncontained system ie freewater diel measurements. However the biological, chemical and physical characteristics of the mesocosm can only mimic freewater changes and as such must still be regarded as possessing certain containment effects.

4.2.2. In vitro measurements

The problems associated with measurements in vitro are severalfold but positively, in vitro incubations do constitute a controlled environment, and the only one in which the 14C-$NaHCO_3$ technique can be successfully and safely employed. The value of in vitro measurements, though lacking in certain respects, still constitutes a utilisable resource when in situ measurements are often not possible.

Containment effects, biological, chemical and physical are detailed in Berman and Eppley (1974), Carpenter and Lively (1980).

In addition, it is now apparent that sampling and manipulation can give rise to large errors (Chavez and Barber 1987, Williams and Robertson in press, Grande et al in press)

Another limitation to in vitro measurements is the small time-scale associated with the incubations, especially those using the 14C-$NaHCO_3$ technique (Strickland and Parsons 1972). These incubations are frequently scaled up in order to provide estimates of diurnal change. Some of the most conflicting comparisons between the 14C-$NaHCO_3$ and oxygen techniques involve problems not just associated with the 14C-$NaHCO_3$ technique uniquely, rather in vitro based production rates themselves (Tijssen 1979, Shulenberger and Reid 1981 and Jenkins and Goldman 1984). The Winkler oxygen technique, in contrast to the 14C-$NaHCO_3$ method, involves incubations of 12 or 24 h duration. These timescales for diurnal changes are more realistic but increase the possible risk of increased error due to containment.

In summary *in situ* measurements whether in freewater or large mesocosms, are difficult to both achieve and interpret. Additionally, this approach is not amenable to the use of isotopes, the most common method currently in use to measure photosynthesis and production. For these reasons *in vitro* measurement remains the most popular method of providing estimates of photosynthesis.

4.3 Planktonic photosynthetic quotients

The second major drawback to the previously discussed comparisons is that it requires the use of a photosynthetic quotient to convert oxygen into comparable carbon units. Any change in the true value of the quotient at that moment will significantly effect the real value of the comparison.

The long history of ^{14}C-$NaHCO_3$ and O_2 comparisons has shown that insufficient thought has been given when dealing with an appropriate quotient and this will prejudice the comparison.

The considerable problems and interest in verifying the ^{14}C-$NaHCO_3$ technique, led on to an increased understanding and appreciation of the compartmentalisation problems associated with use of the tracer. This was however, pursued to the neglect of perhaps a more general and fundamental question being observed during the rush of comparative experiments. Namely, the numerical value of the PQ and RQ being noted.

To a certain extent, the unusual biochemical stoichiometry being suggested by these results (Holligan *et al* 1984, Gallegos *et al* 1983, Johnson *et al* 1983,b Oviatt *et al* 1986, Megard *et al* 1985, Fahnensteil and Carrick 1988) was not pursued due to a fundamental incompatibility of the ^{14}C-$NaHCO_3$ and the oxygen techniques for this purpose.

It is vital to obtain unambiguous and compatible estimates of production, measured simultaneously through changes in carbon and oxygen. Ratios so determined will then be a closer reflection of algal metabolism at that particular point in time and space. With the advent of a more precise method for TCO_2 measurement (Johnson et al 1985, 1987), the question of the true value of quotients was now open to a more detailed examination.

There is a clear need to evaluate the quotient under a range of conditions, both in situ and for comparison in vitro.

4.3.1 Definition and background

It is current practise to measure primary productivity by estimating oxygen flux and then converting to carbon using metabolic ratios in order to assess carbon flow, compare techniques and the finer details of methodology.

The photosynthetic quotient (PQ) of actively photosynthesizing organisms is the molar ratio of the rate of oxygen production to that of carbon dioxide assimilation, the respiratory quotient (RQ) being the inverse.

The rates of oxygen production and carbon assimilation are inevitably linked to each other and to the flux of radiant energy. However, the overall photosynthetic stoichiometry of oxygen, carbon and nitrogen in phytoplankton and natural heterogeneous populations, in particular, can be complex and theoretical expectations are frequently not obtained in practice (Anderson and Sand-Jensen 1980, Johnson et al 1981, 1983, Gallegos et al 1983, Holligan et al 1984, Oviatt et al 1986, Megard et al 1985).

In part, perhaps this is not suprising, as metabolism of oxygen and carbon dioxide are associated with related, but fundamentally different processes, oxygen being associated with energy flux and carbon dioxide fixation with the formation of organic compounds (Sournia 1971, Williams et al 1979, Gallegos et al 1983).

4.3.2 Expected range of quotients

Conventional values for quotients

Over short-time intervals the instantaneous values of these quotients may vary enormously due to a decoupling of O_2 and CO_2 metabolism in the overall plant metabolism - "CO_2 bursts" etc. (Strickland 1960).

However, in the long term (more than a few minutes), the cell cannot harbour an excess or deficiency of reducing power, hence it has been commonly assumed that the PQ should fall within the range expected from stoichiometric biochemical considerations depending on the composition of the end-product. The photosynthetic quotient is most commonly quoted as being in the range 1-1.3 for phytoplankton (Parsons et al 1984).

The respiratory quotient is commonly quoted as being in the range 0.7-1.0 depending on whether fats or carbohydrates are being utilized for energy (Parsons et al 1984).

Precision limits from methodology used to calculate the ratio can be placed on the value of the quotient, and it is not expected that analytical imprecision would normally affect the true value of the quotient by more than 20 %.

4.3.3 Calculated theoretical range

Strickland (1960) was one of the first marine scientists to draw attention to the importance of the form of combined nitrogen assimilated along with the photosynthetic end-products of the cell. He calculated theoretical values for the photosynthetic ratio depending on the constitution of the end-product and the nitrogen source.

Hexose - 1.0
Fat - 1.4
Protein - 1.05 (ammonia as a nitrogen source)
Protein - 1.6 (nitrate as a nitrogen source)

The role of the source of combined nitrogen was taken up and commented on in greater detail by Williams et al (1979) and Davies and Williams (1984).

If nitrate is taken up then it must be first reduced before use to NH_4^+, the energy required for this (ATP and $NADPH_2$) arises from the photolysis of water, which is an oxygen producing process. The overall stoichiometry of the process is outlined in Fogg (1975) and Williams et al (1979).

$$NO_3^- + 2H_2O \Rightarrow NH_3 + OH^- + 2O_2$$

Thus the utilization of nitrate will result in the production of two molecules of oxygen per atom of nitrogen assimilated. Uptake of ammonium requires no additional reduction and so does not influence the relative concentration of oxygen.

During utilisation of nitrate as a nitrogen source, another influencing factor on the value of the quotient is the C:N assimilation ratio.

A theoretical range can be calculated by considering the photosynthetic end-product in addition to the nitrogen source and C:N assimilation ratio. In order to do this it is convenient to separate the PQ into 2 components :

a) A carbon PQ dependent on the end-product
b) A nitrogen PQ dependent on the form of combined nitrogen

(after Williams et al 1979).

'Carbon' PQ

The end product of photosynthesis will determine the quotient. Products of photosynthesis include - hexose sugars, disaccharides, polysaccharides, sugar alcohols (glycerol), organic acids (glycollic acids), lipids, fatty acids and amino acids.

In essence, phytoplankton are protein synthesizing organisms with a capacity for metabolic diversity that permits considerable variability to be superimposed. The nature of this variability is controlled by the environmental conditions and the physiological state of the cell.

Traditionally, photosynthesis is described using hexose formation as the end-product.

$$6CO_2 + 6H_2O \Rightarrow C_6H_{12}O_6 + 6O_2$$

leading to a quotient of 1.0

A lower limit can be theoretically calculated with the formation of an oxidized acid

$$8CO_2 + 6H_2O \Rightarrow 2C_4O_4H_6 + 7O_2$$

leading to a quotient of 0.88

An upper limit would result from say fatty acid formation.

$$CO_2 + H_2O \Rightarrow (-CH_2-) + 1\tfrac{1}{2}\ O_2$$

leading to a quotient of 1.5.

'Nitrogen' PQ

Ammonium is the preferred nitrogen source (McCarthy et al 1982) for phytoplankton and does not require reduction, prior to assimilation. However, for growth on nitrate as a nitrogen source, the C:N ratio will be a major factor determining the PQ.

An upper limit to the C:N ratio may be expected to be 3:1 (Antia et al 1963). A lower limit can be obtained using a C:N ratio of 15:1 (Caperon and Meyer 1972).

It is possible, on the basis of theoretical biochemical considerations to calculate a range to the quotient which involves the nitrogen source, the C:N assimilation ratio and the end-product.

During the formation of proteins, a typical amino acid formed is glycine.

The stoichiometric balance of the formation of glycine provides a photosynthetic quotient of 0.75.

$$4CO_2 + 2H_2O + 2NH_3 \Rightarrow 2C_2NH_5O_2 + 3O_2$$

With a C:N ratio of 2 this gives a total quotient of 1.75
The stoichiometric balance of the formation of phenylalanine provides a photosynthetic quotient of 1.11

$$9CO_2 + 4H_2O + NH_3 \Rightarrow C_9NH_{11}O_2 + 10O_2$$

With a C:N ratio of 9 this gives a total quotient of 1.33.
The stoichiometric balance of the formation of a nucleic acid can be estimated by balancing the formation of a nucleotide, comprising a sugar and a base (Thymine).

$$10CO_2 + 5H_2O + 2NH_3 \Rightarrow C_{10}N_2H_{16}O_6 + 9.5O_2$$

This will give a quotient of 0.95 which in addition to a C:N ratio of 5:1 gives a total quotient of 1.35.

Williams et al (1979) constructed a table using a carbon PQ of 1.25 with varying C:N ratios taken from the literature and so calculated a range of theoretical quotients based on nitrate as a nitrogen source of 1.38-1.92.

Thus it can be seen that a lower limit is set by the formation of an oxidised acid - 0.88, with NH_4^+ as a nitrogen source, whilst a higher limit would be set the use of a nitrate nitrogen source and a low C:N ratio ie 3:1 with a carbon quotient of 1.25 providing a quotient of 1.92 (Williams et al 1979). It must be noted that however the above possible scenarios are not to be expected to occur for more than a short time period. Phytoplankton are essentially protein synthesizing organisms and all other photosynthetic products constitute a small proportion of the total synthesis.

The expected theoretical limits have, however, been frequently questioned in the literature (Anderson and Sand-Jensen 1980, Gallegos et al 1983, Johnson et al 1983, Oviatt et al 1986, Megard et al 1985, Fahnensteil and Carrick 1988).

4.3.4 Factors that may influence the quotient

When comparing the relative rates of O_2 and CO_2 metabolism, there are a number of factors that will interfere with the interpretation of an observed quotient.

First, there are a number of complicating microbiologically mediated processes that may give rise to apparently anomalous ratios. Second, the two gases, oxygen and carbon dioxide may be involved in additional chemical or physiochemical reactions which confuse the interpretation of the quotient. Third, there are a number of planktonic biochemical processes which effect the flux of both oxygen and carbon dioxide, in addition to photosynthesis and respiration. Finally, there is the possibility of errors associated with the methodology and protocol used in order to calculate the quotient.

Microbial activities

There are a series of bacterial reactions (eg nitrification / denitrification, sulphur oxidation and reduction, anoxygenic photosynthesis) that will give rise to quotients quite distinct from conventionally expected algal values. However, the majority of the reactions occur in anoxic or specialised environments and as such would not be expected to have a major influence in open water marine measurements. The exception to this is nitrification which does occur in aerobic conditions, however it is inhibited by light and so is also not expected to be an important influence on planktonic photosynthetic quotient measurements (Horrigan et al 1981).

Chemical and physio-chemical processes

1) Abiotic production/consumption of oxygen

Laane et al (1985) and Gieskes and Kraay (1982) followed oxygen consumption from surface waters and concluded that observed oxygen losses were the result of photo-oxidizing processes. Laane et al (1985) recorded that 5-40% of oxygen produced was affected by photochemical reactions. Ultra-violet emission was the most effective wavelength in causing photo-oxidation with DOC apparently acting as a sensitizer for the reaction.

2) Differential Atmospheric exchange

Exchange rates in the surface layers are approximately ten times greater for O_2 than CO_2 due to a chemical buffering by the carbonate system in both seawater and freshwater.

Most measurements made in situ are corrected for the difference in the exchange rate of the two gases, failure to do so adequately would mean that the PQ and RQ being recorded is a minimum estimate.

3) Dissolution and precipitation of $CaCO_3$

Calcium carbonate precipitation or dissolution can effect CO_2 concentration and therefore the photosynthetic and respiratory quotients.

Dissolution

The saturation horizon for aragonite and calcite has been estimated as being on average 3.4 and 4.3 km respectively in the deep oceans. Although, the actual depth will vary from ocean to ocean and even region to region it can be assumed that the surface waters is supersaturated with respect to both calcite and aragonite. Hence it can be expected that dissolution has little effect on the quotient measured in marine surface waters.

Precipitation

Although supersaturated in the surface $CaCO_3$ does not precipitate out due to the action of Mg^{2+} ions which complex with approximately 70% of free CO_3^{2-} ions. The failure of $CaCO_3$ to usually precipitate out from ocean surface waters seems to be a consequence of the slow kinetics of nucleation or of nucleus growth as a result of the retarding effect exerted by the presence of certain ions (eg Mg^{2+}). Therefore it can be safely assumed that precipitation does not play a significant role in any possible causes of asynchrony in the surface waters being sampled.

4.3.5 Additional biochemical planktonic processes.

1) Diel variation in photosynthetic end-products

O_2 and CO_2 asynchrony manifesting itself in the form of an unusual range of observed quotients may be due to the possibility of significant diel variation in the photosynthetic end products (Verduin 1960).

During the photoperiod extra carbohydrates are produced in addition to protein. At high irradiances and under nutrient stress carbohydrates and lipids are produced, as the light level decreases, the carbohydrate-glutted cells resynthesise protein partially at the expense of hexose (Myers and Cramers 1948). During phosphorus limitation the cell does not produce lipids.

In general, it can be argued that measurements of carbon assimilation are more balance over 24 h as any discrepancy from the 'unbalanced' synthesis of storage products in the light is cancelled out by the inclusion of the dark period.

2) Luxury uptake and storage of HCO_3^-

Raven (1968, 1970, 1974) has provided both experimental evidence and a thorough review of other work and indicates that some algae are capable of assimilating HCO_3^-. HCO_3^- assimilation appears to be via a metabolic influx pump that operates across a cellular membrane. Raven (1970) hypothesised that the mechanism enables algae to photosynthesise at an alkaline pH.

The CO_2 would have to released before subsequent fixation by the Calvin cycle, and the release would have to well regulated so as to maintain oxygen production as light-dependent (Gallegos et al 1983).

Findenegg (1974) has shown that low CO_2 adapted cells of Scenedesmus obliquus possess a Cl^- influx pump that is absent in high CO_2 adapted cells. The uptake of Cl^- is inhibited by HCO_3^- , the presumption by Findenegg (1974) is that the pump can operate as a pump for HCO_3^- in addition.

Berry et al (1976) summarise that the key components theoretically required for a CO_2 -accumulating mechanism based on a HCO_3^- influx pump has been individually characterised in various algae, by a number of workers. However, in no single experimental system, have these observations been integrated.

If and when the uptake of HCO_3^- does occur, this will not effect determination of the photosynthetic quotient as measured. However, active accumulation of HCO_3^- in low CO_2 adapted cells (Berry et al 1976) would lower the value of the photosynthetic quotient but only if the accumulation persisted beyond the timescales involved for incubation purposes.

3) Irradiance levels

The effect of irradiance on the quotient has been frequently observed.

McAllister et al (1964) found that PQ varied with irradiance and concluded that the quotient ratios he ob tained could only be explained by the excretion of organic matter. In response to this Eppley and Sloan (1965) followed the excretion rate along with measuring the photosynthetic quotient. They concluded that the high PQ values were independent of excretion.

Anderson and Sand-Jensen (1980) found that the value of the quotients were correlated to irradiance. They concluded that this was due to an underestimation of gross photosynthesis by the 14C-$NaHCO_3$ technique as compared to the O_2 method. This underestimation was due they hypothesised to the reassimilation of respired CO_2. Reassimilation has been shown to be most important at low photosynthetic rates when the flux of CO_2 into the cell is small (Raven 1972b).

Holligan et al (1984) observed high quotients with the value of the quotient increasing with depth.

Fahnenstiel and Carrick (1988) observed quotients in the range 1.4 - 2.2 for an in vitro O_2 and 14C-$NaHCO_3$ comparison at normal light levels, compared to 2.8 - 4.9 at lower light levels.

Megard et al (1985) found carbon assimilation to be a linear function of oxygenic photosynthesis above a constant lower threshold, and below a varying maximum the rate of carbon fixation becomes independent as photoinhibition proceeds. Megard et al (1985) suggest that quotients are a variable function of irradiance and that light dependent reduction of nitrate is competing with CO_2 for the oxygenic photoreductant.

Earlier work by Syrett (1956) had noted that NO_3 and CO_2 compete for reduction under limited irradiance. Nitrate acts as an alternative acceptor for the photosynthetically produced hydrogen ions.

Van Neil et al (1953) also suggested that nitrate may act as an alternative hydrogen acceptor in photosynthesis.

Studies by Kessler (1959) and Hattori (1962) concluded that the enzymes (nitrate and nitrite reductase) for the reduction of nitrate to ammonium have higher affinities for reductant at low irradiances than the corresponding CO_2 enzymes.

The effect of irradiance, though observed in some work, has yet to explained physiologically or quantified with respect to estimation of algal quotients. However, the effect of low irradiance, if an influencing factor would be to raise the value of the photosynthetic quotient, but not effect the respiratory quotient. Photosynthetic quotients less than a theoretically calculated minimum at low irradiances are difficult to explain by this process if it exists.

4.3.6 Methodological inaccuracy and incompatibility

These errors are due to an inappropriate comparison of chemical and radiochemical derived rates

A quantitative measurement of either gross or net photosynthesis is not possible when using the ^{14}C-$NaHCO_3$ technique to follow carbon uptake. There is no way to estimate respiratory loss of organic matter, importance of photorespiration or the degree of reassimilation (see previous section for a detailed explanation).

In contrast, chemical methods provide unequivocal estimates of net community activity.

Most frequently, short incubations are employed for the radiochemical method and rates measured assumed to be gross estimates of production. If the quotient is calculated by comparison of gross rates obtained radiochemically and chemically then two possible systematic errors can be introduced.

a) Underestimation of gross production by the oxygen method

The above statement will be true if oxygen consumption in the light is greater than in the dark. Light respiration may proceed due to both dark respiratory and photorespiratory pathways. The controversy regarding the role and importance of photorespiration in production estimates is considerable. Most recent estimates of photorespiration (Bender et al 1987) suggest that in comparison to photosynthetic rates, in a healthy population, they are neglible.

b) Underestimation of gross production by the 14C-$NaHCO_3$ method

Underestimation by the method may be due to extracellular production (ECP) and / or reassimilation of respired CO_2. Reassimilation in unicellular algae is variable and can depend on the experimental situation, age and population history (Raven 1972). Algal excretion is a notoriously difficult process to quantify and has been shown to vary enormously depending on a variety of factors (Fogg 1977, Sharp 1977).

Most recent work completed in this field, regarding the interpretation of results, do agree that an underestimation is almost certainly observed (Hobson et al 1976, Dring and Jewson 1982).

Underestimation of GP either chemically or radiochemically will result in increasing the true value of the photosynthetic quotient.

The photosynthetic quotient can also be calculated through the ratio of the measurement of gross production as estimated using two chemical estimates of O_2 and CO_2. This removes the possibility of a systematic error attached to one or the other chemical method for measuring O_2 or CO_2.

4.3.7 Summary

In conclusion, a theoretical range based on biochemical considerations of photosynthetic products would be approximately from 0.88 - 1.9. In practise most algal photosynthetic end-products would provide a quotient of 1.0 - 1.3 depending on the form of combined nitrogen assimilated. Photosynthetic and respiratory quotients have been published in the literature (Anderson and Sand-Jensen 1980, Gallegos *et al* 1983, Johnson *et al* 1983, Oviatt *et al* 1986, Megard *et al* 1985, Fahnenstiel and Carrick 1988) which are difficult, if not impossible, to explain in terms of current understanding regarding biochemical stoichiometry. If these quotients do reflect true biochemical photosynthetic and respiratory processes then a major reconstruction of algal biochemistry is necessary.

There is the possibility of additional factors effecting the true value of the quotient, with potentially the most serious being methodological errors and the level of irradiance.

Errors due to methodology can be removed by the use of a combination of compatible chemical techniques which can provide unambiguous estimates of production. The effect of irradiance can be controlled by use of saturating levels of quantum flux.

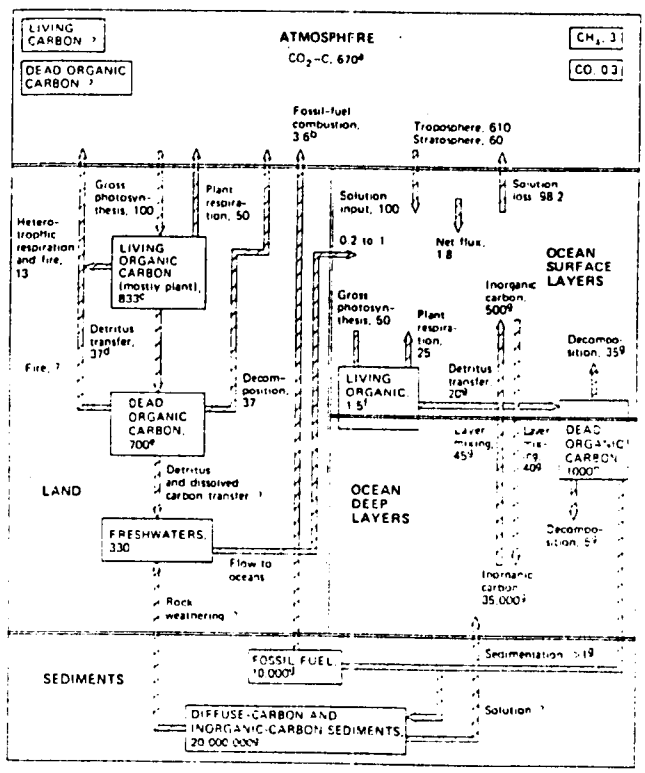
CHAPTER 5

THE CARBONATE SYSTEM IN SEAWATER

5.1 Introduction

The marine carbonate system represents the largest carbon pool in either the atmosphere, biosphere or ocean and therefore is of fundamental importance to the understanding of global biogeochemical cycles.

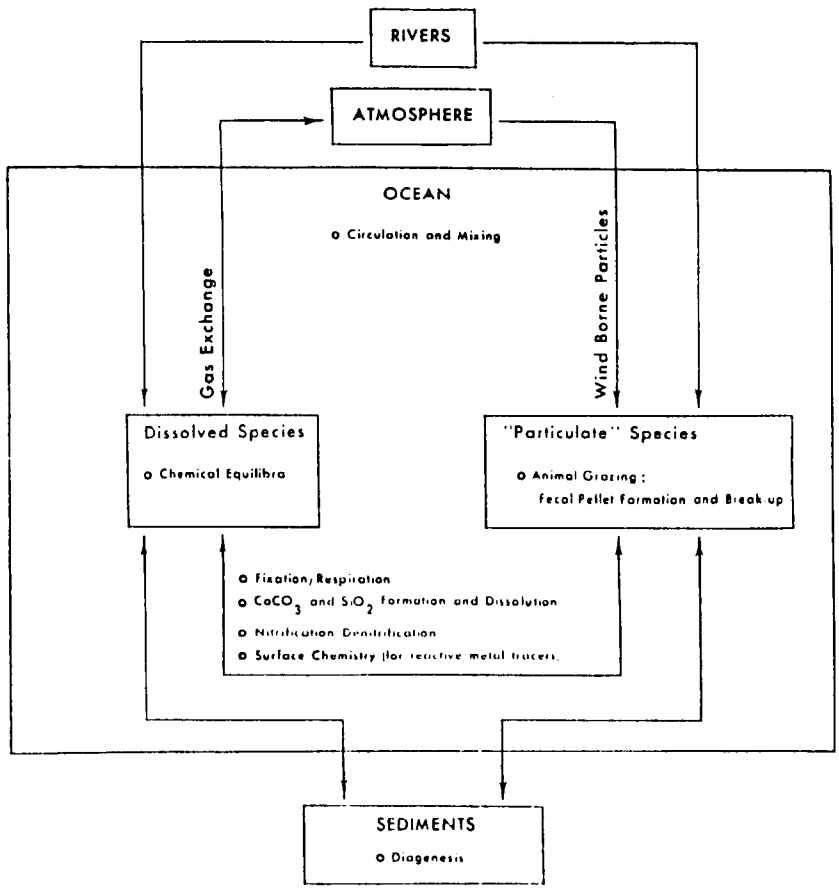
The following diagram shows the principal reservoirs and fluxes associated with the global carbon cycle (Bolin et al 1977).



Diagrammatic model of the global carbon cycle. Estimates are given where possible; sources of these estimates are given below. Question marks indicate that no estimates are available. Figures are all in billions of metric tons of carbon and are derived from estimates of Brookhaven Symposium participants unless otherwise noted. The following are alternative estimates: (a) Other estimates are 683 (SCEP, Ref. 1, page 161) and 700 x 10^9 tons (Bolin);[2] (b) SCEP, Ref. 1, page 304. (c) Bolin[2] estimates 450 x 10^9 tons. (d) Bolin[2] estimates 25 x 10^9 tons (e) Bolin,[2] based on Delwiche's[3] nitrogen estimate and a carbon/nitrogen ratio of 12, an alternative estimate is 9000 x 10^9 tons. (f) Bolin[2] estimates 10 x 10^9 tons. (g) Bolin,[2] (h) Bolin[2] estimates 3000 x 10^9 tons.

The diagram below indicates the connecting pathways and fluxes associated with the oceanic carbon system itself.

SCHEMATIC OF OCEANIC CARBON CYCLE



5.2 Global importance of the marine carbonate system

In the unpeturbed environment, CO_2 transfers across the air-sea and land-air boundaries in gigatonne amounts, with fluxes across these interfaces in approximate balance on a yearly basis.

As a consequence of the combustion of fossil fuels, and almost certainly by land use changes, man has released significant, additional amounts of CO_2, the majority of which has been injected directly into the atmosphere.

Measurements made over the last 25 yrs at the Mauna Loa Observatory (Hawaii) show clearly a steady increase in the atmospheric concentration of CO_2, at a rate of approximately 0.3 % per year, which is attributed to these anthropogenic inputs.

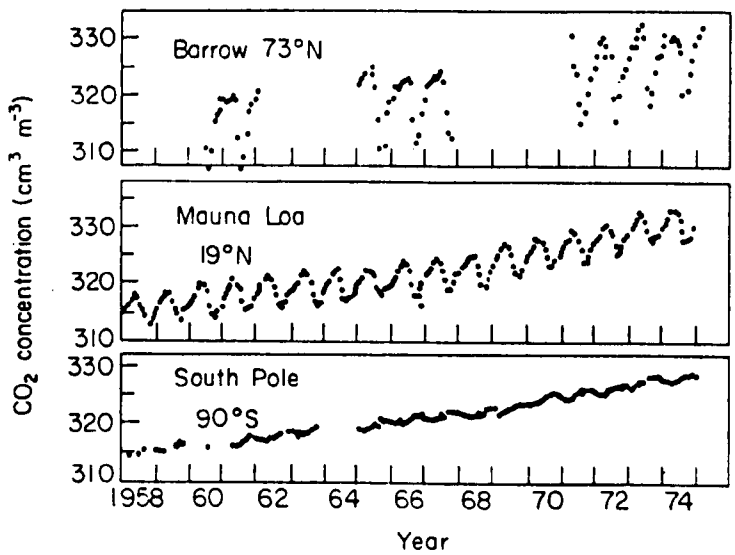


Figure 1. Monthly average atmospheric CO_2 concentrations at Point Barrow, Mauna Loa and the South Pole over the period 1958–1975 **after Brewer et al (1984)**

Carbon dioxide is one of what has become colloquially termed a 'greenhouse' gas, others include water vapour, methane, nitrous oxide and chlorofluorocarbons.

The 'greenhouse' effect is the absorption of infra-red radiation emitted by the Earth's surface following heating by solar radiation. Due to the absorption, the air once warmed re-emits heat, some of which warms the ground once more. This is the 'greenhouse' effect, the gases listed above absorb strongly in the infra-red region and so are responsible for this re-heating of the Earth's surface higher than it would normally be. This action is a natural feature of the Earth's atmosphere, however, post-industrial revolution increases in the atmospheric concentrations of these gases is calculated to be giving rise to an increasing global mean temperature.

The increased release and atmospheric concentration of CO_2 is significantly altering the balance of the carbon cycle between atmosphere, biosphere and ocean reservoirs.

It is no longer questioned that the CO_2 chemistry of the oceans is changing (NAS 1983). The annual increase in the total CO_2 content of the surface ocean waters today should be close to 1 μmol/kg (Bradshaw and Brewer 1988).

Since 1958 to the present day, the observed atmospheric increase in CO_2 approximates to half that emitted by fossil fuel combustion. Recent work has indicated an apparent discrepancy between the estimates of anthropogenic CO_2 taken up by the oceans over the last two decades (Oeschger et al 1975, Broecker et al 1979,1980, Siegenthaler 1983) and the estimates of the amounts released (Bolin 1977, Moore 1981, Houghton et al 1983). This has led to a discussion of the so-called 'missing sink'. What has emerged from this discussion is that there is a real need for comprehensive and reliable information concerning the interactions of released atmospheric CO_2 and the carbonate system in seawater. Current models are incomplete and lack a sound data base on which to develop assumptions.

It is anticipated that the oceans will become an intermediate sink for most of the excess CO_2 in the atmosphere. Broecker et al (1971) estimate that the sea will continue to remove 40 % of the 'excess' carbon and that, within 200 yrs, the acidity of seawater will reach the point at which $CaCO_3$ sediments will begin to dissolve. At that time the sea will be able to take up even larger amounts of CO_2, however the kinetics of physical, chemical and biological processes are slow and this sets a limit to the rate of uptake and in the meanwhile the atmosphere will continue to hold an 'excess' of CO_2.

Assessment of the climatic implications of this excess on both a regional and global basis requires a capability for long term monitoring of the constituents of the CO_2 system. It will be necessary to be able to model realistically and hence predict reliably the rate at which the oceans will take up 'excess' CO_2 along with the implications of such an uptake.

5.3 Anticipated Effects of rising CO_2 levels on Man

A doubling of CO_2 in the atmosphere from the pre-industrial baseline of 270 ppm is expected to produce a globally-averaged temperature rise of about 2^0 C, with larger increases in high latitudes (Crane 1985). At the same time, there will be changes in prevailing winds and in the distribution of precipitation around the globe. Middle and high latitudes of the northern hemisphere may suffer decreased soil moisture levels during the summer.

The rate of climatic change due to the temperature rise will be significant as human society has considerable ability to adapt to changing conditions.

Another effect of a rise in the mean global temperature will be a rise in sea-level. It is anticipated that a global warming of about 2^0 C will increase sea level by roughly 30 cm from current levels (Gribbin 1988).

This increase will be mainly due to the thermal expansion of water, not a melting of the ice-caps as has been popularised in the press.

Some areas of the world are likely to suffer a deterioration in climate while others may benefit. Another important aspect is whether year to year variability will change along with mean climatic state. This would have a far greater impact than a general trend in average conditions (Crane 1985). Specific forecasts of potential effects are not possible as most computer models of global climate are not advanced enough at this stage. Scientists do not have sufficient knowledge of the processes in order to predict a future CO_2 atmospheric concentration from which climate modellers could base their calculations.

5.4 Past history of CO_2 in the atmosphere

Recent analyses of CO_2 trapped in ice cores (Barnola et al 1983) are providing evidence of considerable deviations in atmospheric CO_2 levels during the last 100,000 years, which may be linked in some way to changes in climate. It would appear that far higher levels of CO_2 have existed in the atmosphere at other times without the input of mans activities. A self-regulating system of climate and biological activity, primarily in the oceans, appears to provide a natural homeostatic control on levels of CO_2. The extent to which CO_2 variation contributes as a cause or an effect of the climatic change is not possible to determine as yet. However, the evidence is that man may be pre-empting a natural cycle with unknown consequences.

James Lovelock in 1979 published a book which promoted a concept termed Gaia. This envisages that all living systems belonging to Earth are part of a total organism called Gaia, which has maintained a stable environment suitable for life for millions of years through the operation of natural feedback processes.

The concept of Gaia may be relevant to the current debate about the damage mankind may be doing to the atmospheric environment, and so likely consequences for life on earth. Whether envisaged in terms of Gaia or as an alternative natural biological feedback, it is apparent that the oceans may have previously regulated high levels of CO_2 in the atmosphere (Crane 1985).

5.5 Current status regarding the marine carbonate system

Historically, data concerning the CO_2 chemistry is scarce and often not reproducible. The main reason is the complicated nature of the system under examination. Theoretically any two of several parameters or constituents ie total carbon dioxide, partial pressure of cardon dioxide, alkalinity, pH, CO_3^{2-}, HCO_3^- may be measured in order to define the system. Modern measurements of the oceanic CO_2 system were made on the GEOSECS Atlantic Expedition (1972) and TTO N Atlantic Expedition (1981). These provide the greater part of the oceanic data set now in existence, however, the frequency and quality of the data is not really adequate.

The North Atlantic is the formation area for the North Atlantic Deep Water mass (NADW). In this area the surface water exchanges heat and its chemistry with the atmosphere, and sinks during the winter to the deep oceanic circulation. If this water carried with it significant quantities of dissolved CO_2 from the atmosphere then it may be expected to constitute a major pathway for the removal of industrial carbon dioxide. In addition, since the physical and chemical conditions of high latitude oceans are particularly sensitive to climatic changes, these oceanic areas could play a major role in the climatic-oceanic CO_2 feedback processes (Takahashi et al 1985).

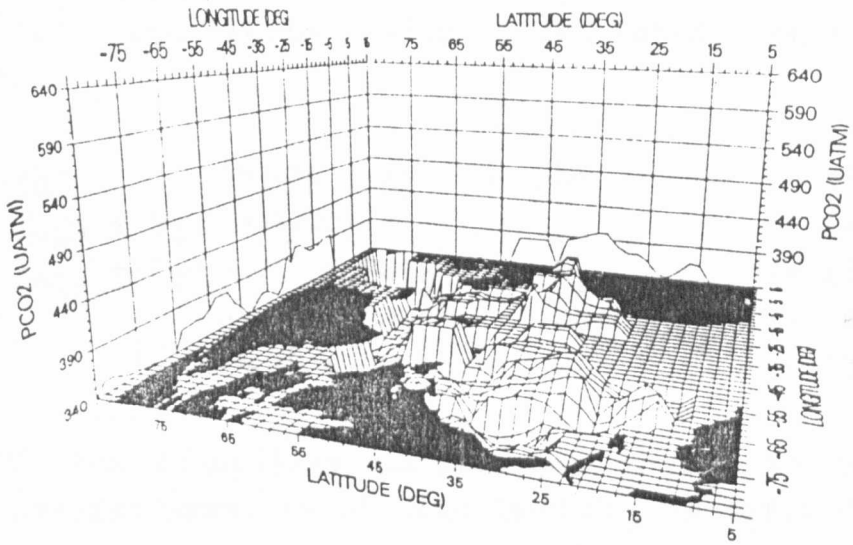


Fig. 9. Three-dimensional plot of surface pCO_2 in the North Atlantic based upon TTO data (surface, 1–15 m). A correction term for the surface excess of O_2 has been applied. The view is from the U.S.A. and from the perspective of atmospheric equilibrium.

after Brewer et al (1984)

For these reasons, the N E Atlantic has been targeted as an important region or 'end-member' of the processes involving the carbonate system in seawater. A new scientific initiative is to start in 1989, this is a series of national research programmes (USA GOFS, Global Ocean Flux Study, UK BOFS, Biochemical Ocean Flux Study), which aim to bring the latest technology and scientific thought to bear in order gain more information and understanding on the controls of the carbonate system in this vital area.

5.6 Carbonate equilibrium in seawater

5.6.1 Measurable parameters

Dissolved CO_2 in seawater can be characterised by a series of equilibria with associated equilibrium constants.

$CO_2\ (G) \rightarrow CO_2\ (AQ)$	K_0	-- (1)
$CO_2\ (AQ) + H_2O \rightarrow H_2CO_3$	K_H	-- (2)
$CO_2\ (AQ) + H_2O \rightarrow H^+ + HCO_3^-$	K_1	-- (3)
$HCO_3^- \rightarrow H^+ + CO_3^{2-}$	K_2	-- (4)
$H_2O \rightarrow H^+ + OH^-$	K_W	-- (5)

K_0 is the solubility coefficient of CO_2 in seawater and the partial pressure of dissolved CO_2 is defined as -

$$pCO_2 = [CO_2\ (AQ)] \ / \ K_0$$

where square brackets denotes concentration.

Most undissociated dissolved gas is in the form of $CO_{2(AQ)}$ and not H_2CO_3. Conventionally, K_H is set to 1 and so $CO_2\ (AQ)$ and H_2CO_3 are considered as one species (hydrate convention Lewis and Randall 1961, UNESCO 1987).

K_1 and K_2 are the first and second mixed equilibrium constants of carbonic acid -

$$K_1 = a_{H+}\ [HCO_3^-] \ / \ [CO_2]$$

$$K_2 = a_{H^+}\ [CO_3^{2-}] \ / \ [HCO_3^-]$$

the activity of water is taken to be 1

Square brackets denote concentrations and a_{H+} is the activity of the hydrogen ion, the value of which depends on which particular pH scale is used along with associated conventions (pH scales are discussed in greater detail in section 5.7.2).

The alkalinity (total or titration - TA) of seawater is defined as the acid neutralizing capacity or proton deficiency.

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [SiO(OH)_3^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4]$$

In calculations of the carbonate equilibria only the carbon dioxide contributions to the TA are considered, defined as the carbonate alkalinity (CA).

$$CA = [HCO_3^-] + 2[CO_3^{2-}]$$

The carbonate alkalinity is calculated by correcting the TA for the contributions of $[B(OH)_4^-] + [OH^-] + [H^+]$, usually the other contributions are ignored as they are negligible.

Total carbon dioxide (TCO_2) is defined as the sum of all forms of inorganic carbon in seawater.

$$TCO_2 = [HCO_3^-] + [CO_3^{2-}] + [CO_{2\ (AQ)}]$$

Finally, the remaining variable used to characterise the carbonate system is pH. this can be defined as -

$pH = -\log a_{H+}$ where the value of a_{H+} is set by the pH scale used to define it.

pH is the so called 'master' variable of the carbonate system in seawater. It controls the acid-base equilibrium in seawater and is therefore responsible for the buffering capacity of the oceans in the long term. On a larger time scale, geologically speaking, additional buffering is controlled by the action of the sediments and rock.

Theoretically any two of the four system properties (pH, pCO_2, CA, TCO_2) may be combined along with appropriate thermodynamic relationships to provide the remaining. The redundancy implied by measurement of three or four variables permits checks to be made on the internal consistency and validity of data of the carbonate chemistry in seawater (Brewer et al 1984, Bradshaw and Brewer 1988, 1988)

5.7 History of measurements of the carbonate system

Historically, accurate measurements of the carbonate system in seawater have been difficult to achieve. Measurements date back to the early 1930s (Wattenburg 1933), however the data is scarce and not generally reproducible or verifiable.

5.7.1 Alkalinity

Gripenberg (1937) and Greenberg et al (1932) both estimated alkalinity by treating the sample with a measured excess of strong acid, driving off the liberated CO_2, and back-titrating the sample to a pH of 6-7 (at which boric acid is negligibly ionised).

A more rapid method was first documented by Thompson and Anderson (1940) based on a single pH determination. This was later modified (West and Robinson 1941, Anderson and Robinson 1946, Bruneau et al 1953 and Culberson 1980). Precision has been published as 0.4% (Culberson et al 1970).

A potentiometric titration method was originally described by Gran (1952). Development was due to the work of Dryssen (1965) and Dryssen and Sillen (1967). Edmond and Gieskes (1970) and Takahashi et al (1970) subsequently used this procedure on the GEOSECS expedition (1969).

Hansson and Jagner (1973) described an improved procedure based on the use of Gran plots to describe the titration curve. This approach was used on the TTO expedition (1981) by Brewer et al (1984), overall precision was published as 0.1% (Bradshaw and Brewer 1988).

A photometric titration method was described by Graneli and Anfalt (1977) and adapted to shipboard use by Anderson (1981), precision published as 0.1 % .

Grasshoff (1981) compares the precision and limitations associated with all the 4 approaches and concludes that the need for high precision requires the use of potentiometric and photometric titrations. These are slow to perform manually but can be speeded up considerably with the use of computers and automation.

5.7.2 pH

pH is now almost exclusively determined by means of ion-specific electrodes (glass electrodes). Prior to this pH was measured by means of colour indicators, however this was not very sensitive and the application of a considerable salt error was necessary before any real accuracy could be achieved (Grasshoff 1981).

Most sources of error in the determination of pH in seawater result from an improper understanding of the fundamental principles of the pH concept and instrumentation used. pH is defined as the negative logarithm of the activity of hydrogen ions. Another view is to see it as a potential of a cell to shift the acid-base equilibria. Hence measurements of EMF (electromotive force) are used to obtain pH readings.

Cell potential - electromotive force

In order to relate the electrochemical energy associated with a cell to various thermodynamic parameters, the cell must behave reversibly. In truth cells never behave reversibly, however the assumption is still used.

The potential of a reversible electrode to the general half cell reaction

$$M \leftrightarrow M^{N+} + ne^-$$

is given by

$$E_M = E_M^0 + (RT/nF) \ln a_{MN+}$$

Where E_M^0 is the standard potential of the electrode and a_{MN+} is the activity of M^{N+} in solution. The activity can be expressed in terms of concentration by use of a single activity coefficient (γ).

$$a_M = [M^{N+}] \times \gamma_{MN+}$$

In reality, the half-cell reaction does not occur in isolation but is paired, an example of which is the following

$$Pt/H_{2(G)} \; / \; H^+_{(AQ)}Cl^-_{(AQ)} \; / \; AgCl_{(S)}/Ag_{(S)}$$

H_2 electrode / determine pH / reference electrode

$$H_2 + AgCl_2 \quad Ag + 2H^+ + 2Cl^-$$

As previously shown,

$$E_{HCL} = E_{HCL}^0 + RT/F \ln (a_{H+} \cdot a_{CL-})$$

By adopting certain conventions a single ion activity is given to a_{CL-} and hence then a_{H+} can be estimated and thus pH as,

$$pH = - \log a_{H+}$$

Activity is a thermodynamic function and it is necessary to assume more conventions in order to be able to define pH in terms of concentration, which we can then measure. There are two main approaches:

1) Infinite dilution scale

If we adopt an infinite dilution scale as a reference scale for the activity of chloride ions then -

$$\gamma_{CL-} \rightarrow 1 \text{ as } [Cl^-] \rightarrow 0$$

therefore

$$a_{H+} = [H^+] \text{ at infinite dilution}$$

therefore

$$pH = [H^+]$$

The infinite dilution scale has several drawbacks when used in seawater. Cations and anions in solution experience mutual electrostatic attraction and repulsion due to their ionic charges. These will be non-existent in very dilute solutions when the ions are widely separated in space. However, in seawater due to the ionic strength, the effect cannot be ignored. The overall effect is to decrease the availability of ionic species that are free to react as the ionic strength increases. Hence the effective concentration is less than the true concentration. For this reason use of the infinite dilution scale in order to ignore the calculation of single activity coefficents is not rigorously correct. Activity does not become equivalent to concentration, rather 'effective' concentration. The two are related by the activity coefficient which depends on ionic charge and sample composition.

2) Use a non-thermodynamic approximation ie the Guggenheim approximation

$$CL^- = \frac{-A.z^2.\sqrt{I}}{1 + 1.5\sqrt{I}}$$

I = ionic strength
A = constant
z = charge on the ion

The Guggenheim's approximation is only suitable for solutions of low ionic strength ie less than or equal to 0.1M, so not suitable for seawater. The approximation is based on the Debye-Huckel limiting Law which is empirically based and so no reason to consider it thermodynamically sound. An alternative approximation, Davies (Stumm and Morgan 1981), can be used for solutions up to and including 0.5M, however it is based on a single electrolyte in solution, again not suitable for seawater.

pH electrodes

A thorough description of the types of electrode available for pH measurement can be found in Culberson (1981) along with sampling procedure. The standard pH reference electrode is the hydrogen electrode. However, due to sensitivity it is impractical to use in most field measurements of seawater. This has generated one of the most serious problems associated with pH measurements in seawater: that of the reference electrode. The electrode (usually glass or calomel) contains a liquid / liquid phase junction.

As previously stated -

$$E_{H+} = E_{H+}^0 + RT/F \ln (a_{H+})$$

A more correct representation is -

$$E = (E_{H+}^0 + E_R + E_J) + RT/F \ln (a_{H+})$$

Whereas the standard (E_{H+}^0) and residual (E_R) potentials can be defined, the liquid junction potential (E_J) varies in an unpredictable manner and so makes total accurate determination impossible.

The value of E_J depends on -

1) The difference in ionic strength between sample and electrode solution.
2) Permeability of the junction.
3) Type of ions in solution.
4) Temperature and pressure.

The value of E_J needs to be kept constant in order to allow comparisons between different measurements, in response to this, Hansson (1973) defined a new pH scale, based on the use of artificial seawater buffers and on an ionic medium scale for the conventions associated with activity measurements (based on the work by Sillen 1967, Dryssen and Sillen 1967).

Ionic Medium Scale

The ionic medium scale defines

$$\gamma_{H+} \rightarrow 1 \qquad \text{as} \qquad [H^+] \rightarrow 0$$

for a constant value of I (ionic strength). Use of this scale removes the need for determination of single activity coefficients and non-thermodynamic Debye-Huckel type approximations. There have been two approaches to the measurement of pH based on the ionic medium scale.

A) Total Hydrogen Ion pH scale

Hansson (1973) defined a total hydrogen ion pH scale where total concentrations of hydrogen ions ($[H^+]^T$) were equal to the sum of all free hydrogen ions ($[H^+]^F$) and any complexes

$$[H^+]^T = [H^+]^F + [H^+](\text{complexes})$$

This approach assumes that the ratio $[H^+]^T$ / $[H^+]^F$ remains constant over the range of conditions considered. This is certainly true for acids and bases present in SW at low concentrations (Pytkowicz and Hawley 1974). At high acidity $[H^+]^T$ is no longer proportional to $[H^+]^F$ and it is necessary to allow explicitly for the formation of species such as HSO_4^- and HF (Hansson and Jagner 1973).

This scale is thermodynamically sound and as the sample and buffer are nearly identical in composition, inconsistent errors in the liquid junction potential are removed. However due to use of the ionic medium scale, Hansson buffers are extremely sensitive to changes in temperature and salinity and a range of buffers have to be used for differing salinities.

B) 'Free' Hydrogen Ion concentration scale

A more rigorous approach is to use a 'free' scale and include the formation of bisulphate and HF (Bates 1975, Bates and Macaskill 1975, Bates and Culberson 1977, Khoo et al 1977).

$$pH_F = - \log [H^+]_F$$

As yet, there are no acidity constants determined using a 'free' hydrogen scale for evaluating titration data in SW. Dickson (1984) in a comparison of pH scales recommended use of the 'free' hydrogen scale in preference to total hydrogen. Dickson concludes that this scale is conceptually clearer and so should be employed.

In conclusion, more than 10 years have passed since Hansson (1973) and Bates (1975) introduced the concept of the ionic medium scale for defining both pH and the carbonate system. Nevertheless, most workers still use NBS buffer scales, based on the convention of infinite dilution.

The various approaches discussed above are still the subject of considerable debate (Culberson 1981, Dickson 1984, Whitfield et al 1985 and Millero 1986). Culberson (1981) concluded that the most profitable approach would be to design a reproducible liquid junction than adopt either of the ionic medium scales, especially in estuarine waters when the ionic strength is not known prior to sampling. This is reinforced by Whitfield et al (1985), who describe the use of a free diffusion liquid junction for use in an estuarine situation.

Dickson (1984) and UNESCO (1987) both recommend the use of the Hansson and Bates approach. UNESCO (1987) propose the adoption of the new dissociation constants for carbonic acid in seawater computed by Dickson and Millero (1987) derived from the data of Hansson (1973) and Mehrbach et al (1973) after adjustment to a common scale. They note that the recommended constants are based on the ionic medium scale and it is therefore necessary to adopt this scale in measuring pH.

5.7.3 pCO_2

The partial pressure of carbon dioxide in the aqueous phase is defined as the relative concentration of dissolved CO_2 gas in the water relative to that in the atmosphere.

Determination of pCO_2 is particularly useful in the study of both biological processes and atmospheric exchange. The parameter is involved with most biological activity and directly involved with air-sea exchange.

The pH glass electrode can be used to record partial pressures of gases which hydrolyse in water to give acidic or basic reactions ie CO_2 or ammonium. The glass electrode suitably adapted (Whitfield 1975) provides a pH measurement which is proportional to the pCO_2. Whitfield (1975), claims a precision of 10-20 % which is an order of magnitude less than gasometric procedures.

Hence not adequate for measurements of the carbonate equilibria in seawater. In addition, the probe is sensitive to stirring as a diffusion equilibrium has to be set up across the membrane.

An alternative approach is by simply determining the CO_2 content of a bubble of air shaken into equilibrium with the sample (Krogh 1910, Buch 1939a,b). More recently, methods make use of infra-red (IR) analysis of air which has been equilibrated with the sample in a carrier gas of nitrogen, at a known temperature and pressure. A description and evaluation of data collected by this method are described by Kanwisher (1960), Takahashi (1961), Keeling, Rakestraw and Waterman (1965), Broecker and Takahashi (1966), Teal and Kanwisher (1966), Keeling and Waterman (1968), Li et al (1969), Takahashi et al (1970) and Codispoti et al (1982).

Copin-Montegut (1985) describes an IR method for continuous measurement of pCO_2. In this approach complete equilibrium is not possible due to the mean residence time in the equilibrator, so a correction is used to facilitate this rapid, continual profiling.

Two different types of equilibrator were used on the GEOSECS intercalibration cruise (Takahashi et al 1970). One as described by Broecker and Takahashi (1966) for continuous measurement in surface waters, another for discrete, deep water samples (Li et al 1969). An overall precision for GEOSECS IR pCO_2 measurements was quoted at +/- 2.0 % (Takahashi et al 1970).

A more recent development has been the use of a gas chromatographic system (GC) to measure the air equilibrated at a known temperature and pressure and carried by hydrogen (Weiss 1981). This method was used during the 1981 TTO N.Atlantic programme and has been quoted as having a precision of 0.04% (Weiss 1981).

The GC pCO_2 method is comparable to the best measurements possible on an IR pCO_2 approach also it has distinct advantages in that it utilizes much smaller samples, calibrates much quicker and finally the response for CO_2 is essentially independent of gross composition so no corrections are needed analogous to the pressure broadening correction that is required by the presence of oxygen in the IR analyser (Weiss 1982).

5.7.4 Total Carbon Dioxide

Total carbon dioxide (TCO_2) is defined as the summation of all forms of inorganic carbon in seawater including that present as dissolved CO_2.

The analytical chemist has used a wide variety of methods in order to calculate TCO_2, both direct and indirect.

Direct Evaluation

Traditionally, classical gravimetric and volumetric methods have been used and although somewhat tedious they have the advantage of being based on theoretical considerations rather than empirical calibrations.

Antia et al (1963), Strickland and Parsons (1972) claim a precision of 0.3% for measurement with a modified van Slyke apparatus. Another approach has been that of gas chromatography. Curl and Davey (1967) published data with a precision of 1.0 % using GC analysis. Weiss and Craig (1973) using a ship-borne apparatus obtained a precision of 0.3 % . Recently, Weiss has further improved the technique and using flame-ionisation and GC analysis can produce data with a quite remarkable precision of 0.04 %

Broecker and Takahashi (1966) following a different approach used infra-red analysis to measure TCO_2. Wong (1970) obtained a precision of 0.15 % Other advocates of this technique (Johnson et al 1981, 1983a) claim a ship-borne precision of 0.4-0.8 %

A recent development has been the introduction of coulometry to the measurement of TCO_2 (Johnson et al 1985, 1987). Coulometric analysis relies on the electron as the primary standard and so difficult standardisation techniques are not necessary. The coulometric approach is well-suited to automation and with a precision of 0.05 % which is comparable to the best in GC analysis (Johnson et al 1987).

Indirect Evaluation

Indirect calculation of TCO_2 is possible using a potentiometric or photometric titration (Anderson 1981). The accuracy of this approach must depend on the suitability of the acid-base model of seawater chemistry used. Dickson and Riley (1978), Bradshaw and Brewer (1988) quote a precision of 0.2 % in determining TCO_2 titrimetrically.

The current, purely inorganic model has been recently questioned (Bradshaw and Brewer 1988,1988) and the validity of this traditional approach must now be in doubt. Bradshaw and Brewer (1988), in comparative measurements of TCO_2 by gas extraction (manometry, coulometry) versus titrimetric data on natural seawater yielded discrepancies of up to 21 μmol CO_2 / kg with the difference decreasing with depth. The perturbation of the buffer system in freshwater by organic acids is well known (Herczeg et al 1985). Bradshaw and Brewer (1988) hypothesize that the discrepancy is due to the presence of organic acids masquerading as CO_2 in the titration procedure. This would require far greater dissolved organic carbon (DOC) levels than currently measured (0.6 - 2.0 mg C / l, Williams 1975) in the surface waters (ie < 100m).

Recently, a novel technique for measuring DOC in seawater has been published by Sugimura and Suzuki (1988). This is a high temperature catalytic oxidation method using direct injection of seawater.

The authors claim that this method measures four times as much DOC in the surface waters and twice as much in deep waters as with traditional methods.

The highest priority is now apparent to make concurrent measurements of the carbonate system, both titrimetrically, manometrically and using the "new" DOC method. If DOC is identified as the 'missing' organic acids then all previous data regarding the carbonate system must be placed in doubt. These measurements being made currently will provide the benchmark for future marine chemists regarding the carbonate system in seawater.

5.8 Summary

The need for comprehensive data concerning the carbonate system is vital in order to aid modellers to predict the fate of excess fossil fuel in the atmosphere. The complexities of the carbonate system and the difficulties in measuring the necessary parameters has been reviewed. A major challenge exists to marine chemists in the observation of changes, and the prediction of their consequences, for the anthropogenic change is small relative to the large natural abundance of CO_2 in seawater. The annual anthropogenic change is about 1 μmole/kg TCO_2. The actual variability recorded globally is roughly 2300 - 2500 μmoles/kg, hence, a sensitivity of around 0.05 % is required to follow the signal.

Analytical errors (Takahashi et al 1970) and possible discrepancies in the current assumptions regarding the carbonate system in seawater (Bradshaw and Brewer 1988) make it highly desirable to overdetermine and define the carbonate system by measuring at least three variables simultaneously.

Measurements of the system are especially important in the area of the N.E.Atlantic, which is regarded as a sink for current 'excess' CO_2 levels in the atmosphere (Takahashi *et al* 1985), and as such seen as a vital end-member for any discussion regarding the role of the oceans as a sink for atmospheric CO_2.

CHAPTER 6

METHOD

6.1 Instrumentation: Determination of TCO_2

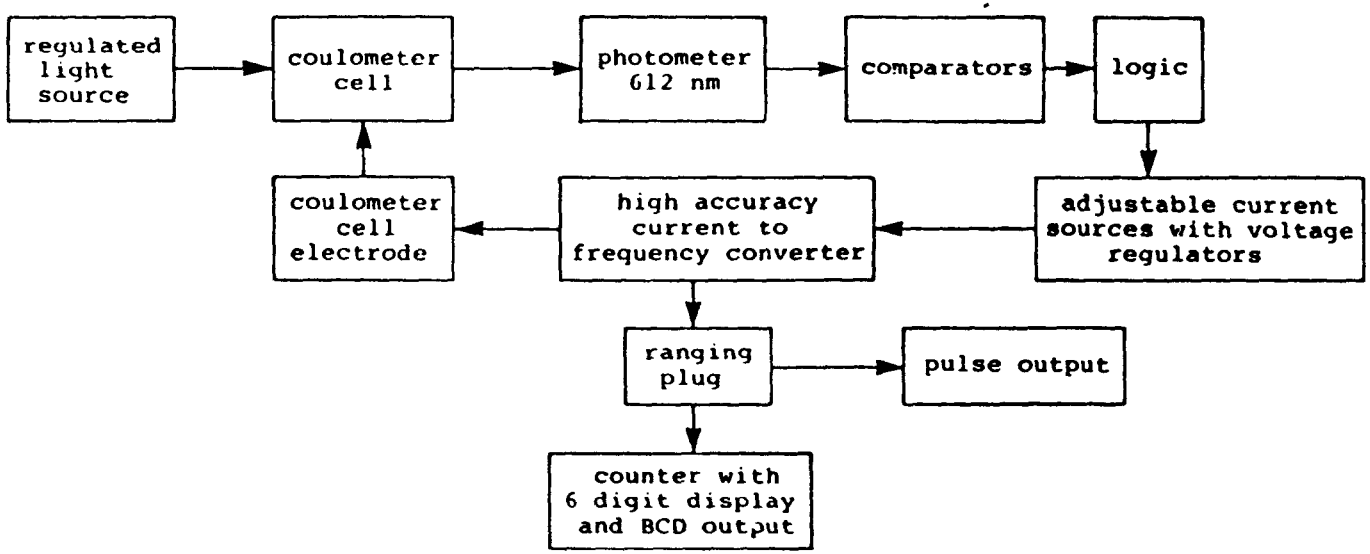
The coulometric back-titration method for determining TCO_2 in seawater used during this study is based on the pioneering work of Johnson et al (1985, 1987). The coulometric determination of CO_2 is a standard method (ASTM Publication D 513-82) and has been adapted for determination of TCO_2 in marine waters by Johnson et al (1985). Subsequent to the description given by Johnson et al (1987) (where the system is described as UG-I in order to differentiate from an earlier system), several modifications have been made to both the software, hardware and sampling protocol.

6.1.1 Coulometric determination

The coulometric titration is based on Faradays Laws and was originally invented by Szebelledy and Somogyi (1938) with descriptions of the technique given by Lingane (1958), Boniface and Jenkins (1971), Sawyer and Roberts (1974), Skoog and West (1976) and Huffman (1977).

Carbon dioxide is detected using a Coulometric Inc. (Golden, CO, USA) coulometer, model 5010. A block diagram of the coulometer system is given (Figure 6.1). The coulometer cell and all reagents are supplied by Coulometrics Inc.

Figure 6.1



Block diagram of coulometer system.

after Coulometric Inc., Manual for the Coulometer Model 5010

In coulometry, the number of coulombs of electrons required to convert all of a chemical species to a different one is measured. Faradays Laws relates the coulombs of electricity to equivalents of titrant generated and so to CO_2 determined. The reaction of CO_2 and ethanolamine produces a weak acid ; hydroxy-ethylcarbamic acid. This acid is titrated by a base with OH^- ions generated by the reduction of H_2O at a platinum cathode. The equivalence point is detected photometrically with thymolphthalein as an indicator. The following equations summarise the electrochemical processes taking place in the cell (after Johnson et al 1985).

Neutralisation

$$2CO_2 + 2NH_2(CH_2)_2OH \Rightarrow 2HO(CH_2)_2NHCOOH$$

$$2HO(CH_2)_2NHCOOH + OH^- \Rightarrow 2HOH + 2HO(CH_2)_2NHCOO^-$$

Oxidation-reduction

$$2Ag^o(s) \Rightarrow 2Ag^+ + 2e^- \qquad \text{(anode)}$$

$$2HOH + 2e^- \Rightarrow H_2 + 2OH^- \qquad \text{(cathode)}$$

Complexation

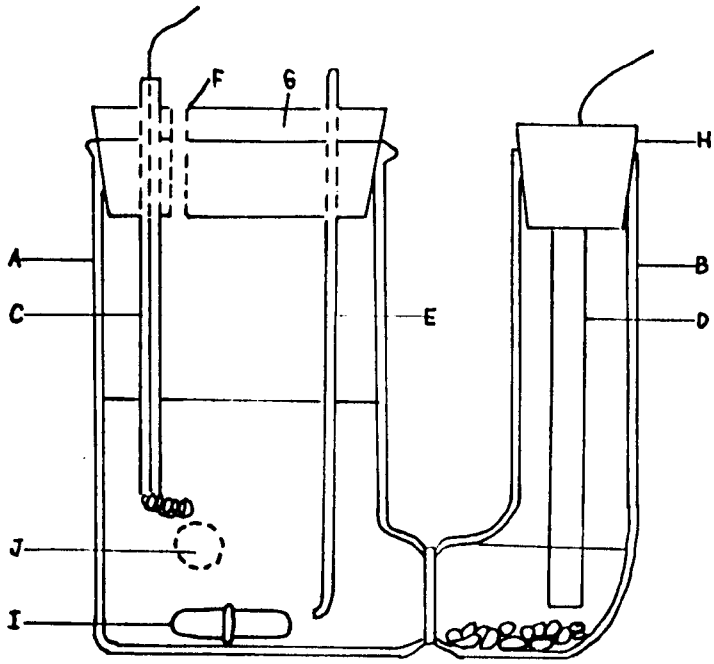
$$2Ag^+ + 4I^- \text{ (saturated KI)} \Rightarrow 2AgI_2^- \qquad \text{(anode)}$$

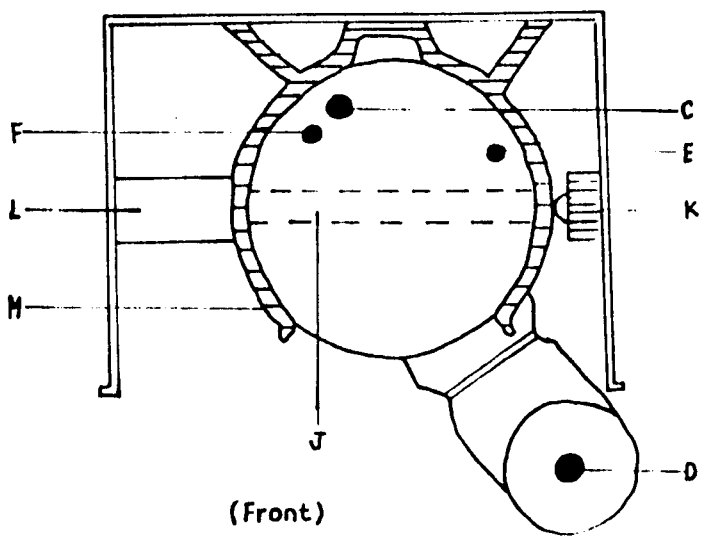
Net reaction

$$Ag^o + 2I^- + CO_2 + NH_2(CH_2)_2OH \Rightarrow AgI_2^- + \tfrac{1}{2}H_2 + HO(CH_2)_2NHCOO^-$$

To be quantitative the reduction of water must occur without the involvement of other chemical species and each faraday of electricity must bring about a chemical change corresponding to one equivalent of the analyte.

A diagram of the cell, front and top view is given below (Figure 6.2 taken from the Coulometrics Inc. manual for the Model 5010)





A. Cell Body

B. Cell Anode Compartment (side arm)

C. Platinum Electrode

D. Silver Electrode

E. Gas Inlet Tube

F. Gas Exit (Vent)

G. Cell Top

H. Anode Top

I. Stir Bar

J. Light Path

K. Light Source

L. Detector

M. Cell Holder

The cell solution used for a coulometric determination is clear initially with an excess of CO_2 being present and then turns deep blue as the CO_2 is titrated and an end-point is reached. The coulometer titrates at a maximum rate of about 750 μg C / min. The coulometer includes anticipatory circuitry to switch the coulometric current from high to low to off as the end-point is reached. Coulometrics Inc. claims that the detection limit is 0.01 μg C. The digital readout is from 0.00 through to 9999.99 micrograms of carbon. Accuracy is quoted as being 0.1 % for samples containing over 1 mg of carbon (3.7 mg CO_2). Coulometric Inc. suggest that cell solutions are changed daily and replaced if over 100 mg of carbon have been titrated.

In practice, the maximum single operating period for one operator, meant that total carbon titrated rarely exceeded 45 mg of carbon for a single filling of the cell with the solutions. Johnson et al (1987) suggest that the maximum limit to one cell solution should be 25 mg C titrated, however totals greater than this were frequently reached and did not appear to affect precision and so within the limits set by Coulometrics Inc. cell solutions were changed only when the machine was to be switched off. Cell solutions could not be kept and re-used adequately, this caused a deposit to be formed on the platinum cathode which then prevented reasonable titrations.

Johnson et al (1987) suggested that an improved precision was obtained by filling the cell with the solutions and leaving to stand overnight, however I failed to confirm this and so this procedure was not adopted for the majority of the titrations. Johnson et al (1987) gave detailed instructions on cleaning the cell and frit after extended use. In addition, a black deposit was observed to collect on the frit over time.

This was found to be a residue of silver and could be removed by dissolving in aqua regia.

6.1.2 Computer control

The microprocessor used during the study is a Hewlett-Packard (HP 86) with monitor, disc drive and printer. The controlling programme is in BASIC and was considerably modified from the original as described by Johnson et al (1987). The modifications consisted mainly of rationalisation and the introduction of user friendly, interactive command procedures along with a series of safeguards in order to prevent incorrect use by an inexperienced operator. The changes to the programme were carried out in conjunction with a fellow post-graduate student, Mr. O. Calvario-Martinez.

The programme controls the sampling sequence, displays information regarding the analysis, reads the coulometer, records the measurements, determines the end-point, completes the calculations and provides statistical analysis of the data.

An on-line power conditioner was routinely used for both the computer and coulometer during ship board measurements.

6.1.3 Gas sampling unit

The original polycarbonate container was used along with the basic arrangement of valves and glassware as described by Johnson et al (1987) for UG-I. Figure 6.3 is a diagrammatic representation of the sampling system along with modifications from the previous diagram of Johnson et al (1987). Changes introduced during the period of this study have been marked with a star for reference.

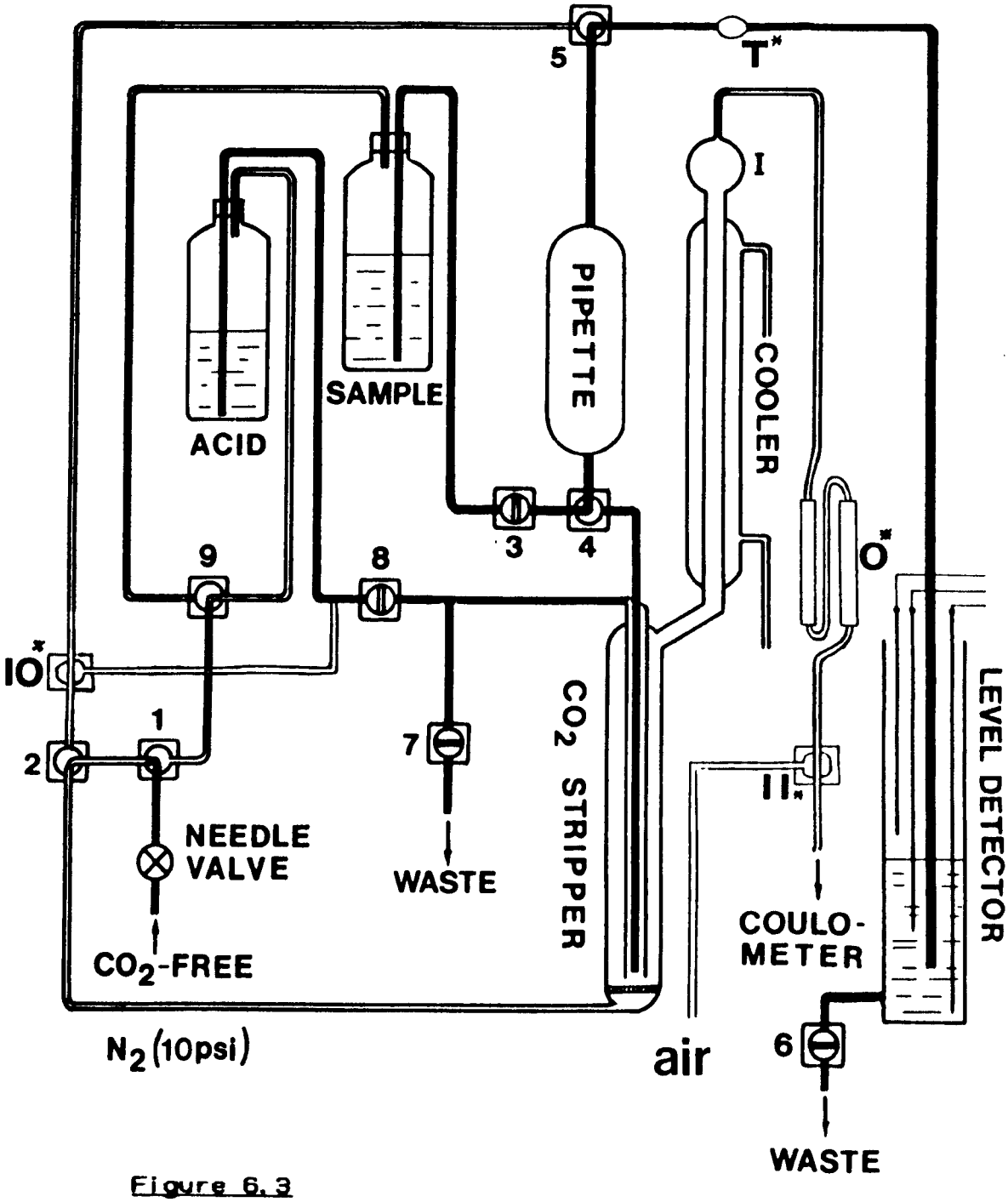

5
T*
I
PIPETTE
COOLER
SAMPLE
ACID
3
4
9
8
O*
IO*
1
2
7
CO2 STRIPPER
LEVEL DETECTOR
II*
NEEDLE VALVE
WASTE
COULO-METER
CO2-FREE
N2 (10psi)
air
6
WASTE

Figure 6.3

Changes introduced

1) The stainless steel 3-way valve (valve 11) replaced a previous check value that exerted an constant back pressure on the system. The back pressure allowed the stripper to be drained at the end of a titration. This valve failed on several occasions and so was replaced by a valve that was intermittently switched on prior to draining, so reducing the wear on the valve. The stainless steel three way value served a dual purpose in that the other inlet port was used to facilitate the passage of air from the air pump to the coulometer cell (see below).

2) Air Pump - a modified air pump, the kind commonly used in a small aquarium, was introduced into the system for two purposes. First, the air flow was occasionally used to push samples around the system, in place of the usual O_2 free nitrogen carrier gas. Second, the air was slowly bubbled into the cell so that the cell could be left for long periods without attendance, this prevented formation of a deposit that occasionally would coat the cathode.

3) Thermistor (T) - an in-line thermistor was placed in the out flow from the pipette and prior to filling the level sensor. The thermistor was interfaced into the computer and allowed the temperature to be recorded automatically, replacing the manual entry as described by Johnson et al (1987).

4) Level sensing electrodes - these electrodes were replaced with rhodium plated probes in order to reduce corrosion on the probes.

5) Acid addition - an extra glass inlet was attached to the tubing in advance of the acid inlet. The new inlet was attached to the carrier gas flow (via stainless steel valve 10) and facilitated the addition of acid into the extractor by purging the acid added along the tube and down into the extractor.

5) Repositioning of the solenoid and stainless valves - the general design, though not analytical sequence, was considerably altered for convenience and safety reasons. The new centre board was machined in order to place all solenoid valves at right angles through the section. The level sensor was repositioned in the front of the polycarbonate container, along with the acid bottle. This meant that all of the 'wet' side of the sampling sequence was on the front part of the container, whilst all the wiring and electronics, and gas handling is to the rear.

6) Sample pipette - a new pipette was installed and insulated against temperature changes. Glass tubing was introduced to the top and bottom of the pipette replacing previous silicone tubing, the intention being to increase the delivery precision of the pipette. The pipette was recalibrated as described by Johnson et al (1987).

7) Tubing - all teflon tubing used within the system was replaced by stainless steel tubing to minimise the contamination of the gas-line with atmospheric CO_2 .

8) Orbo tubes (marked on diagram as O) - the Orbo trap referred to in Johnson et al (1987) of dry Orbo-53 silica gel was introduced to prevent any possible acid mists interfering and entering the coulometer cell. Frequently, the tube became contaminated with water vapour and prevented a free flow of the carrier gas and also appeared to affect the coulometric titration.

Hence the single tube was modified to include a double set of Orbo tubes. This allowed one tube to fail whilst the other could continue to function.

6.1.4 Channel controller

The original custom-made 16 channel controller as described by Johnson et al (1987) was extensively rewired and a transformer inserted in order to allow the 110v solenoid and stainless steel valves to be connected to the 240v power suppply. A dedicated channel was given over to switching on power to the transformer before any of the valves could be operated. Another channel functioned as a switch and turned on the power to the air pump, following a command from the programme.

6.1.5 Calibration Unit

The original unit as described by Johnson et al (1987) was substantially rebuilt and reorganised. A Digitron model 1804 hand held temperature probe attached to a platinum resistance probe was used to record the temperature within an insulated block holding the loop connected to the Vici GC valve. Atmospheric pressure was recorded using a Druck Digital Barometer (Model DPI-250) calibrated against a mercury reference barometer by Druck Ltd (Croby, Leics, England). A functional wooden box was used to hold the reference gas cylinder, valves and wiring, with a front panel providing easy access to the gas cylinder, regulator and temperature readout. The unit provided a relative calibration, useful for checking the system for leaks and potential faults. The system did not provide an absolute calibration.

6.1.6 System blanks

A so termed 'blank' value is routinely obtained from the coulometer even though no titration is occurring. This 'blank' is presumed to proceed at a similar rate during a titration. A thorough description of the blank and potential causes are discussed in Johnson et al (1985). In agreement with previous findings the blank appears to be an integral function of the cell and associated solutions. There is a tendency for the blank to decrease during the process of titrating and so needs to be re-evaluated periodically. Johnson et al (1985) states that the source of the blank is not known but is seldom from CO_2 infiltration from the gas handling apparatus or the failure to scrub CO_2 from the carrier gas. Most probably it is due to a dirty frit (Johnson, pers.comm.), however, extensive cleaning and drying of a cell prior to use does not consistently reduce the value of the blank. Even with these considerable precautions the value of the blank can be somewhat erratic and seldom predictable.

A series of measurements were made in order to follow the progression of the blank with time. The signal was recorded whilst the cell was attached to the gas sampling unit. The carrier gas was bubbled through a small amount of the phosphoric acid remaining in the bottom of the extractor (Figure 6.3), through the cooling column, dryer and Orbo tubes and finally to the cell. The programme was altered so that the coulometer was read every second, when a rise in titrated carbon was noted, the quantity was recorded along with the time it occurred. The time taken along with the addition is recorded in a series of plots, which are given in Chapter 10.

6.2 Instrumentation: Determination of dissolved oxygen

All oxygen determinations carried out during this study were based on the Winkler method, using the automated photometric titration as described by Williams and Jenkinson (1982) and subsequently modified by Williams (pers. comm.). No modifications were made to the instrumentation. The reagents and procedure used followed closely the recommendations of Carritt and Carpenter (1966), Williams and Jenkinson (1982).

6.3 General sampling and analysis procedure: Mesocosm

All water samples analysed during both mesocosm experiments were initially obtained using a 10 dm^3 General Oceanics Niskin water sampler. A small part of the bottle was machined out and a watertight perspex window fitted in order to enable to follow the water level in the sampler as it drained. The water bottle was lowered on a line suspended above the centre of the raft, using a block and tackle at the apex of an A-frame aluminium ladder at the Swedish mesocosm or from a gantry over the Loch Ewe bag. The line was marked at 1 m intervals enabling discrete sampling at nominated depths.

6.3.1 Oxygen determinations

Oxygen determinations were made using an automated, precise Winkler procedure with photometric end-point detector, based on the system described by Williams and Jenkinson (1982).

All glassware and tubing used were cleaned initially by soaking overnight with cold 10% Decon (Decon Laboratories Ltd, Conway St, Hove, BN3 3LY), a proprietary decontaminating reagent, rinsed five times with distilled water, followed by a further soaking overnight with 6% HCL, 2% HNO_3 and then a final three rinses with distilled water. The bottles used were nominally 125 ml borosilicate Pyrex glass bottles. Individual bottle volumes (corrected to 20 ^{o}C) were determined by weight to a minimum precision of 0.01%.

Once rinsed, the bottles were left between experiments containing the titrated sample. Prior to use, they were rinsed in hot water and then twice in seawater (c.f. Williams and Jenkinson 1982).

Bottles to be analysed for in situ measurements were filled directly from the Niskin sampler, on the raft, using silicone tubing. Care was taken to avoid excessive bubbling, agitation and prevent bias during filling. Four replicates were taken for each depth except for the one metre depth at Loch Ewe where only two replicates were taken. During filling the bottles were flushed with at least three times their volume of sample. Prior to fixation the temperature is recorded for all samples using a micro-probe and a Electromedics Model thermometer.

All bottles were shaded whilst being filled and fixed within 10 minutes of being sampled. The bottles were then returned to the shore by boat, still shaded from full sunlight. The time between in situ measurements varied from three to twelve hour intervals.

For in vitro incubations a new, clean and rinsed 30 dm^3 polyethylene container was filled with water sampled several times from the same depth by the Niskin bottle. The resulting sample was well mixed and shaded whilst the incubation was being set up. For convenience, incubations at the Swedish bag were set up on the shore and then returned to the bag.

At the Scottish bag, all *in vitro* incubations were set up on the floating laboratory moored close to the bag prior to being returned to the bag for incubation.

When setting up the incubation, the same procedure for filling bottles for *in situ*, as described above, was used. Five replicates were used for the zero times with four light and four dark replicates during the Swedish experiment, four replicates for the zero, light and dark times at the Scottish bag. The zero times were fixed immediately, the remaining bottles being returned, shaded, to the raft. The light bottles were laid lengthways down on wire mesh trays and suspended at 3 m depth inside the bag. The dark bottles were enclosed in 4-5 layers of black polyethylene and then suspended at an indeterminate depth inside the bag.

Typically, samples were incubated from dawn to dusk, with another incubation running consecutively, dusk to dawn and so on. All bottles, on completion of an incubation, were removed from the bag, shaded, and fixed within 10 minutes of removal. The fixed samples were shaded and returned to the laboratory, where the oxygen samples were stored under water prior to titration. All samples were titrated within 48 h of fixation, in an order that prevented bias during the determination.

6.3.2 TCO_2 determinations

TCO_2 determinations were carried out using an automated coulometric back-titration procedure, as described by Johnson *et al* (1985,1987). The general sampling routine was similar to that described previously for oxygen determinations, with a few exceptions.

First, no routine fixation of samples occurred during the Swedish mesocosm experiment. All samples were analysed immediately on return to the laboratory.

Samples were titrated within one and one half hours of being taken from the raft. Samples were stored for the intervening period in a fridge at 5 ^{o}C. During the Loch Ewe experiment all samples were routinely fixed with 100 μl of saturated $HgCl_2$ within 10 mins of being taken. Subsequent to fixation the samples were placed in a darkened cool-box for transport back to the laboratory. Samples were titrated within 6 hours of being taken from the raft.

Second, nominally 250 ml Pyrex borosilicate glass bottles were used for all TCO_2 in situ measurements. One bottle was filled for each depth in situ, three replicates being taken from the one bottle during the Swedish experiment and typically two replicates during the Scottish experiment. The same initial cleaning procedure was used as described for the oxygen bottles, but once analysed the emptied bottles were left filled with seawater and approximately 1 ml H_2SO_4. Prior to use, they were rinsed with hot water, then twice in seawater .

Third, in vitro incubations undertaken during the Loch Ewe experiment used the same size bottle that was used for in situ measurements, with one bottle being used for the zero time, light and dark replicates respectively. Two replicates were taken from each bottle with an extra one being titrated if the precision of the coulometer was poor. All bottles to be used for incubation purposes, either as a light or dark bottle, were 'clean' bottles in that they had not previously contained $HgCl_2$ and had been cleaned according to the initial cleaning procedure described above. During the Swedish experiment the same bottles described for the determination of oxygen were used for all in vitro incubations. In vitro incubations consisted of 3 replicate bottles for the zero times and two for the light and two for the dark. Two titrated data points were possible from each of the smaller bottles

giving a total of 6 replicates for the zero times and 4 each for the lights and darks.

6.4 General sampling and analysis procedure: Cruise

6.4.1 Determination of TCO_2

During the Challenger 16/87 cruise (8 June - 3 July) a number of determinations of TCO_2 were taken using a coulometric back-titration system similar to that described by Johnson et al (1985, 1987). The system varied from the previous version due to a number of modifications described earlier in section 6.1.

Sampling Procedure for surface water measurements

A total of 351 surface TCO_2 concentrations were obtained by titration of samples collected from the non-toxic surface water supply. Surface samples were taken at regular intervals along the ships track with temperature, salinity, position and time (GMT) being noted at the time of sampling.

Sampling consisted of first rinsing, then filling a Pyrex borosilicate glass bottle of nominally 250 ml volume. The bottle was filled gently in order to excessive agitation and bubble formation. The sample was then analysed immediately, typically three replicates being taken from the one sample, although this was increased to four when the precision of the analyses was reduced.

Sampling Procedure for CTD stations

In addition to surface samples, vertical profiles were obtained with water collected from water bottles at 20 of the CTD stations occupied during the cruise. Up to twelve sampling depths were selected according to the main gradients in light transmission, dissolved oxygen and chlorophyll fluorescence.

All depths selected were also sampled for discrete oxygen and alkalinity samples. Sampling consisted of first rinsing and then slowly filling one bottle for each depth, from which three replicates were later analysed. All bottles were fixed immediately after filling by adding 100 μl of saturated $HgCl_2$. All samples were shaded and stored underwater prior to titration. Most samples were titrated within six hours of collection.

Methodology for comparative in vitro incubations between O_2, TCO_2 and 14C techniques.

A total of four on-deck incubations were set up and a comparison carried out between radiochemical and chemical carbon uptake combined with following estimated rates of production by measuring oxygen flux. Water samples were taken at chosen stations using a 30 dm^3 General Oceanics water sampler. The depth chosen was the depth of the chlorophyll maximum as determined by a previous CTD cast. Unfortunately a combination of poor precision and low production rates meant the TCO_2 measurements were not sufficiently sensitive to enable a true comparison. These incubations are not discussed further in the text.

6.5 Additional details and measurements: Swedish Mesocosm

6.5.1 Dimension and construction of the bag

The experiments were carried out in a mesocosm of approximately calculated 100 m^3 volume. The bag was based on a design evolved by the Department of Agriculture and Fisheries Science (The Marine Laboratory, Aberdeen, Scotland), in studies at Loch Ewe, Scotland (Davies et al 1980). The bag was anchored in a small bay off the Asko Laboratory (University of Stockholm, Sweden), see Figure 6.4 for the position of the bag.

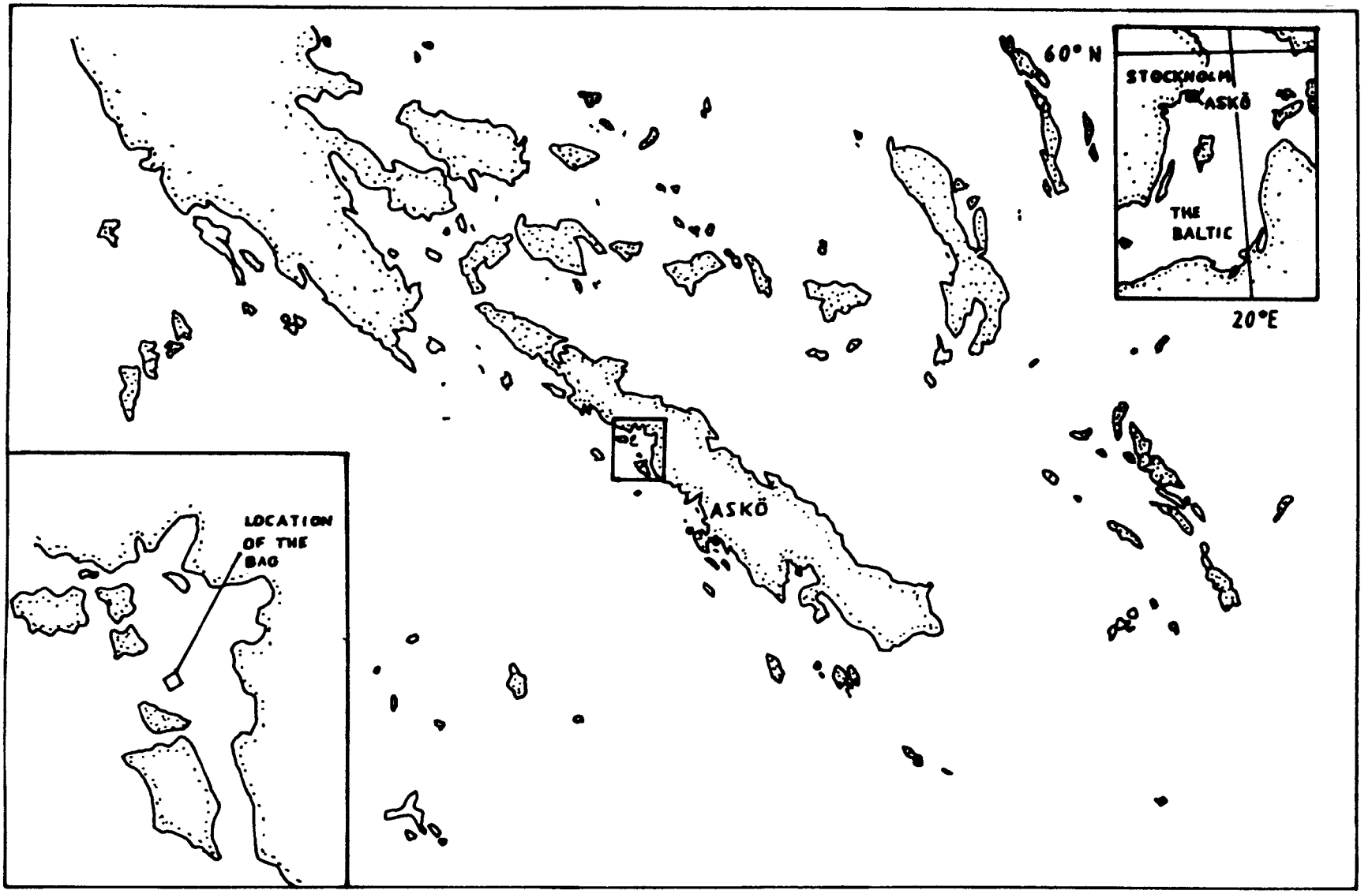


Figure 6.4

The site was close to the laboratory for easy access by small boat and protected from excessive wind and waves. At the same time it was in water regarded as typical of this region of the Baltic coast.

The bag is made of Plastolene 946, which is a flexible vinyl sheet reinforced internally with woven polyester fabric, total thickness 0.5 mm. The bag is a cylindrical open tube approximately 8.8 m long tapering to a cone 4 m from the top (Figure 6.5, after Wulff and Koop, in press). The diameter at the opening is 4.8 m (Wulff and Koop, in press).

The bottom cone of the bag has a 500 mm diameter polythene funnel attached by means of sealing tape. The funnel leads to a flexible hose connected to a pump on the surface.

The flotation collar (Model SF 3000 COMBI, Svenska Flytblock AB, Hedemora, Sweden), was galvanised steel 5.2 by 5.2 m attached to floating walkways on all sides. The structure was fitted with a wooden gangplank across the middle allowing easy access to the water sampler, which was suspended from the apex of an A-frame aluminium ladder by means of a block and tackle (Wulff and Koop, in press).

Before the beginning of the experiment the bag was partly filled and left to leach for several days. The bag was then collapsed on the bottom, taking care not to stir up the sediment and drawn up to the surface manually. This achieved about 80-90% fill and the bag was topped up by means of a diaphragm pump. Once any suspended sediment had sedimented out through the bottom of the bag, the bag was sealed. Subsequently, sedimented material was removed from the cone daily, using a small diaphragm hand pump.

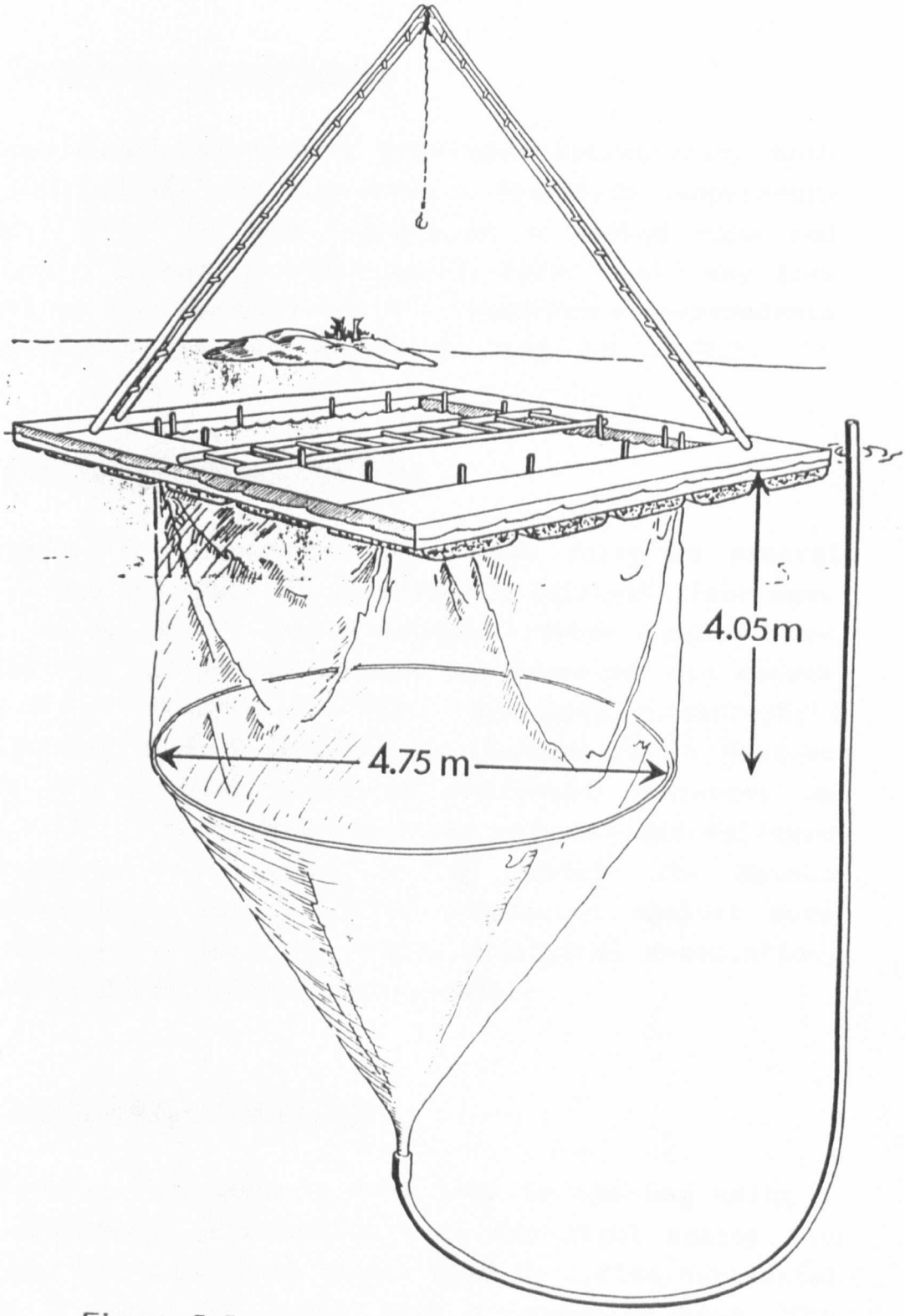


Figure 6.5

6.5.2 Temperature measurements

Temperature measurements were made sporadically both within and outside the bag using a Braystoke temperature recorder. The probe was lowered on a marked rope and temperature recorded for each depth, once on the way down and again on the way back up. All temperature measurements were taken by Dr. P. Tett and Dr. D. Mills (U.C.N.W.).

6.5.3 Chlorophyll determinations

Chlorophyll measurements were made daily at several depths within the bag. All chlorophyll determinations were carried out by Dr. P. Tett (U.C.N.W.) Water samples were collected with the Niskin sampler and decanted into vacuum flasks for transport to the laboratory. Chlorophyll concentrations were determined by fluorometry on acetone extracts of particulate matter extracted overnight on Whatman GF/F filters. Procedure and calculations followed that suggested by Parsons et al (1984). The Aminco fluorocolorimeter was initially calibrated against pure Chl_a, supplied by Scottish Marine Biological Association, Oban, Scotland (Dr P. Tett, pers. comm.).

6.5.4 Irradiance measurements

Irradiance measurements were made in the bag using a Levell multimeter attached to a Li Cor light sensor for use in air and water. The sensor head is a flat horizontal surface, a cosine collector with a corrected head. The sensor was lowered on a cable marked at 1 m intervals. The sensor had been calibrated under water against a Li Cor quantum sensor (Dr P.Tett, pers. comm).

Quantum sensors are designed to respond equally to all quanta within the photosynthetic range, regardless of wavelength. The sensor was positioned so as to record downwelling light, once on the way down and again on the way back up. The resulting profiles were corrected for dark current interference and an average irradiance taken for subsequent calculations.

In addition to irradiance measurements within the bag, a continuous recording of solar irradiance was kept. A Kipp and Zonen solarimeter on the roof of the Asko laboratory recorded hourly irradiance values.

6.5.5 Nutrient additions

Nutrients were added to the bag on the first and sixth day of the experiment. Approximately 35g ammonium sulphate and 7g sodium hydrogen phosphate were first dissolved in five dm^3 of seawater using a polyethylene container. The resultant mixture was then added to the bag at night and mechanically mixed in.

6.5.6 Bag Blackout

The high latitude coupled with the time of year meant that only 5-6 h darkness occurred each day. In order to measure a diurnal change the bag was artificially darkened so as to provide a longer period of darkness. A 'curtain' was constructed using black agricultural film, Silathene (Gore and Associates UK Ltd, Queensferry Rd, Dunfermaline). The curtain was lowered at dusk and raised at dawn on 3 successive night-time periods, the eighth, ninth and tenth of July.

6.5.7 Wind speed measurements

Wind speed was measured and recorded during most sampling periods on the raft. The wind speed was recorded using a hand-held anemometer. The anemometer was held at a height of roughly 2 m above the sea surface for typically one minute, the speed being noted as an average value of that observed during the minute.

The original intention of recording the wind speed was to correct for air-sea exchange processes. The small number of measurements meant that realistic estimation of exchange coefficients was not possible. The manual logging of windspeed with sufficient frequency would have involved a considerable commitment. Preliminary scaling along with previous experience of working with mesocosms (Williams pers. comm.) suggested that the correction would be minor in relation to the fluxes being observed within the bag. Consequently, a minimal data set was obtained.

6.5.8 ^{14}C-$NaHCO_3$ and TCO_2 comparisons

A number of comparative incubations were undertaken during the experimental period between radiochemically determined uptake and chemically determined uptake of carbon. Dr. D. Mills (UCNW, Bangor) was responsible for all aspects of the preparation, innoculation and subsequent determination. The radiocarbon values obtained proved however to be unsatisfactory. Low precision coupled with high time zeros and dark bottle counts meant that these experiments are not pursued or commented on further in this text.

6.6 Additional details/measurements: Scottish Mesocosm

6.6.1 Dimensions and construction of the bag

The experiments were carried out in a mesocosm of approximately calculated 300 m^3 volume. The bag was designed and constructed by the Department of Agriculture ans Fisheries Science (The Marine Laboratory, Aberdeen, Scotland). The bag was anchored in Loch Thurnaig, a sheltered embayment of Loch Ewe, a sealoch on the west coast of Scotland. (See Fig 6.6). The bag was positioned over a mud bottom in a water column of 25-30 m depth.

The bag is made of HT nylon, a flexible plasticide coated PVC. The bag is a cylindrical open tube approximately 20 m long tapering to a cone 17 m from the top (Fig 6.7 after Davies and Williams 1984). The diameter at the top is 4.7 m. The bottom cone terminated in a 50 cm diameter polythene funnel attached to the bag material by means of large hose clips and mastic. The funnel was attached to a plastic sampling hose which was attached to a pump on the surface support raft.

The flotation collar was constructed of octagonal steel sections and polystyrene blocks, the collar served as both a splash barrier and sampling access platform. A 38 cm wide steel slatted walkway spanned the diameter of the bag.

The bag were partially filled and left to leach for four days before the final filling. The bag was filled by collapsing the bag and then drawn up to the surface manually. Once any suspended sediment had been sedimented out through the bottom of the bag, the bag was sealed. This achieved about a 80-90% fill and the bag was then topped up by means of a diaphragm pump.

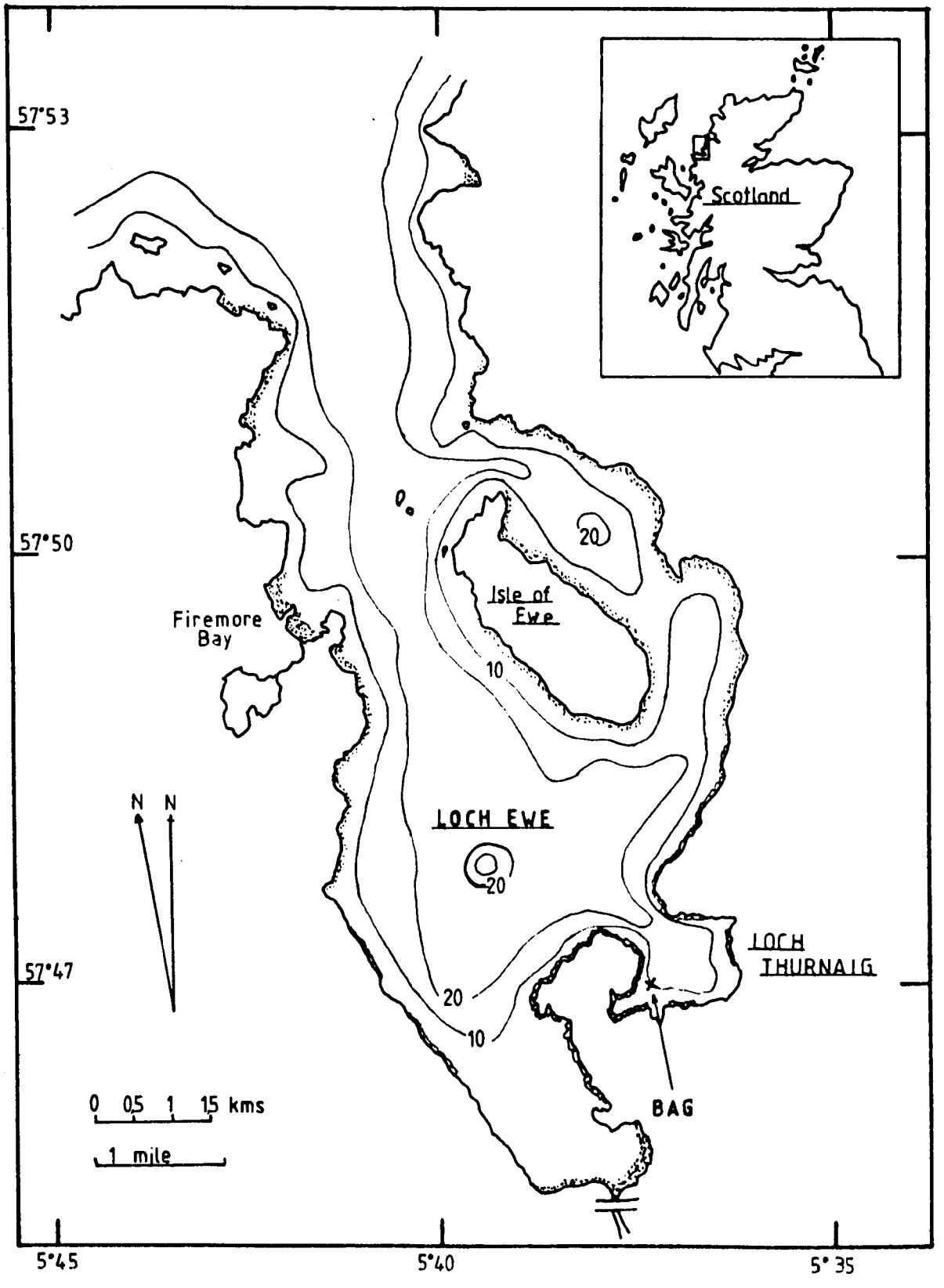

57°53
57°50
57°47
5°45
5°40
5°35
Scotland
Firemore Bay
Isle of Ewe
20
10
LOCH EWE
20
LOCH THURNAIG
20
10
BAG
N N
0 0.5 1 1.5 kms
1 mile

Figure 6.6

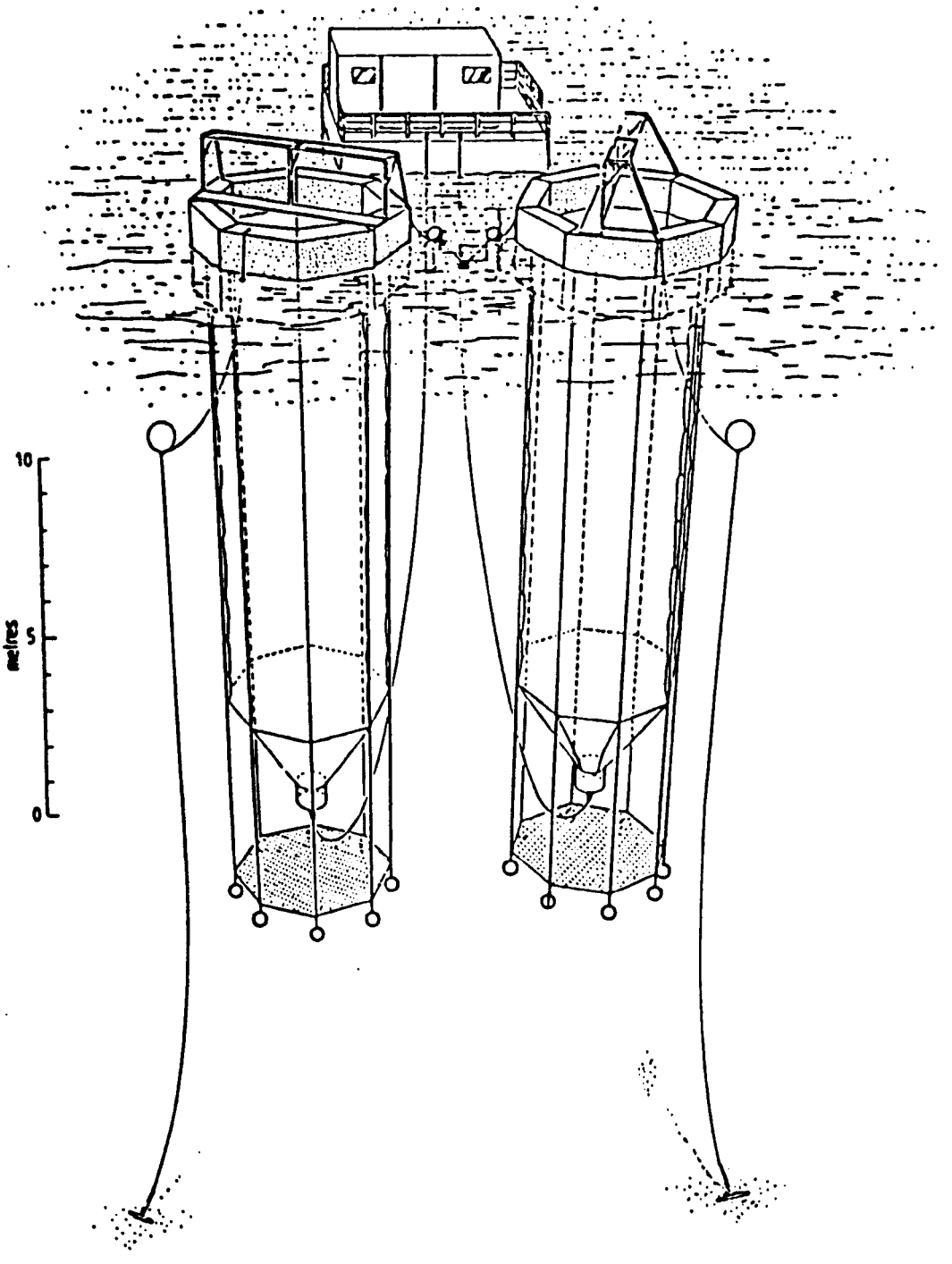


Diagram of the Loch Ewe bags with attendant laboratory raft.

Figure 6.7

6.6.2 Irradiance measurements

Irradiance measurements were made in the bag using a Li Cor LI-185 irradiance meter with a quantum sensor for use in air and water. The sensor head is a cosine collector with a corrected head. Measurements were made for both upwelling and downwelling irradiance.

Solar irradiance was recorded as two hourly totals by a Kipp and Zonen solarimeter placed on the roof of the laboratory moored close to the raft.

6.6.3 Wind speed measurements

Wind speed measurements were made on the raft each time sampling occurred. Wind speed was noted using a hand-held anemometer. Usually the anemometer was held at a height of 2.5-3.0 m height above the sea surface and the average speed noted during a one minute duration. Twice during the experimental period additional wind speed measurements were taken at a height of 1 m above the sea surface.

Extrapolation then enabled all wind speed measurements to be given to a height of 10 m above the sea surface.

Two approaches to the estimation of the coefficient and hence estimated gas flux are used, both of which utilise the 'stagnant film' model (Whitman 1924, Lewis and Whitman 1924) for gas exchange. The results are given in section 8.3, Chapter 8. Realistically it is difficult to envisage a uniform, constant stagnant film at a liquid surface and other models do exist, but Dankwertz (1970) has shown that fluxes resulting from calculation by the boundary layer, film replacement and more elaborate models differ by only a few percent.

The uncertainty in the value of diffusion coefficients and error associated with the normally limited data set of a few wind speed values reduces the importance of choosing one model over the other. The stagnant film model provides an adequate first order approximation to much more complex processes and so it is reasonable to continue to use the model in this study.

Gas transfer can be summarised by the two following equations :

$$F = K [P_{atm(g)} - P_{w(g)}] \quad (1)$$

$$K = D \cdot \alpha \cdot h^{-1} \quad (2)$$

where

$P_{atm(g)}$ = Partial pressure of the specific gas in the atmosphere. (units = atm)

$P_{w(g)}$ = Partial pressure of the specific gas in the water. (units = atm)

K = Gas exchange coefficient (units = mol m^{-2} hr^{-1} atm^{-1})

F = Gas flux (units = mol m^{-2} hr^{-1})

D = Molecular diffusivity (units = m^2 s^{-1})

α = Solubility (units = mol m^{-3} atm^{-1})

h = Surface film thickness (units = m)

Solubility

The solubility of oxygen at a known temperature and salinity is taken from Weiss (1970).

Molecular Diffusivity

These are tabled as a function of temperature in Broecker and Peng (1982).

Film thickness

Film thickness (h) is not a simple parameter, rather some inverse function of wind speed. Kanwisher (1960) suggested that D x h^{-1} (known as the piston velocity) was related to the square of the wind speed. However it should be noted that the piston velocity will be sensitive to the effects of waves and bubble entrainment (Jahne et al 1979, Merlivat and Memery 1983).

These processes will decrease h and so accelerate gas flux. Use of a squared function ensures that the brief storm will have the predominant effect on the flux and so errors are likely to be substantial with use of an averaged daily wind speed.

Broecker et al (1978) argue that both theoretically and experimentally (using a wind-wave tunnel) piston velocity should vary linearly with wind speed above some theoretical speed, and that the observed non-linearity is likely to be due to the effects of waves and bubbles.

Ledwell (1982) showed that gas exchange rates of He, CH_4 and N_2O in a wind tunnel follow the square root of the diffusivity dependence as predicted by the film replacement model.

Liss (1973) suggested that the exchange coefficient was proportional to the wind speed squared based on work in watertanks and wind wave tunnels.

Smith (1985) suggests that a main difficulty in making generalised statements regarding h as a function of wind speed concerns the type of wind measurement made. Commonly 2 types are utilised - drag velocity measured 10cm above the sea surface or the common 10m elevation standardised by meterologists.

Smith reworked several data points to a common 10m height and fitted an exponential regression line expressing h (cm) as a function of W_{10m} ($m.s^{-1}$).

$$h = 0.072.e^{-0.215.W10} \quad (R^2=0.80) \qquad (3)$$

The first method for calculating gas exchange utilises the relationship of K being a square function of wind speed (Tijssen and Eijgenraam 1982). The second is the exponential relationship between h and wind speed given by Smith (1985).

6.6.4 Chlorophyll measurements

Profiles of fluorescence and temperature were made both within and outside the bag using a Chelsea Instruments Flow-through Fluorimeter and Turbimeter Aquatracka. The fluorimeter was linked to a deck unit placed nearby on the laboratory moored close to the raft. The fluorimeter was lowered using a cable and rope marked at 1 m intervals.

In order to calibrate the fluorescence profile a number of discrete water samples were taken at various depths, using the Niskin sampler. The water samples were decanted into marked, darkened bottles and placed in a cool box for transport back to the laboratory. Chlorophyll concentrations were determined by fluorometry on acetone extracts of particulate matter extracted overnight on Whatman GF/F filters. A Perkin-Elmer LS1 fluorometer was used and this was initially calibrated against pure Chl a by Mr I Baird, of DAFS (The Marine Laboratory, Aberdeen, Scotland).

Procedure and calculation followed that recommended by Parsons et al (1984) with the addition of exposing the filter to sonification for 30 secs prior to centrifuging.

6.6.5 Temperature measurements

In situ temperature profiles were taken using both the Chelsea Instruments Aquatracka and a MC5 bridge, recording both temperature and salinity. Profiles were taken both within and outside the bag. Both instruments were calibrated prior to use at Loch Ewe by DAFS (Dr. B Turrell, pers. comm.).

One Aanderaa thermistor chain was used to provide a time series of temperature changes within the bag. One channel was placed at the surface the remaining ten at one metre intervals down to 10m. The thermistor data was computed as hourly means.

6.6.6 Nutrient additions

Nutrients were added two days before sampling began and then once a day. Initially, 300 mg of KNO_3 and 30 mg of NaH_2PO_4 was added to the bag. The chemicals were dissolved in a polyethylene container with approximately five dm^3 of seawater taken from the bag. The resultant mixture was then poured down a length of plastic tubing, the length of the bag, that hung down inside the bag. The tubing was maneuvered into the centre of the bag and then pulled out of the water, aiming to leave a column of nutrient enriched water dispersed throughout the whole water column.

Following the initial addition, subsequent daily additions were made using 3 mg of KNO_3, using the same approach described above.

6.6.7 Physical mixing of the bag

Following the first series of *in situ* measurements it was apparent that a large gradient existed in the bag, in both O_2 and TCO_2 concentrations with depth. The bag was mixed in order to equalise the gradients. Mixing consisted of hauling a 1m plankton net (350 μm net size) quickly up through the bag. The net was open at both ends and had a 75 kg weight attached to the tail in order to facilitate sinking after having been brought to the surface. A total of 10-15 hauls were made at each mixing attempt. The bag was mixed a total of 4 times.

6.6.8 Dye experiment

A solution containing 0.12g of the red fluorescent Rhodamine B dye was initially injected into the bag at 1430 h on 27/8/87. The raw commercial dye was 40 % by weight red Rhodamine powder in an aqueous solution of ethanoic acid.

The dye was added slowly using tubing placed onto the surface of a polysterene disc weighted to be submerged to just below the sea surface in the bag.

The dye was tracked subsequently with the aid of a Turners designs fluorometer fitted with a continuous flow through cuvette and linked to a chart recorder. The fluorometer operating system uses ultra-violet light to excite fluorescent material in the flow cell. Via a photomultiplier and phase sensitive detector, the intensity of this light gives a measure of fluorescence and, after calibration, absolute dye concentration (Carter 1974).

Water was pumped via an inlet hose marked at 1m depth intervals. The hose was lowered or raised at a continuous rate and the delay time recorded (94 secs) and accounted for in subsequent calculations. All profiles were measured on channel 1 of the fluorometer except for profile 5 which required channel 2 for increased sensitivity.

The fluorometer chart recorder trace must be calibrated for both depth and concentration. The depth scale was determined on site by timing the rate of descent of a rope marked at 1m intervals, approximating the rate of descent and ascent used when operating the sampling hose. The concentration scale on the fluorometer was calibrated after the experiment by Dr. B. Turrell (DAFS, The Marine Laboratory, Aberdeen, Scotland).

A digitizing table was then used to create a data file of the calibrated chart record of concentration versus depth, having established a baseline of zero concentration at the natural background fluorescent level of seawater (Dr B. Turrell, DAFS, The Marine Laboratory, Aberdeen, Scotland).

6.7 Additional details/measurements: Cruise 16/87

During June 1987 (8 June - 3 July) a cruise was undertaken on the R.R.S. Challenger, in order to investigate carbon fluxes in the N.E. Atlantic (55-65^{o}N, 01-21^{o}W).

Details of the cruise track and station sampling positions are shown in Figures 6.8 and 6.9. The hydrography of the area is given for reference in Figure 6.10.

RRS CHALLENGER CRUISE JUNE 1987

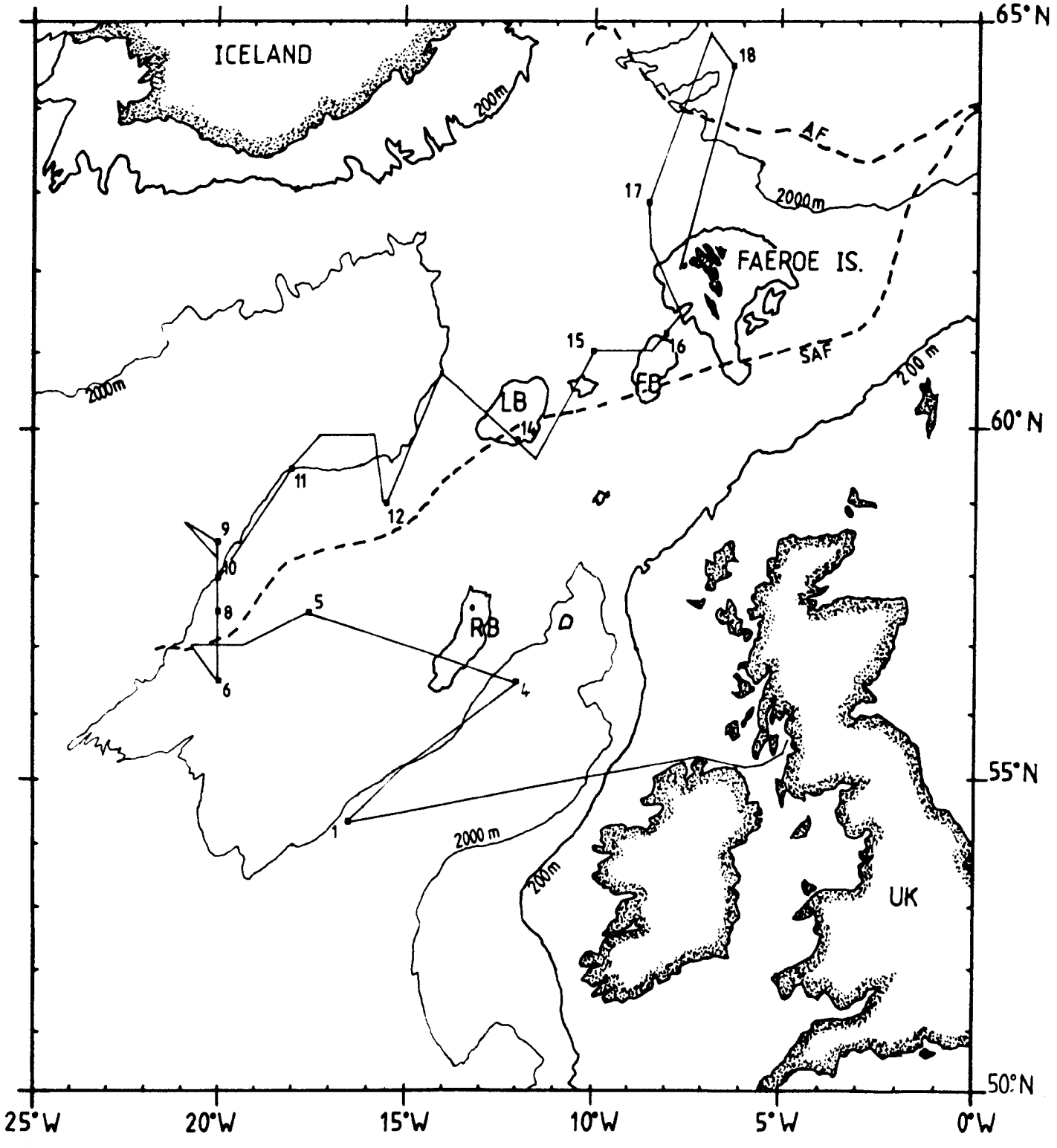


Figure 6.8

•=CTD Station 1st Leg
8-22 JUNE

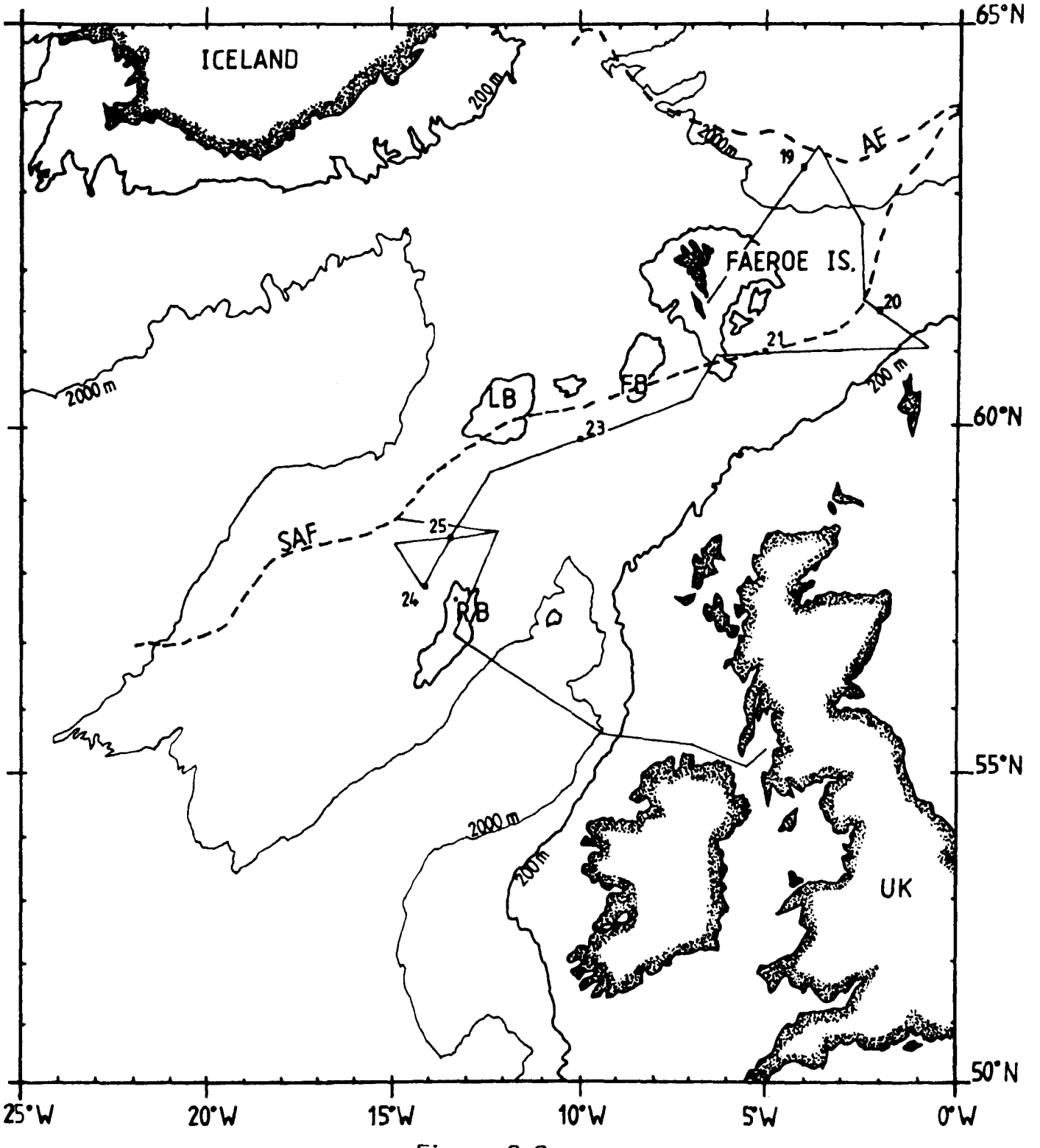


Figure 6.8

• = CTD Station 2nd Leg
23 JUNE - 3 JULY

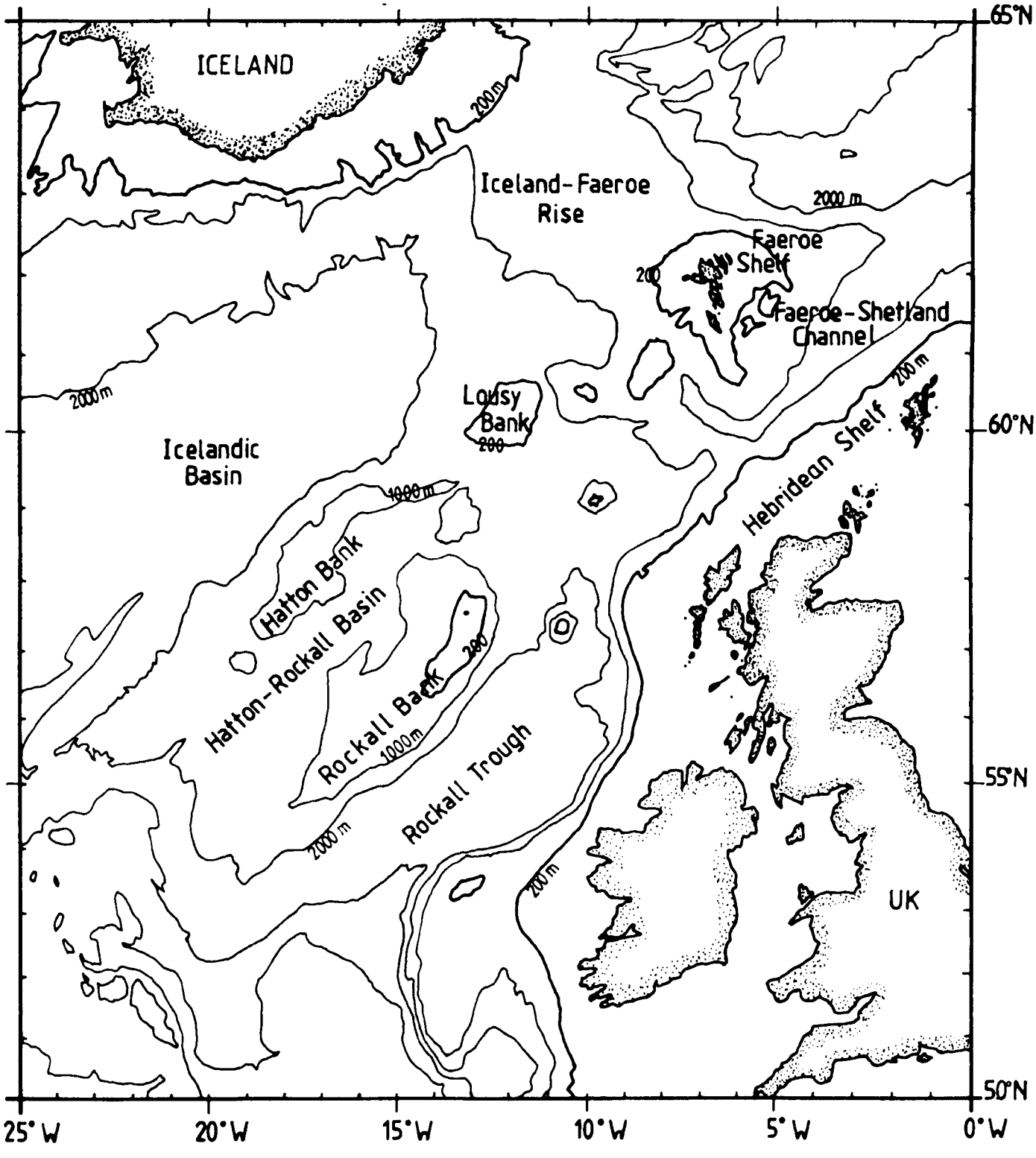

RRS CHALLENGER CRUISE JUNE 1987
ICELAND
200m
Iceland-Faeroe Rise
2000 m
Faeroe Shelf
200
Faeroe-Shetland Channel
2000m
Lousy Bank
200
200m
Hebridean Shelf
Icelandic Basin
1000m
Hatton Bank
Hatton-Rockall Basin
200
Rockall Bank
1000m
Rockall Trough
2000m
200m
UK
65°N
60°N
55°N
50°N
25° W
20° W
15° W
10° W
5° W
0° W

Figure 6.10

Continuous measurements of temperature, salinity (TSG103 Thermosalinograph, Ocean Data Equipment), chlorophyll fluorescence (Chelsea Instruments fluorometer), light transmission (Sea Tech 25 cm transmissometer), dissolved oxygen (YSI oxygen electrode), inorganic nutrients (nutrient autoanalyser) were made along the cruise track, using the ships non-toxic water supply (intake depth approximately 3 m). In addition, discrete samples were taken for pH, alkalinity and TCO_2 surface mapping purposes. A total of 28 CTD casts were made using a Neil Brown Instruments System Mark IIIB 'Conductivity, Temperature, Depth Profiler', a Chelsea Enviromental Instruments Mark II 'Aquatracka' submersible fluorometer, Sea Tech 25 cm Transmissomter, and a General Oceanics Inc. Rosette sampler with 12 x 1.2 L Niskin bottles. A total of 20 stations were sampled up to a maximum of twelve depths, for discrete oxygen, TCO_2 and alkalinity concentrations.

The CTD unit was linked to a 1150 data terminal and both BBC and 'ABC' (Nerc Research Vessels Services, Barry, Wales) computer systems used for data logging and processing.

6.7.1 Alkalinity measurements

A total of 91 in situ samples were taken using water collected by the CTD rosette sampler. For most casts 10 alkalinity samples were taken throughout the water column. Sampling depths were selected according to the main gradients in dissolved oxygen, chlorophyll fluorescence and light tranmission. An additional depth sampled on each cast was as close to the sea floor as it was possible to take the CTD.

All depths sampled for alkalinity were also sampled for TCO_2 and discrete O_2 values.

A total of 53 surface alkalinity samples were collected from the ships non-toxic surface water supply (taken in at a depth of 3 m). Sampling coincided with surface TCO_2 measurements and temperature, salinity recordings taken using the ships thermosalinograph.

Surface samples were routinely taken to coincide with alternate TCO_2 measurements, however at high surface fluorescence or low transmission values, additional samples were taken.

Sampling details

Roughly 500 ml of seawater was filtered through a 0.45 µm (Whatman GF/C) filter for each alkalinity sample taken. The filtrate was placed in a clean, rinsed, labelled plastic bottle. Following instructions from Dr. M. Whitfield of the Marine Biological Association (Plymouth UK), one ml of chloroform was then added to each sample bottle. The samples were initially cooled in a fridge ($5^{o}C$) prior to freezing. All samples were kept frozen until just prior to analysis.

Several methods were subsequently used in the analysis of the samples.

1) Potentiometric method

This method was originally described by Gran (1952) and subsequently modified (Dryssen 1967, Hannson and Jagner 1973). The method follows that described by Grasshoff (1981), with modifications and software developed by Dr D. Turner (Plymouth Marine Laboratory, The Citadel, Plymouth).

2) Photometric method

Two alkalinity samples were sent to the Department of Analytical and Marine Chemistry, University of Goteborg, Sweden for analysis by Dr L. Anderson. The method was originally described by Graneli and Anfalt (1977) and subsequently modified by Anderson and Wedborg (1982).

3)Single point pH method

The method was followed as described by Culberson et al (1970) and Grasshoff (1981). The exception being that all samples were left to equilibrate for up to six hours after addition of the aliquot of acid.

4) Determination of calcium concentration

A number of alkalinity samples were analysed using a Varian atomic absorption spectrophotometer for calcium concentration. The results were inconclusive and insufficient precision did not enable information to be obtained from the samples.

6.7.2 pH measurements

An automated pH system controlled by an APPLE computer was used on its first field-test during the cruise. The system was designed by Dr M Whitfield at Plymouth Marine Laboratory, The Citadel, Plymouth. The system proved after a series of runs to be inadequate for recording continuous pH from the non-toxic seawater supply. In addition to the automated system, a conventional pH electrode (Orion Ross combination Model 8102SC) and meter (Orion Expandable Ion Analyser EA-920) was brought from UCNW in order to provide an additional record of surface pH values using the non-toxic seawater supply. The electrode and an automatic temperature compensation probe (Orion ATC Model 917002) were placed in a machined perspex cell connected to the non-toxic seawater supply and allowed to overflow into the sink.

The pH meter was linked via an RS232 interface to BBC logging system. Unfortunately drifting of the electrode meant that despite extensive recalibrations the data was unreliable and not used in any further calculations.

In addition to measurements of the carbonate system, a number of other variables were recorded and used subsequently in the analysis of data.

6.7.3 Transmission

This was recorded continuously using the non-toxic seawater supply connected to a Sea Tech 25 cm transmissometer linked up to a BBC computer and home-made logging unit. A full data set of transmission values along with time and date was supplied after the cruise by John Wood (PML, Plymouth).

Continuous profiles of transmission were also obtained during the CTD casts with a similar unit being attached to the CTD frame. Printouts of transmission against depth were provided via the BBC computer and logging system at the end of each cast.

In order to change transmission percentages to an attenuation coefficient the following relationship was adopted (Jerlov 1976)

$$\text{Attenuation } (m^{-1}) = \frac{1}{L} \cdot \ln \frac{I_o}{I}$$

where L = length of beam of light (0.25m)
where I_o = full transmission ie 100 %
and I = observed transmission as a percentage.

6.7.4 Fluorescence

Fluorescence was recorded continously from surface waters using the non-toxic seawater supply with a Chelsea Environmental Instruments fluorometer linked up to a BBC computer and home-made logging unit. A full data set of fluorescence and time recorded was supplied after the cruise. Continuous profiles were obtained during the CTD casts and printouts made available after each cast with fluorescence logged against depth.

Frequent water samples were taken both from the non-toxic SW supply and CTD casts in order to calibrate both fluorometer outputs. Phytoplankton was concentrated from a 100 ml water sample onto a 0.45 μm membrane filter (Whatman GF/F) and the filters then frozen until fluorometric analysis. Prior to analysis, the photosynthetic pigments were extracted for 18-24 h into a known quantity of 90 % neutralised acetone (Parsons et al 1984). Pigments were estimated from measurements of fluorescence before and after acidification, using a Turner Designs filter fluorometer. The unit had been previously calibrated against a chlorophyll a standard whose concentration had been determined spectrophotometrically (Holligan per. comm.).

A linear correlation model was fitted to the natural log of the chlorophyll concentration against output from the fluorometer used during the CTD casts. The method of least squares fit was used to obtain the correlation equation ;

$$\text{Fluorescence} = 2.49 + 0.810\ (\ln \text{Chl a})$$

R^2 adjusted = 73.8%

(after Fasham et al 1985)

All fluorescence output from the CTD was calibrated using the above equation and converted into units of mg/m^3.

Fluorescence from the continuous surface output was calibrated in a similar manner and the calibrated chlorophyll data supplied by PML, Plymouth after the cruise logged against time and date.

6.7.5 Temperature and salinity

Temperature and salinity were recorded continuously using the ships non-toxic seawater supply and displayed using a BBC computer and logging system. At each surface sampling point, both temperature and salinity were noted down manually. Later calibration of the salinometer meant all values were corrected for an offset of - 0.25 . A printed log of both temperature and salinity was produced after each cast for each depth sampled.

6.7.6 Dissolved oxygen

Levels of dissolved oxygen in the surface water were recorded using a YSI oxygen electrode linked to a BBC computer and data logger. Discrete samples analysed using an automated Winkler technique were taken at certain intervals in order to calibrate the probe. All oxygen sampling and subsequent calibration was carried out by Dr D.Purdie and Mr G.Parkes, Southampton University.

A Beckman polarographic oxygen sensor was mounted on the CTD and produced a continuous recorded signal that was later calibrated by use of discrete samples analysed using the Winkler technique (Mr G.Parkes).

All discrete sampling depths were chosen according to the main gradients in oxygen, fluorescence and light transmission and matched with sampling for TCO_2 and alkalinity.

6.8 Preservation Experiments

Johnson et al (1987) reported that the poisoning of water samples with $HgCl_2$ was unsatisfactory for coulometric determination of TCO_2. It was apparent at the beginning of this study that a reliable preservation technique was vital for maximum exploitation of the method.

A series of experiments were carried out using algal cultures in order to determine the suitability of $HgCl_2$ as a fixing agent. The cultures were provided by Mr. M. Budd from the algal culturing facilities at UCNW. The cultures were not axenic and were diluted to volume using non-sterile, filtered seawater. All cultures were counted using a coulter counter prior to incubation, so that approximate cell densities could be recorded for each incubation. All bottles were incubated in the dark and the effect of $HgCl_2$ on respiration recorded. Several different concentrations of $HgCl_2$ was used and bottles were both cleaned and not cleaned prior to incubation.

CHAPTER 7

MESOCOSM EXPERIMENT, ASKO, SWEDEN

The following section deals with results obtained during a series of experimental measurements undertaken in a mesocosm at Asko, Sweden. The mesocosm or bag was raised on the last day of June and the experiment was run through until the eleventh of July 1986.

7.1 Chlorophyll

Discrete water samples were taken at several nominated depths throughout the experimental period. These were analysed fluorometrically for chlorophyll, individual data is tabulated in the data appendix for Sweden. All chlorophyll measurements were taken and subsequently processed by Dr P. Tett (UCNW Bangor).

Figure 7.1 shows a chlorophyll concentration averaged from all readings taken from the surface down to seven metres depth. This represents an overall picture of the change in chlorophyll with time within the bag. Figure 7.1 also has for comparison three measurements taken at the surface outside the bag. Figure 7.2 shows the development of the algal biomass, as represented in this instance by chlorophyll concentrations, for three individual depths (surface, 3 m, 6 m). It is apparent that nutrient addition to the bag on the 1/7/86 and 6/7/86 (marked on the first graph Figure 7.1) produces a rapid chlorophyll increase whilst outside the bag chlorophyll levels remained steady and comparatively low.

7.2 Temperature

It has become convenient, for biological and chemical studies to undertake experiments within enclosures that are semi-submerged within the water column. The assumption of the experimentalist is that 'real' conditions are simulated within a more controlled environment, hence hypotheses tested within the bag can be applied to external systems.

In order to estimate fluxes of the gases, oxygen and carbon dioxide due to biological activity, the dynamics of circulation within the bag must be determined. The effects of physical mixing within the bag will determine in part the observed distribution of these gases at any particular time.

A classical approach to describing the circulation is to adopt the hypothesis that heat transfer through the water column is a one-dimensional heat diffusion process occuring in the vertical axis (McEwen 1929). This then enables temperature profiles to be used as a diagnostic tool to correct observed fluxes for inherent physical participation (Hesslein and Quay 1973).

Temperature profiles were taken inside the bag at regular intervals with three main objectives.

1) First, to establish the similarity of temperature structure and so physical characteristics in and out of the mesocosm.

Figures 7.3, 7.4 and 7.5 are temperature profiles taken on different days both inside and outside the bag, from the surface down to a depth of seven metres. The profiles were taken concurrently on each date sampled. The temperature structure within the bag is similar to that observed outside. The thermocline is deeper within the bag (maximum of 1 m), however the gradient is similar both within and without the bag.

2) Second, a number of time series measurements were made of temperature in order to establish a region of comparative stability in the water column within which chemical flux could be followed with the minimum physical correction being required.

Figure 7.6 is a time series of temperature measurements taken approximately hourly, for each 1m depth, from the surface to 7 m. The plot covers the period 6/7/86 0900 h to 6/7/86 1650 h.

Figure 7.7 is a similar plot with the same depths being shown as in Figure 7.6, with measurements taken roughly every three hours for the period 7/7/86 0920 h to 8/7/86 0205 h.

Figure 7.8 is a similar plot again the equivalent depths as shown in Figures 7.6 and 7.7. In addition six measurements of the air temperature, just above the surface of the bag are plotted for comparison. Temperature was recorded approximately every three hours. All three Figures 7.6, 7.7 and 7.8 indicate that a comparatively stable region exists in the bag between 2 and 4 m.

Figure 7.9 represents the time period of 7/7/86 0920 h through to 8/7/86 0200 h, a series of successive depth profiles were taken approximately three hourly. This is best represented by a contour diagram of temperature with time elasped in hours being plotted against depth. Two regions are of interest, surface warming occurs during the day followed by a period of mixing and cooling at night down to nearly 2 metres. At night a cooling and progression upwards of cooler water at night to just below 5 m depth. Once again this plot suggests that the most stable region occurs between 2 - 4 m.

3) The third aim of recording temperature changes in the mesocosm is to provide data to allow the calculation of eddy diffusivity coefficients. These coefficients are calculated under the previously described assumptions regarding the one-dimensional vertical diffusion model applied to the water column. The coefficients can then be applied to observed gaseous flux in order to correct for physical mixing processes (Appendix 2).

Calculation of eddy diffusivity coefficients

The frequency and timing of temperature measurements made within the bag did not permit an extensive series of Kz (eddy diffusivity coefficient) values to be calculated. Only two periods of successive temperature measurements, 2/7/86 1210 h to 3/7/86 0630 h and 7/7/86 1100 h to 7/7/86 2200 h provided sufficient evenly spaced measurements to permit a calculation of Kz for the 3 m depth.

In the calculations, the effect of radiant heating due to the solar input was ignored as previously temperature profiles showed it to be minimal at that depth. Horizontal advection was assumed to be zero. Calculated values for Kz, a worked example of which is given in Appendix 1, are given below.

The Kz values obtained vary considerably and illogical negative coefficients have been obtained. This suggests that the simple one dimensional Fickian diffusion model is too simplistic and other processes unaccounted for are influencing the observations. An alternative hypothesis is that the insufficient number of adequate temperature measurements meant that any illogical coefficients obtained could not realistically be disregarded.

Calculated values of the eddy diffusivity coefficient (Kz)

Depth = 3m

Day	Time(h)	Kz (cm^2/sec)
2/7	1210	0.853
	1520	1.235
	1820	0.839
	2110	0.370
	0030	0.517
	0345	0.595
	0630	-0.090
7/7	1100	-0.555
	1315	1.000
	1545	9.524
	1820	-2.174
	2200	0.617

Due to the nature of the coefficients obtained it was decided to procede using an average Kz coefficient (0.2 m^2/h) taken from examining the relevant literature (Hesslein and Quay 1973, Steele et al 1977, Dillon and Caldwell 1980, Oakey and Elliott 1982, Denman and Gargett 1983). Although describing vertical mixing as a diffusion process must have limitations, other workers (Steele et al 1977) have shown it to be a useful simplification and not wholly inaccurate.

Hence although coefficients calculated from the temperature observations in the bag were not as anticipated, a value from the literature was taken in the expectation that it would provide a reasonable estimate of a diffusion correction and so provide the means to determine the importance of corrections due to physical processes.

7.3 Irradiance

Irradiance profiles were taken at regular intervals inside the bag using an underwater cosine collector. Solar radiation, over a range of 350-2800 nm, was recorded using a Kipp and Zonen pyrheliometer.

Irradiance was followed within the bag in order to ensure that the bag structure and material did not substantially or adversely alter conditions compared to the external light field.

Irradiance measurements were taken both inside and outside the bag. All measurements are plotted as the natural logarithmic ratio of Iz to Io , where Io is the irradiance at the surface and Iz the irradiance measured at the specific depth z. The attenuation coefficient (K) remained reasonably constant with a value in the range 0.4 to 0.9 m^{-1}. The attenuation in the intensity of light is assumed to follow Beers Law ie

$$Iz\ (t) = Io\ (t)\ .\ e^{(-K.z)}$$

Figure 7.10 is a profile of irradiance in the bag compared to that outside taken on 8/7/86 at 1545 h. Measurements were taken every one metre depth from 1 to 7 metres. Profiles within the bag (Figure 7.10) are more irregular than those taken outside.

This irregularity suggests that the bag is itself effecting the attenuation characteristics of the water.

Figure 7.11 is a similar profile taken within the bag with the curtain lowered and then raised. These measurements were taken at 0730 h on 9/7/86. It is apparent from Figure 7.11 that the black curtain used had a neglible effect in reducing irradiance entering the bag. The majority of light entering the bag appparently must do so through the surface.

Figures 7.12 and 7.13 indicate a succession of irradiance profiles taken within the bag over a certain time period. Figure 7.12 indicates the presence of a shadow in the bag, due to a shading effect at 1030 h on 10/7/86. Figure 7.13 shows the development of the shadow within the bag from 0900 h through to 1810 h on 2/7/86. This shading effect is not suprising considering the low angle of the sun at this latitude, during the experimental period.

7.4 Chemical measurements of O_2 and TCO_2 concentrations

Chemical measurements taken during the experimental period can be divided into three sections.

The first section consists of *in situ* profiling of both oxygen and carbon dioxide concentrations every three hours for a total of 24 h from 2/7/86 1030h through to 3/7/86 0900h. Initially, concentrations were recorded at two and five metres depth, this was then changed at 1845h 2/7/86 to three depths; two, four and six metres depth.

Table 7.1 contains the record of observed *in situ* measurements of O_2 concentration at certain depths, during the period 2/7/86 1030 h to 3/7/86 0900 h. Values are given as mean taken from three replicates and associated standard error (S.E.). The data is represented graphically in Figure 7.14.

Table 7.2 has comparable measurements of TCO_2 for the same depths and time interval. This data is plotted in Figure 7.15. An opposite or symmetrical diurnal pattern is obvious for all depths and for both gases.

As discussed previously, it is possible to correct observed data to take account of vertical diffusion using a certain value for Kz. Table 7.3 contains observed and corrected data for the 4 m depth for both oxygen and carbon dioxide. All observed data has been recalculated using a Kz value of 0.2 m^2/h. A worked example for the correction of observed data is given in Appendix 2. Figures 7.16 and 7.17 show the observed and corrected profiles for 4 m, given in Table 7.3.

Although there are differences between the two profiles, the overall metabolic rates vary little between and observed and corrected measurements. If the correction made (Kz = 0.2 m^2/h) is reasonable, and previous literature supports this, then it would appear that a correction for physical processes in the bag is minimal in comparison to the overall rates being observed.

It is possible to calculate a series of molar ratios (fluxes determined <u>in situ</u>) for both observed and corrected data. The appropriate ratios are given in Table 7.4, along with associated standard errors.

A worked example for the calculation of a standard error for a ratio is given in Appendix 3. One of the main criteria associated with the calculation of error bars for a ratio, is that the individual errors must be less than the associated mean values used in the calculation. In this first experimental section, low rates were observed for the three hourly sampling intervals, and in most cases the error exceeds the mean rate of change observed with either gas. As confidence limits cannot be adopted for a number of the molar ratios an alternative approach was taken.

All paired CO_2 and O_2 measurements are plotted against each other and a correlation calculated using the method of least squares fit (Figure 7.22). A poor correlation of 37% is obtained initially with a molar ratio of 1.89. One point, circled on the correlation plot, appears to be unduly influencing the regression and without this point a correlation of 49% is obtained with a molar ratio of 1.45.

The second experimental period follows a similar approach to that discussed above, however different sampling depths have been chosen. The series of measurements covers the interval 7/7/86 1030 h to 0230 h 8/7/86.

Observed O_2 and TCO_2 concentrations at two, three and four metres depth for this period are given in Tables 7.5 and 7.6. Mean values taken from three replicates are given plus the associated standard error. This data is shown in Figures 7.18 and 7.19 respectively. Once more, an opposite and symmetrical diurnal curve is apparent for the distributions of the two gases throughout the water column.

Values corrected as described before using a Kz = 0.2 m^2/h at 3 m depth are given in Table 7.7 for both O_2 and TCO_2. Figures 7.20 and 7.21 show the observed and corrected concentrations for both O_2 and TCO_2 respectively at three metres depth. Some differences occur between the two profiles but again the overall rates are still similar.

Calculation of molar ratios is in principle possible, however, a similar problem to that during use of data obtained over the first sampling period is encountered, namely small rates that inhibits calculation of the associated standard errors. In response to this as for the first sampling periods, all pairs of observed oxygen and carbon dioxide concentrations are correlated.

The regression line is drawn through the points using the method of least squares fit (Figure 7.23).

The gradient of the line is taken to represent an averaged molar ratio for the time period in question. For the interval 7/7/86 1030 h through to 8/7/86 0230 h an averaged ratio of 1.30 with a correlation of 84% is obtained (Figure 7.23).

The third and final series of measurements consisted of a set of seven comparable and consecutive *in vitro* incubations and *in situ* profiles. Measurements were made every twelve hours, at dawn and dusk.

Rates of gross and net production along with respiration estimates as estimated by use of *in vitro* incubations are given in Table 7.8. Also included are appropriate photosynthetic and respiratory quotients and associated standard error. A full data set showing individual replicates for each *in vitro* incubation is given in the data appendix for Sweden.

The range of photosynthetic quotients observed *in vitro* is from 0.99 - 1.17, very close to the conventionally adopted value of 1.00, or 1.20 (Parsons *et al* 1984). Conversely, the range observed for respiratory quotients is much greater and significantly different from the accepted value of 1.00 (Parsons *et al* 1984). The range observed is in this instance is 0.52 - 2.87.

For comparison, Table 7.9 contains comparable estimates of net community activity as estimated through both *in vitro* and *in situ* measurements. The net activity for *in situ* estimates are observed values, temperature measurements are insufficient to permit correction, however examination of previous correction for the first two experimental periods suggest that it could be a minor correction.

Neither O_2 or TCO_2 estimates of net community activity agree consistently either between *in vitro* and *in situ* measurements or between the two gases. Considerable differences can be seen between both gases and both sampling methods. Most frequently, *in vitro* estimates are lower than those observed *in situ*.

The range of respiratory and photosynthetic quotients observed from *in vitro* measurements during the experimental period are given in Table 7.10.

Figure 7.24 is a histogram of observed *in situ* molar ratios measured during the night period (during the first and second parts of the experimental period), one value 13.10 (1845 h to 2200 h 2/7/86) is not included to simplify scaling of the plot. Included in the figure are observed molar ratios measured during the daylight. These ratios are given in Table 7.10.

Figure 7.25 is a histogram of corrected *in situ* molar ratios measured during the night period (during the first and second parts of the experimental period). Two values have not been included, 8.55 (1845 h 2/7/86 - 0600 h 3/7/86) and -14.08 (1845 h 2/7/86 - 0300 h 3/7/86). Once again these two extreme values were excluded in order to present the major part of the data. Included in the figure are the corrected molar ratios measured during the daylight periods. The ratios obtained and then corrected are given in Table 7.10.

7.5 Summary

An opposite and symmetrical diurnal rhythmn was observed from *in situ* measurements of both O_2 and TCO_2 within a mesocosm. A correction for air/sea exchange was not possible but presumed to be neglible compared to the scale of fluxes being observed within the bag.

A simple one-dimensional diffusion model was applied to temperature measurements and assumed to represent the physical processes occurring within the mesocosm. Unusual eddy diffusivity coefficients were obtained and so a value taken from the literature was subsequently used in order to correct observed fluxes for the result of physical mixing. The correction did not significantly affect overall metabolic rates observed.

A number of photosynthetic and respiratory quotients were calculated from *in vitro* incubations. The range of PQs was close to conventionally adopted values, whilst the RQ range was substantially larger and differed from expected values.

A number of molar ratios were calculated from the *in situ* measurements, these varied enormously with suprisingly large and occasionally negative ratios being obtained. Correction for physical mixing processes did not alter the range calculated.

In vitro estimates of respiration, gross and net production by both O_2 and TCO_2 rates are reasonably close. A comparison of *in situ* and *in vitro* estimates of net community activity as determined from O_2 and TCO_2 rates suggest significant differences between both the technique and the sampling approach.

As a consequence of the above results an additional series of measurements were undertaken in another mesocosm situated in a sealoch, Scotland. The results of this experiment are discussed in the following chapter.

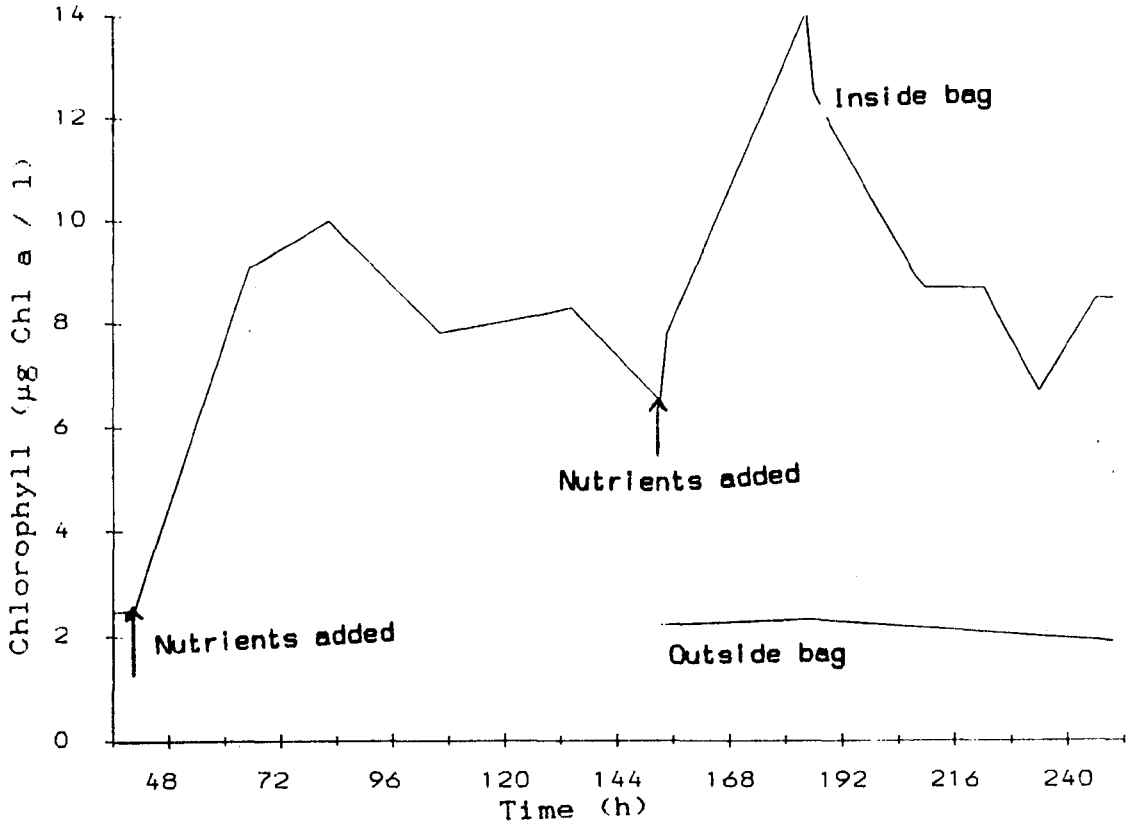
FIGURE 7.1

Change in chlorophyll (μg Chla/l), averaged from the surface to seven metres, during the mesocosm experiment.

FIGURE 7.2

Change in chlorophyll (μg Chla/l) at the surface, 2m, 3m and 6m during the mesocosm experiment.

Figure 7.1



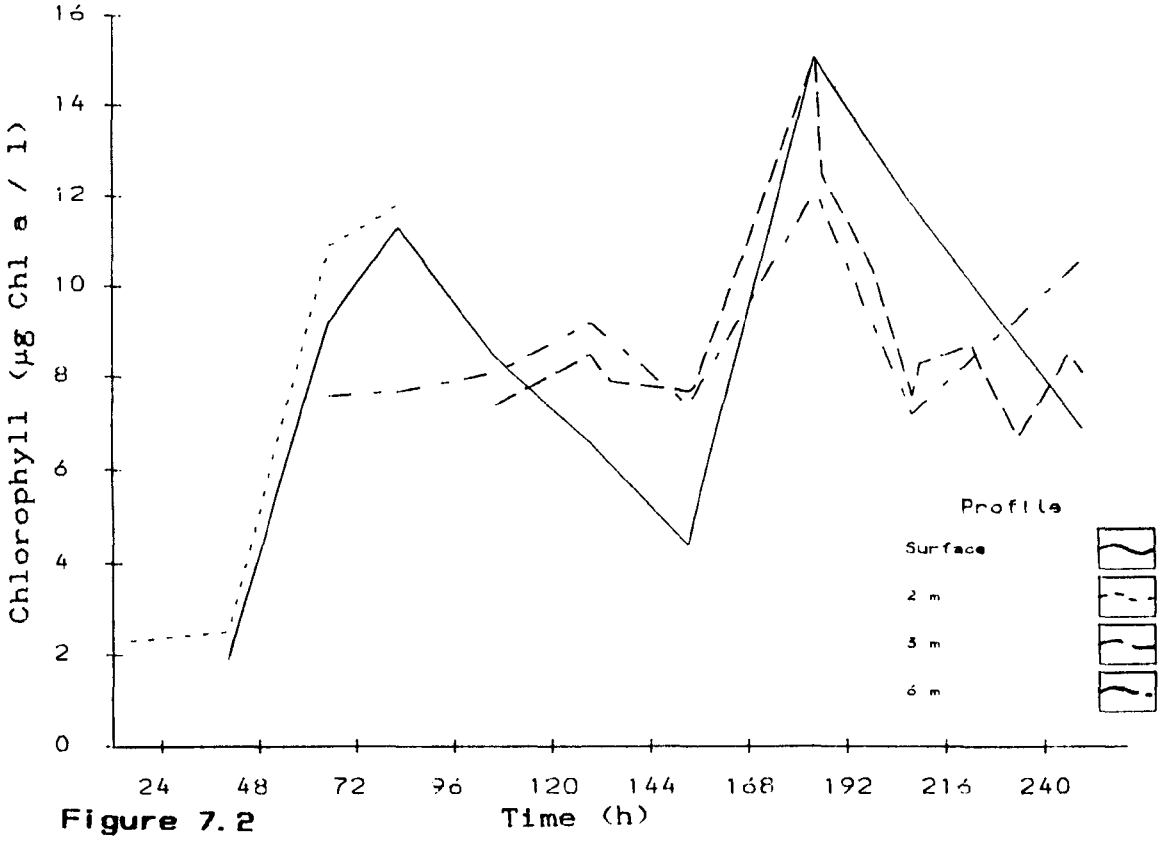


Figure 7.2

FIGURE 7.3

Temperature profiles taken
inside and outside the bag.
(Surface to seven metres)

FIGURE 7.4

Temperature profiles taken
inside and outside the bag.
(Surface to seven metres)

Figure 7.3

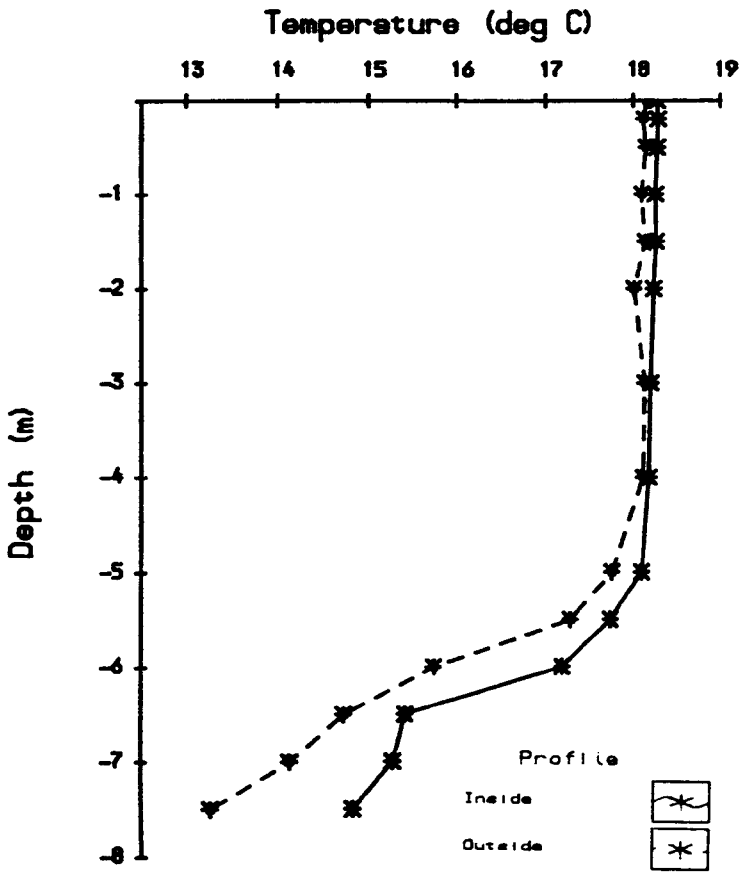


Figure 7.4

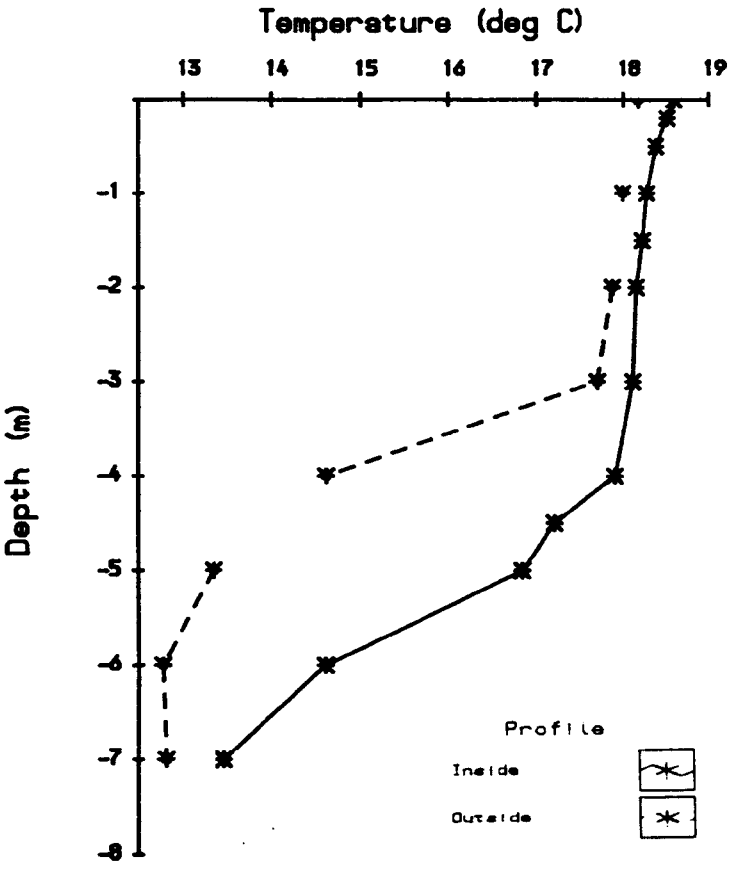


FIGURE 7.5

Temperature profiles taken
inside and outside the bag.

(Surface to seven metres)

Figure 7.5

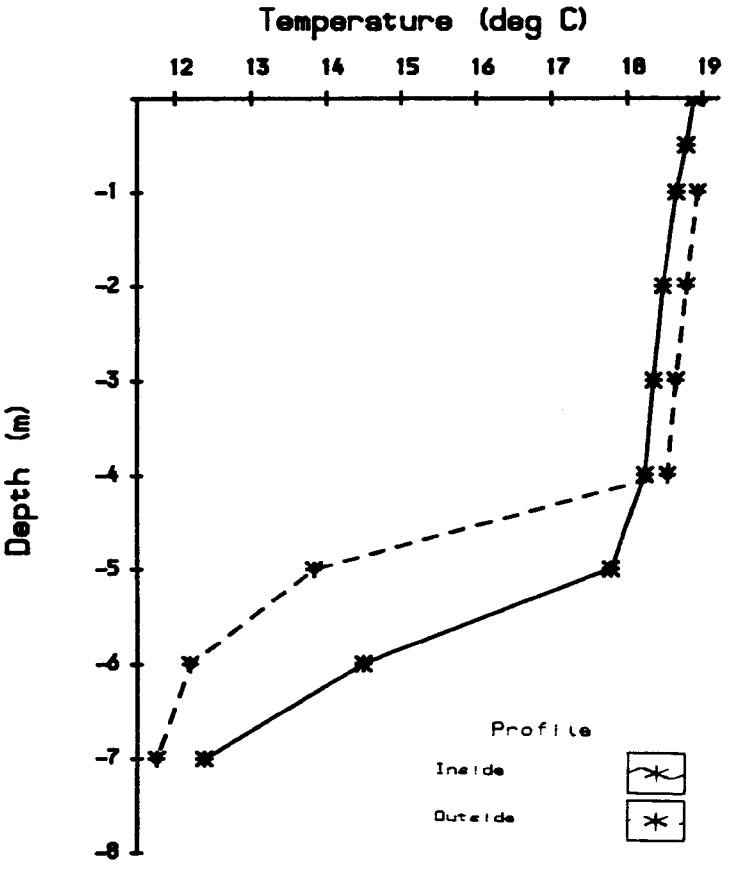

Temperature (deg C)
12
13
14
15
16
17
18
19
Depth (m)
-1
-2
-3
-4
-5
-6
-7
-8
Profile
Inside
Outside

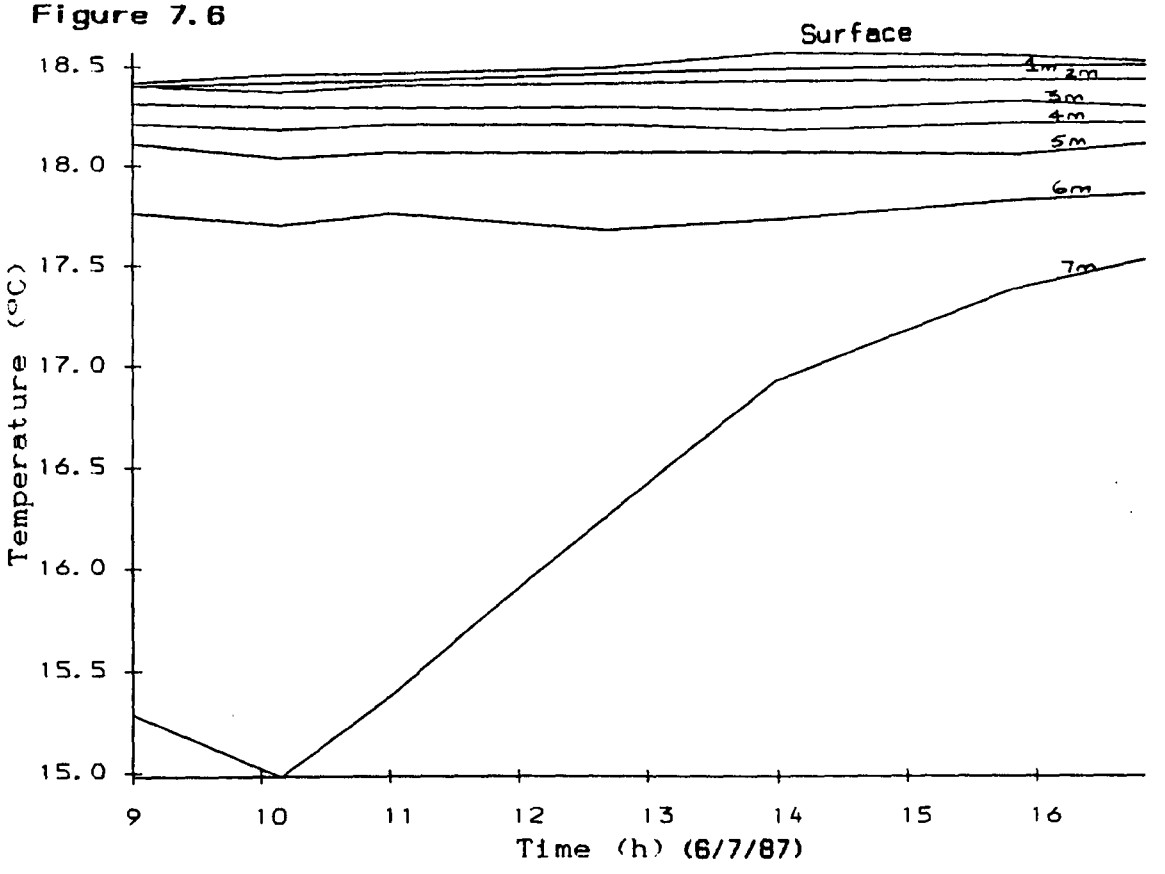
FIGURE 7.6

Time series of hourly temperature profiles
(6/7/86 0900 h to 6/7/86 1650 h)

FIGURE 7.7

Time series of three hourly temperature profiles
(7/7/86 0920 h to 8/7/86 0205 h)

Figure 7.6



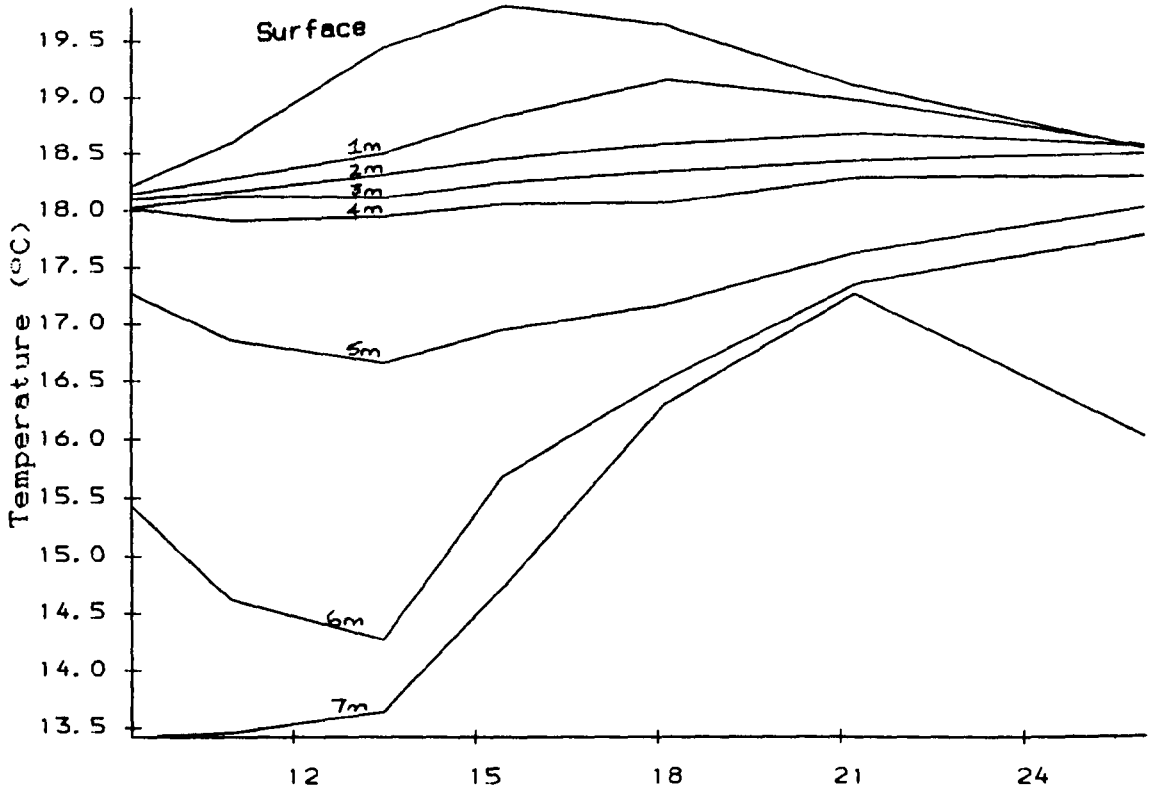


Figure 7.7

FIGURE 7.8

Time series of temperature profiles
Air temperature superimposed for contrast.
(1/7/86 to 3/7/86)

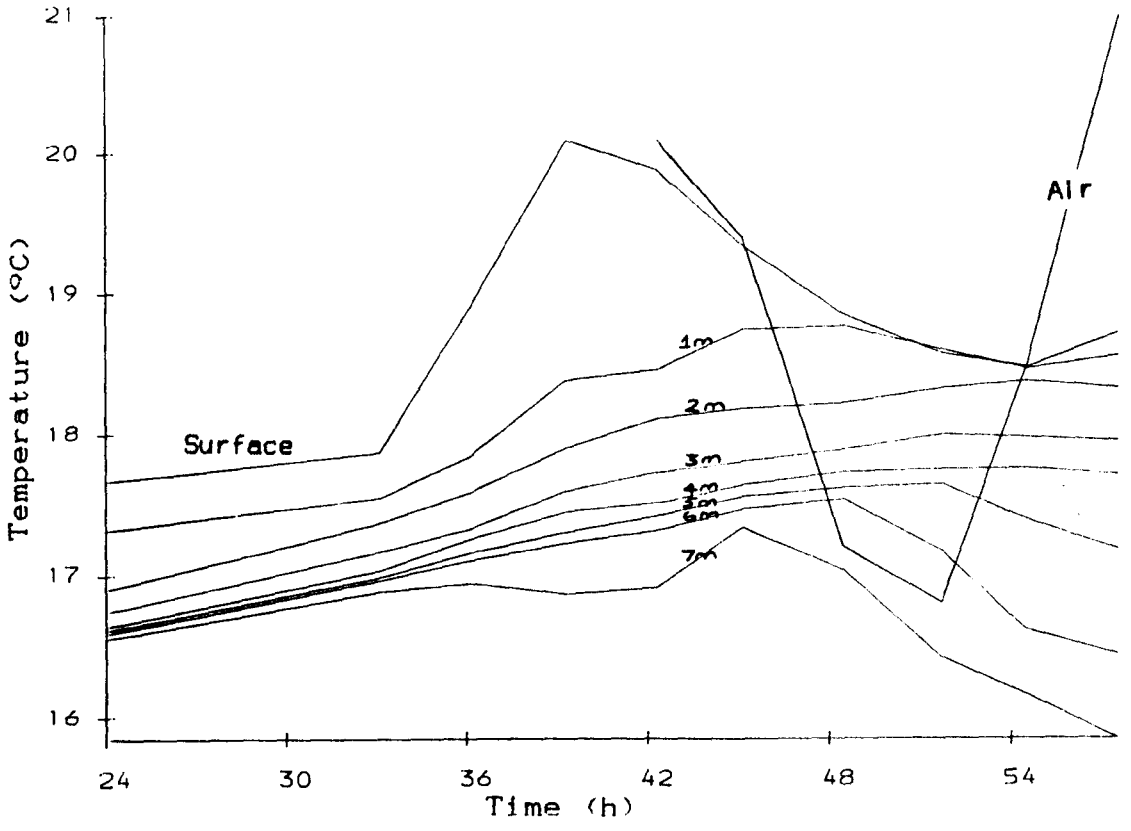


Figure 7.8 (1/7/87 - 3/7/87)

FIGURE 7.9

Contour diagram of temperature recorded every three hours and plotted as time elasped against depth.
(7/7/86 0920 h to 8/7/86 0200 h)

Figure 7.9

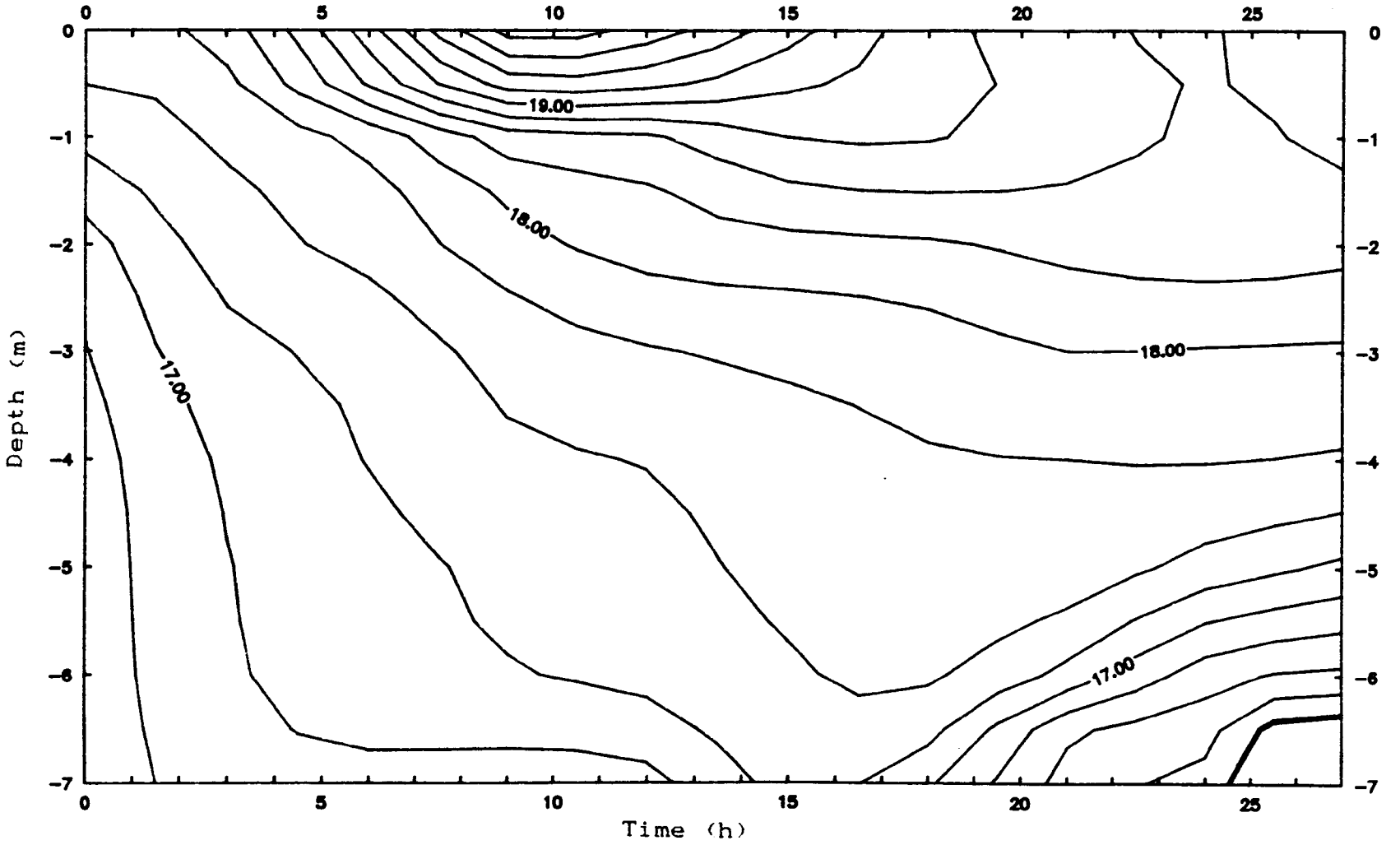


FIGURE 7.10

Irradiance profiles for inside
and outside the mesocosm.
(One to seven metres)

FIGURE 7.11

Irradiance profiles inside the bag
with the curtain raised then lowered.
(One to seven metres)

Figure 7.10

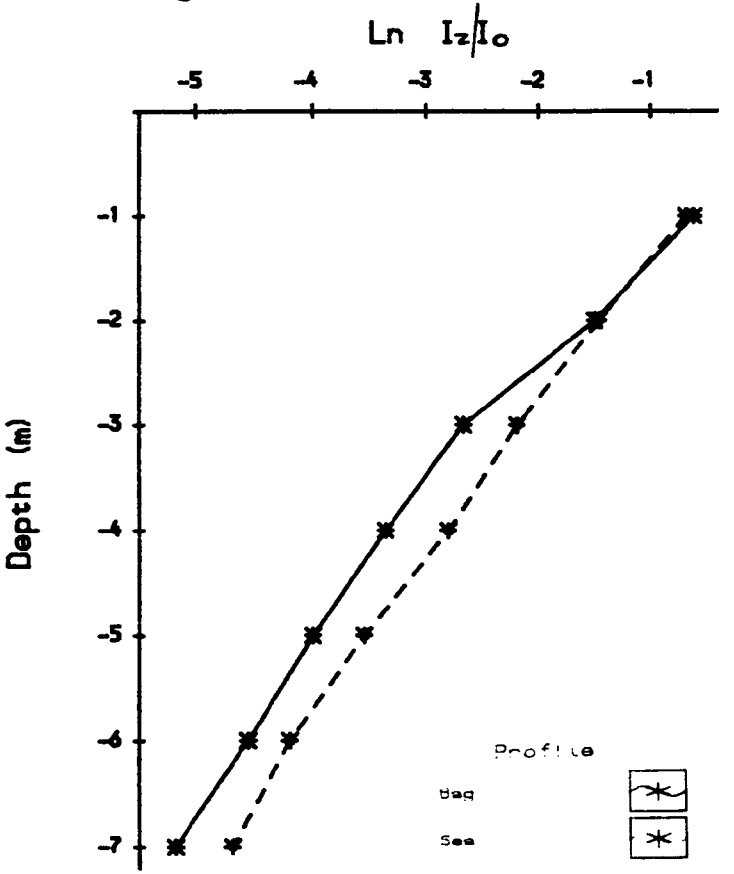


Figure 7.11

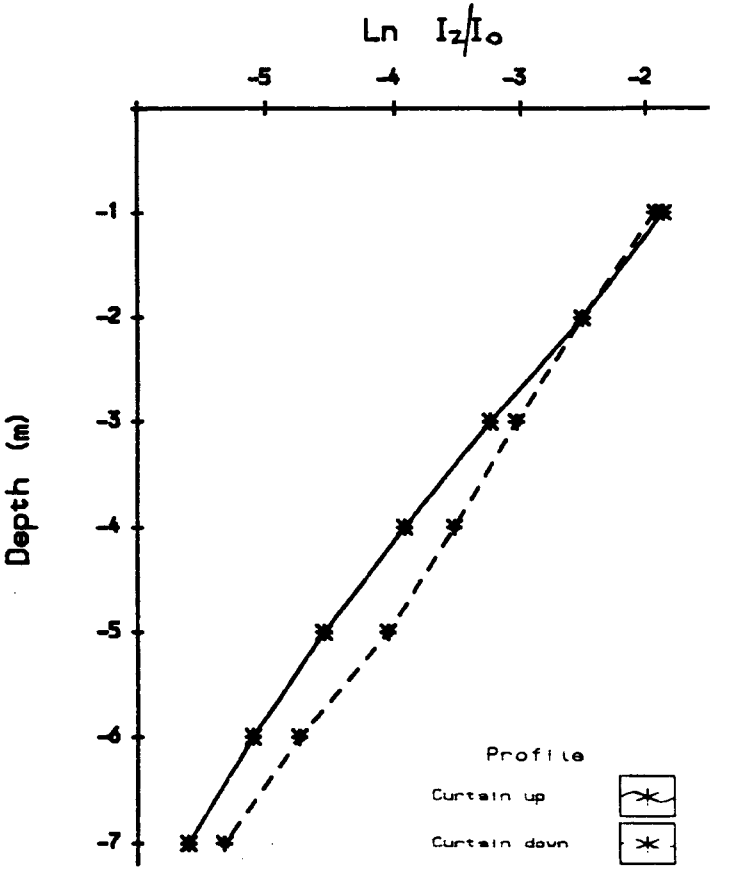


FIGURE 7.12

Irradiance profiles taken within the bag
Profiles at 1030 h and 1400 h 10/7/86.

FIGURE 7.13

Irradiance profiles taken within the bag
Profiles at 0900, 1200 and 1810 h 2/7/86.

Figure 7.12

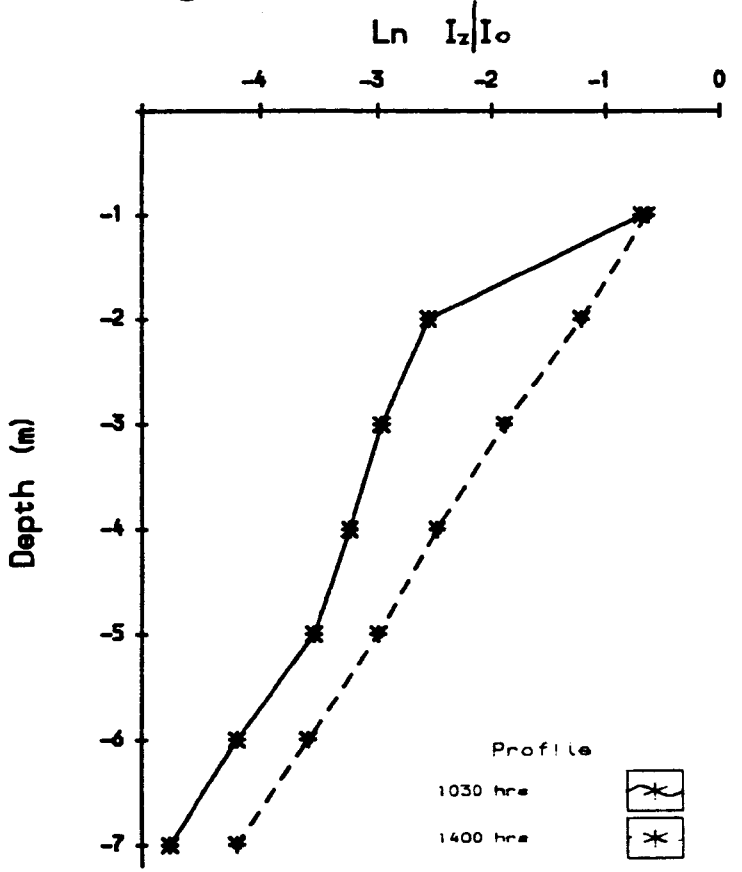


Figure 7.13

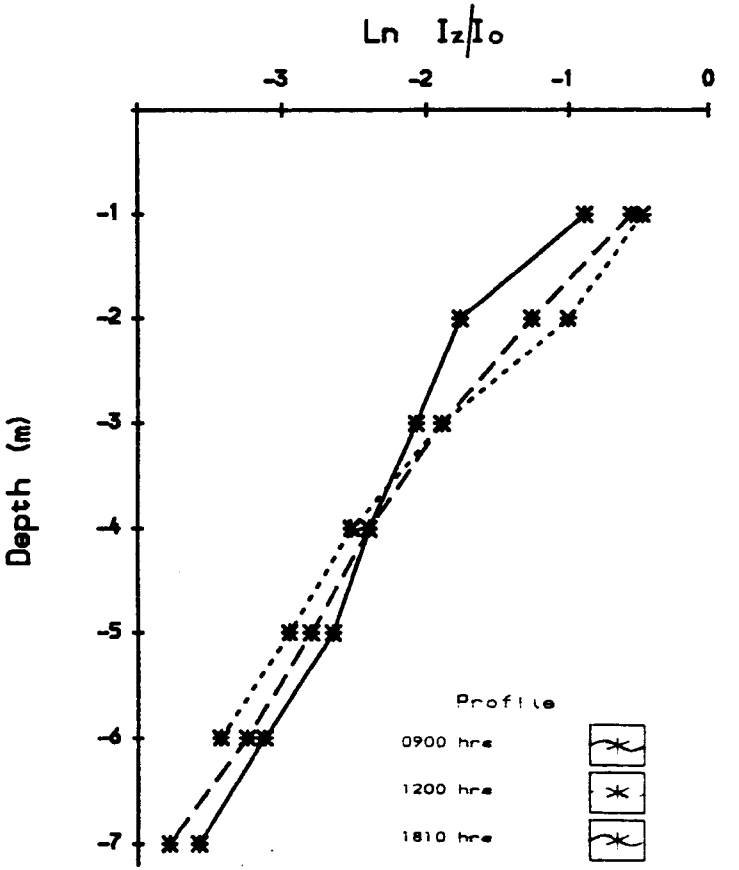


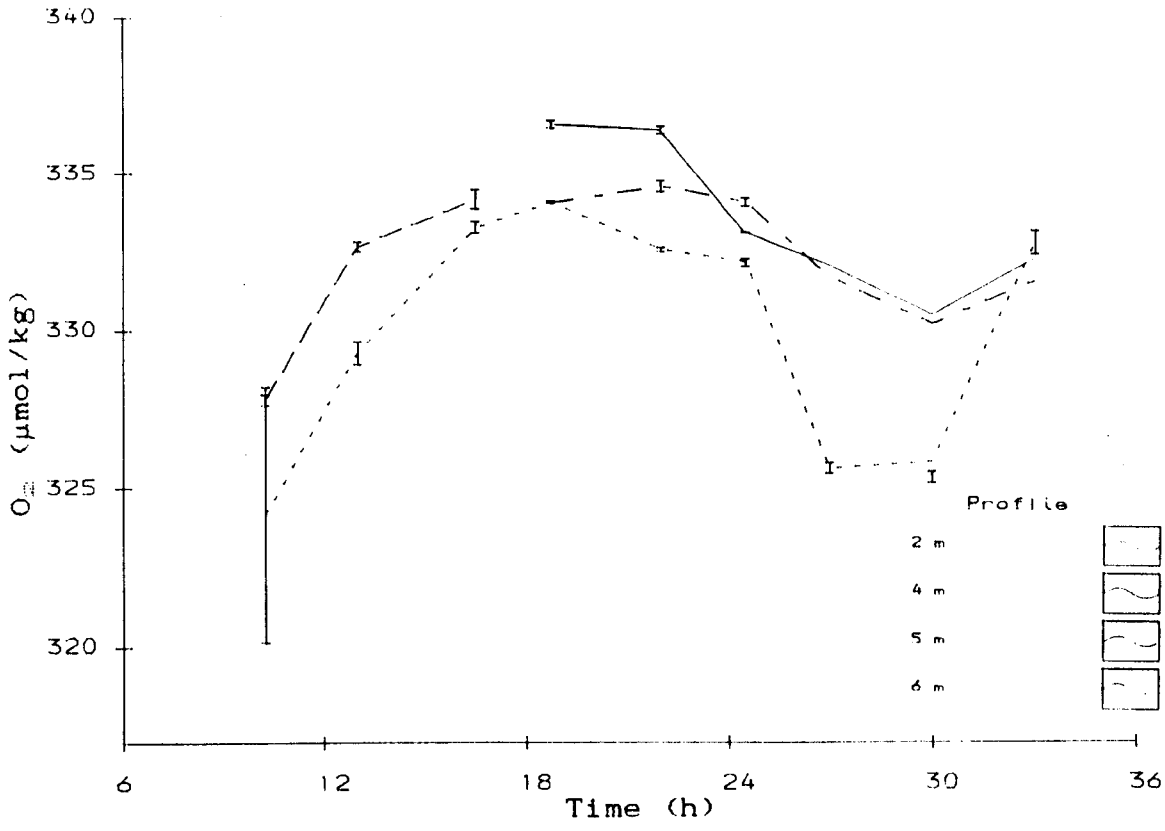
FIGURE 7.14

Observed *in situ* oxygen concentrations
at depths 2m, 4m, 5m and 6m.
(1030 h 2/7/86 to 0900 h 3/7/86)
Note :
Molar scale on Y axis not equivalent in Fig. 7.15

FIGURE 7.15

Observed *in situ* TCO_2 concentrations
at depths 2m, 4m, 5m and 6m.
(1030 h 2/7/86 to 0900 h 3/7/86)
Note :
Molar scale on Y axis not equivalent in Fig. 7.14

Figure 7.14



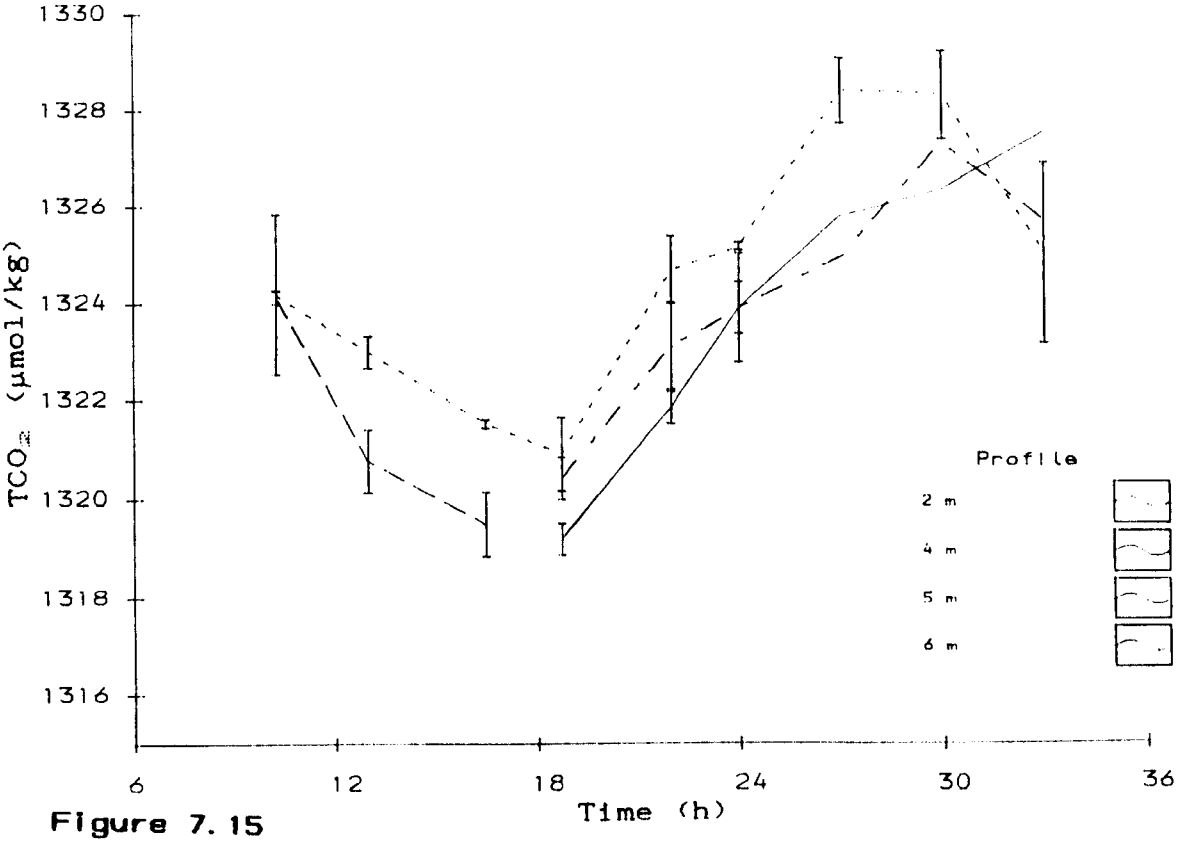


Figure 7.15

FIGURE 7.16

Observed and corrected profile of oxygen
in situ concentration at 4 m depth.
(2/7/86 1030 h to 3/7/86 0900 h)

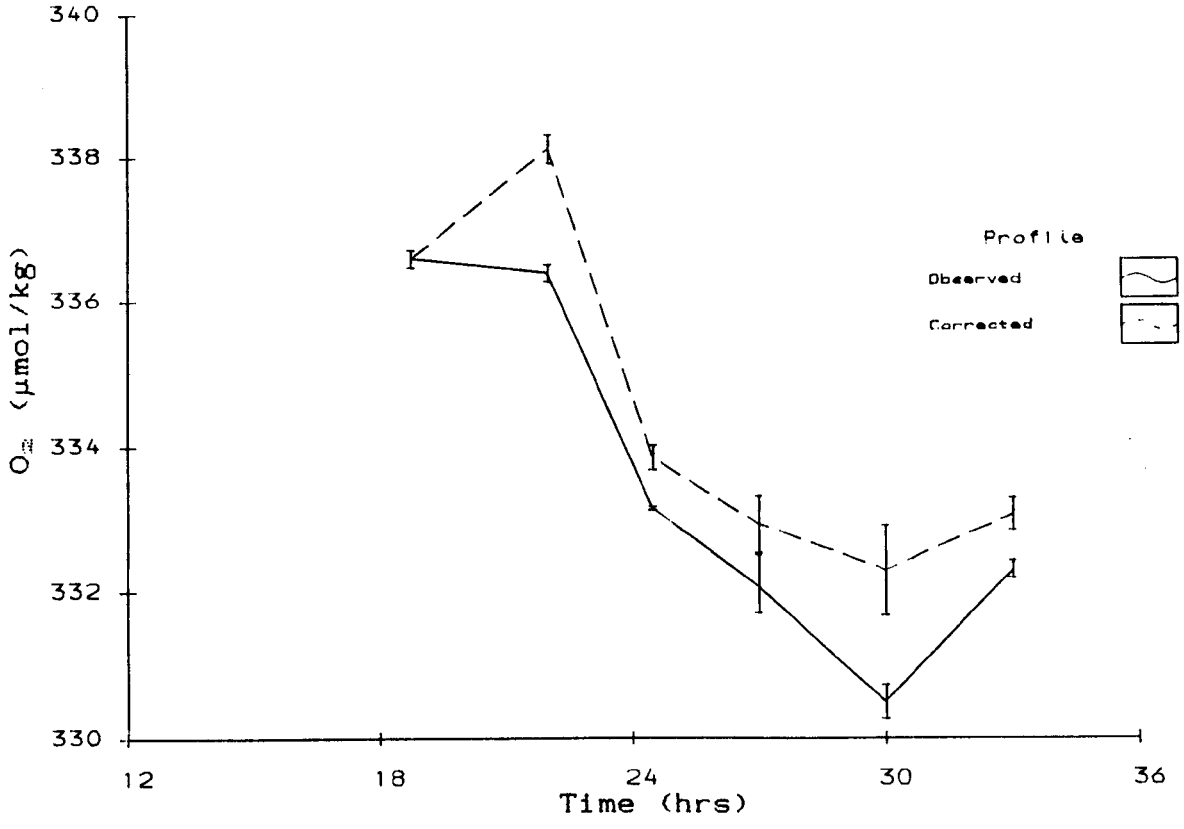
Note :
Molar scale on Y axis not equivalent in Fig. 7.17

FIGURE 7.17

Observed and corrected profile of TCO_2
in situ concentration at 4 m depth.
(2/7/86 1030 h to 3/7/86 0900 h)

Note :
Molar scale on Y axis not equivalent in Fig. 7.16

Figure 7.16



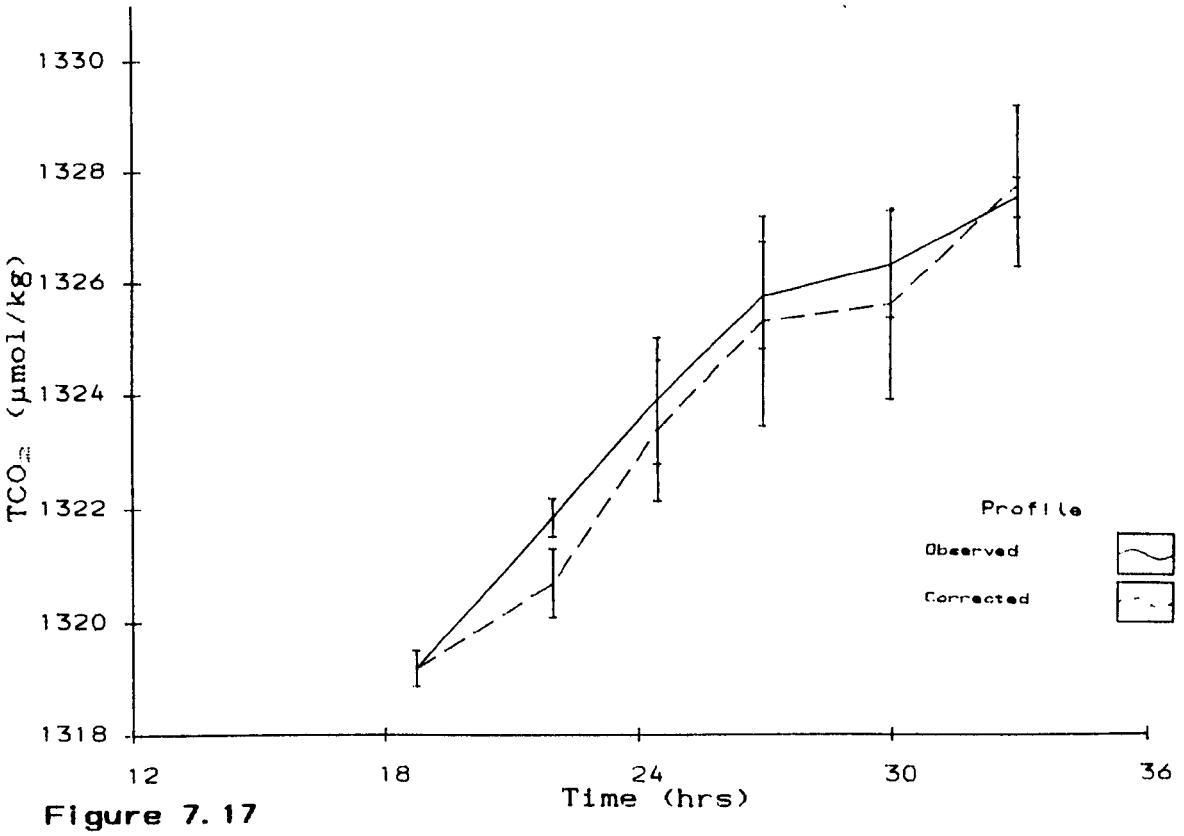


Figure 7.17

FIGURE 7.18

Observed *in situ* oxygen concentrations
at depths 2 m, 3m and 4 m.
(7/7/86 1030 h to 8/7/86 0230 h)

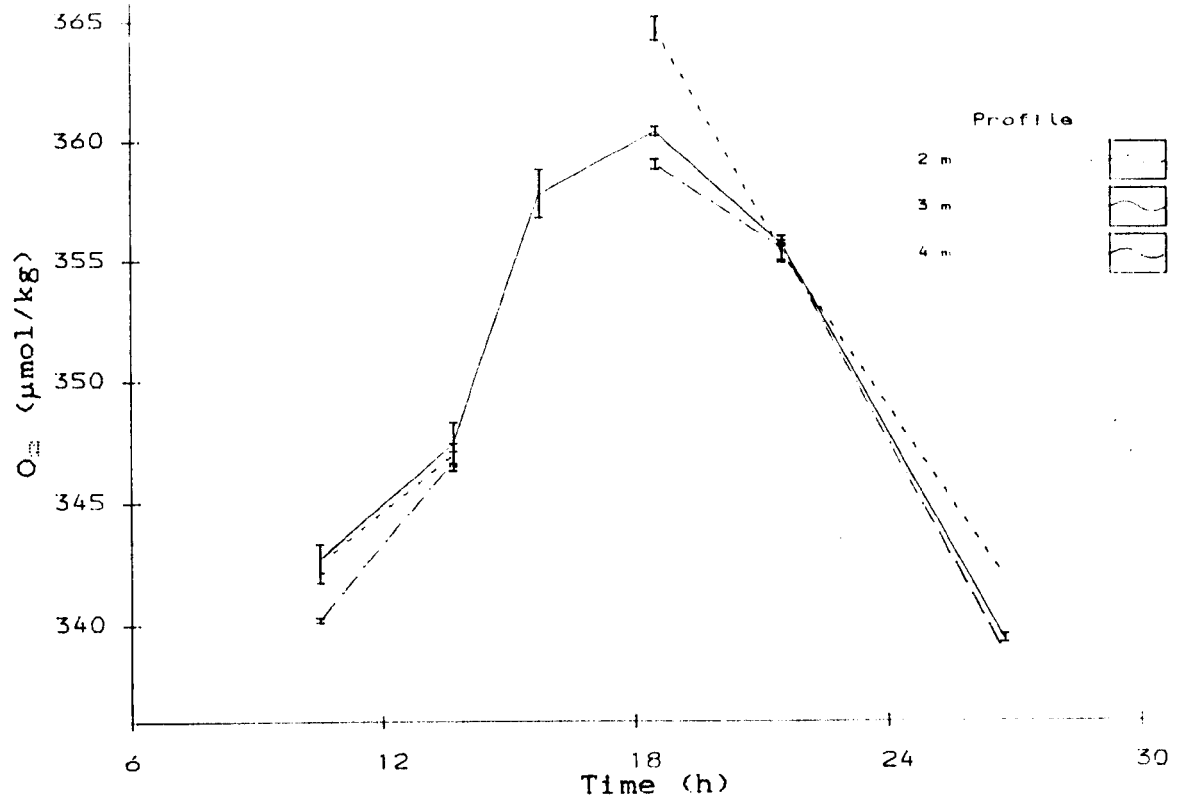
Note :
Molar scale on Y axis not equivalent in Fig. 7.19

FIGURE 7.19

Observed *in situ* TCO_2 concentrations
at depths 2 m, 3 m and 4m.
(7/7/86 1030 h to 8/7/86 0230 h)

Note :
Molar scale on Y axis not equivalent in Fig. 7.18

Figure 7.18



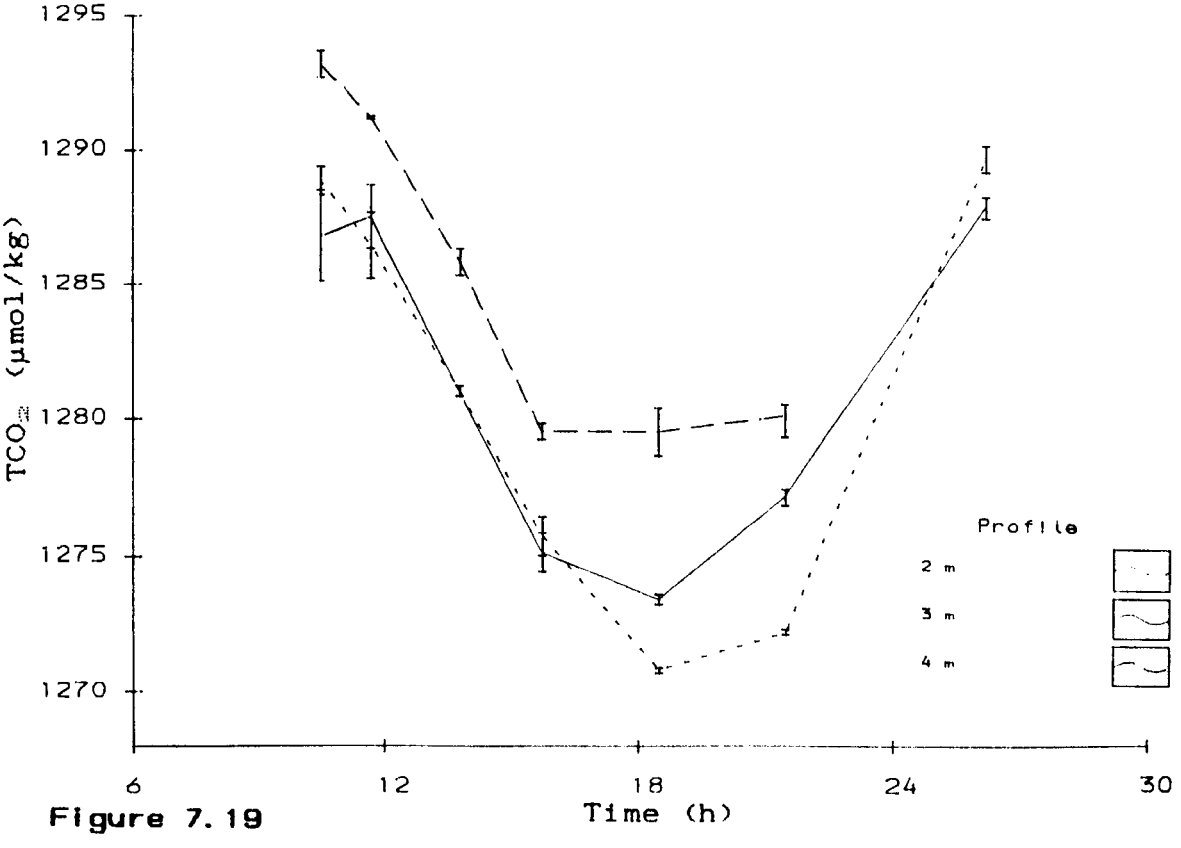


Figure 7.19

FIGURE 7.20

Observed and corrected profile of oxygen
in situ concentration at 3 m depth.
(7/7/86 1030 h to 8/7/86 0230 h)

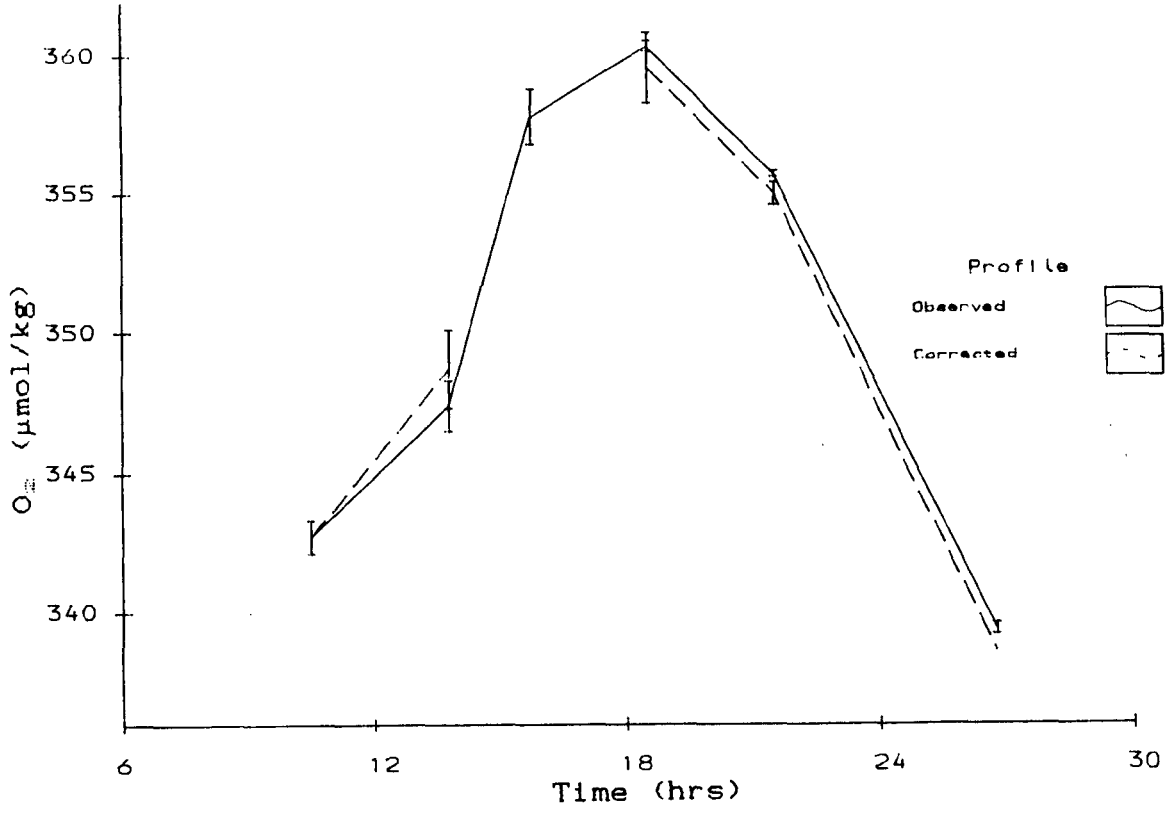
Note :
Molar scale on Y axis not equivalent in Fig. 7.21

FIGURE 7.21

Observed and corrected profile of TCO_2
in situ concentration at 3 m depth.
(7/7/86 1030 h to 8/7/86 0230 h)

Note :
Molar scale on Y axis not equivalent in Fig. 7.20

Figure 7.20



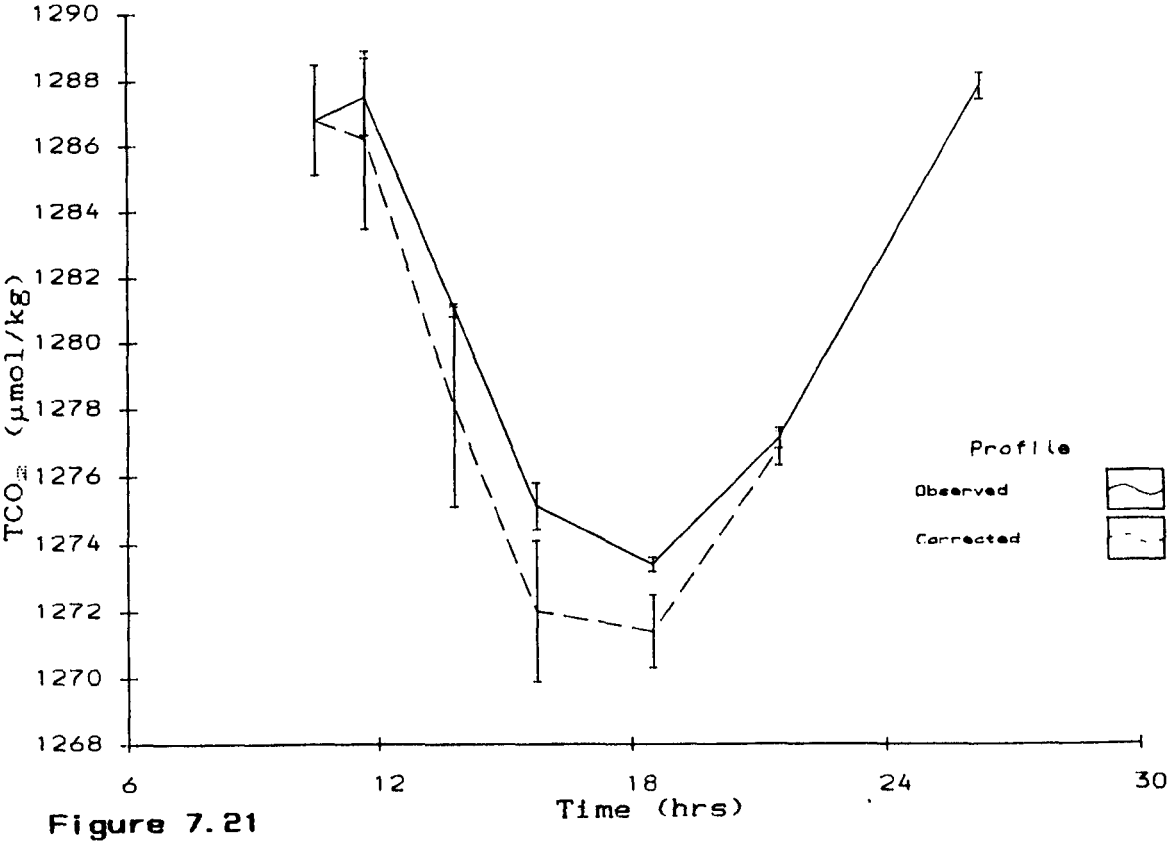


Figure 7.21

FIGURE 7.22

Correlation and regression line of all paired *in situ* concentrations of TCO_2 and oxygen measured during the period (2/7/86 1030 h to 3/7/86 0900 h)

Correlation = 37 % Molar ratio = 1.89
With one data point removed as indicated on the diagram
Correlation = 49 % Molar ratio = 1.45

FIGURE 7.23

Correlation and regression line of all paired *in situ* concentrations of TCO_2 and oxygen measured during the period (7/7/86 1030 h to 8/7/86 0230 h)

Correlation = 84 % Molar ratio = 1.30

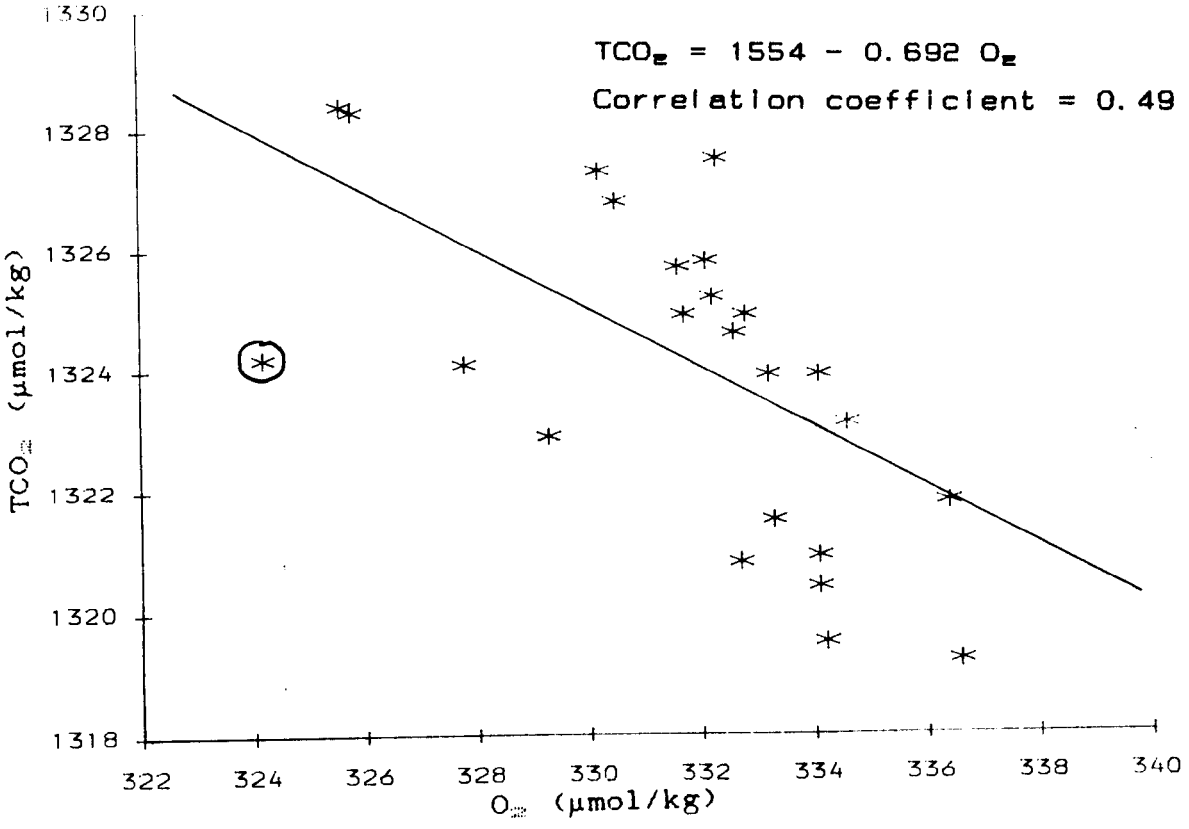
Figure 7.22

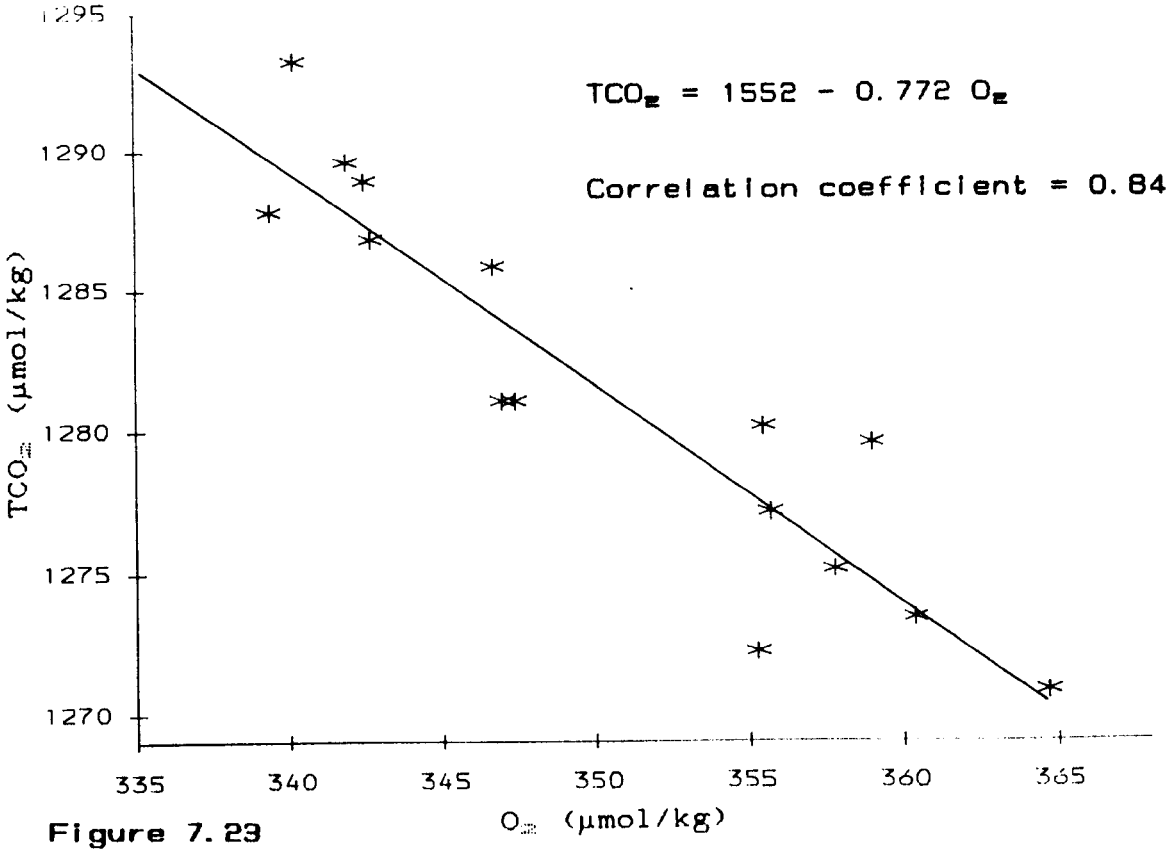
$TCO_2 = 1499 - 0.528\ O_2$

Correlation coefficient = 0.37

$TCO_2 = 1554 - 0.692\ O_2$

Correlation coefficient = 0.49





$TCO_2 = 1552 - 0.772\ O_2$

Correlation coefficient = 0.84

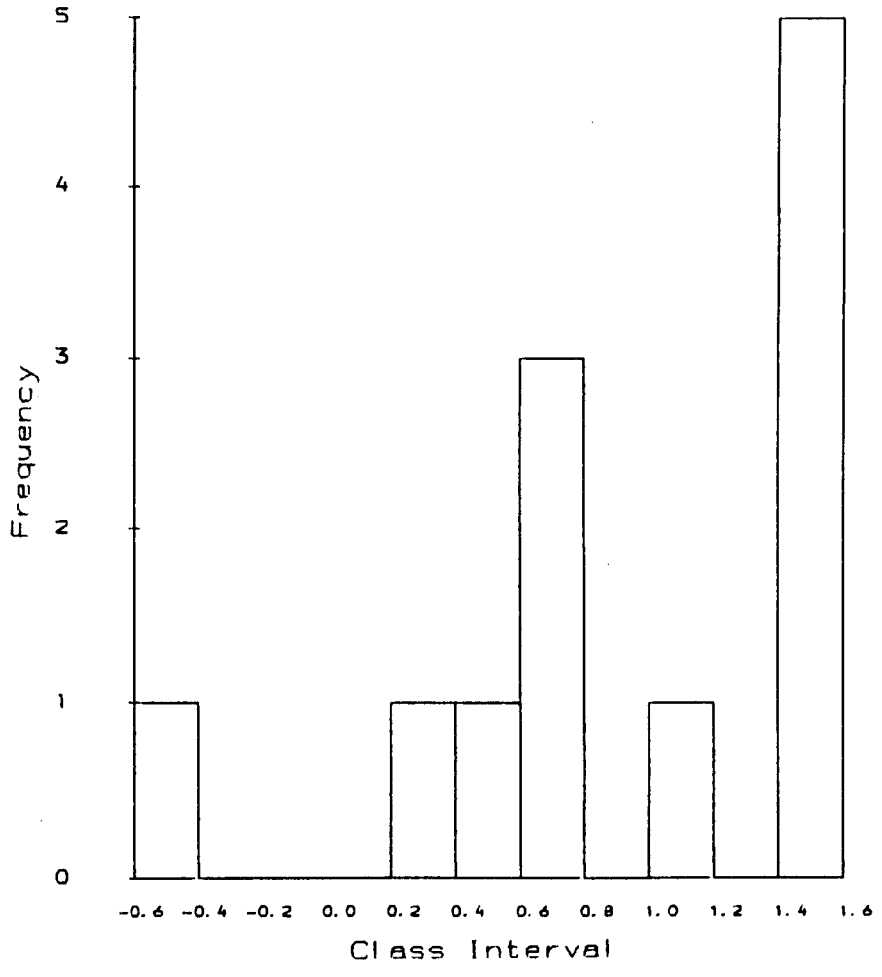
Figure 7.23

FIGURE 7.24

Frequency histogram of observed
molar ratios (night-time measurements)

Daytime molar ratios : 0.41, 1.33, 1.38, 1.43

(Taken from Table 7.10)



* Missing ratio = 13.10

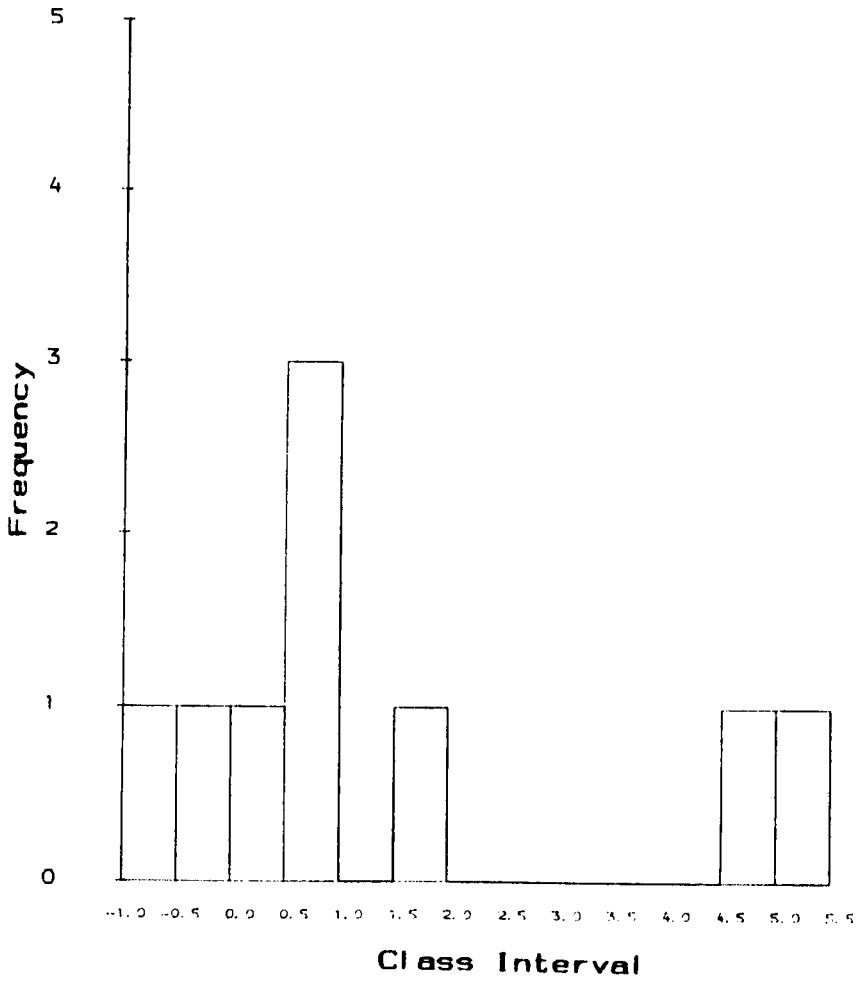
Figure 7.24

FIGURE 7.25

Frequency histogram of corrected
molar ratios (night-time measurements)

Daytime molar ratios : 0.72, 0.80, 1.10, 1.39

(Taken from Table 7.10)



* Missing ratios = -14.0, -8.55

Figure 7.25

TABLE 7.1

2-3 July observed oxygen concentration
In situ (µmol/kg, mean +/- 1 S.E.)

TABLE 7.1

2-3 July observed oxygen concentration in situ (µmol/kg)

Time/ Date	1030 2/7	1300 2/7	1630 2/7	1845 2/7	2200 2/7	0030 3/7	0300 3/7	0600 3/7	0900 3/7
Depth									
2 m	324.2 +/- 4.0	329.3 +/- 0.4	333.3 +/- 0.2	334.1 +/- 0.1	332.6 +/- 0.1	332.2 +/- 0.1	325.6 +/- 0.2	325.8 +/- 0.7	332.8 +/- 0.4
4 m				336.6 +/- 0.1	336.4 +/- 0.1	333.2 +/- 0.1	332.1 +/- 0.4	330.5 +/- 0.2	332.3 +/- 0.1
5 m	327.8 +/- 0.2	332.7 +/- 0.2	334.2 +/- 0.3						
6 m				334.1 +/- 0.1	334.6 +/- 0.2	334.1 +/- 0.1	331.7 +/- 0.3	330.2 +/- 0.6	331.6 +/- 0.4

TABLE 7.2

2-3 July observed TCO_2 concentration
In situ (μmol/kg, mean +/- 1 S.E.)

TABLE 7.2

2-3 July observed TCO_2 concentration in situ (μmol/kg)

Time/ Date	1015 2/7	1300 2/7	1630 2/7	1845 2/7	2200 2/7	0000 3/7	0300 3/7	0600 3/7	0900 3/7
Depth									
2 m	1324.2 +/- 1.7	1322.9 +/- 0.3	1321.5 +/- 0.1	1320.9 +/- 0.7	1324.6 +/- 0.7	1325.2 +/- 0.1	1328.4 +/- 0.7	1328.3 +/- 0.9	1324.9 +/- 1.9
4 m				1319.2 +/- 0.3	1321.8 +/- 0.3	1323.9 +/- 1.1	1325.8 +/- 1.0	1326.3 +/- 1.0	1327.5 +/- 0.4
5 m	1324.1 +/- 0.1	1320.8 +/- 0.6	1319.5 +/- 0.7						
6 m				1320.4 +/- 0.4	1323.1 +/- 0.9	1323.9 +/- 0.5	1324.9 +/- 1.0	1327.3 +/- 1.2	1325.7 +/- 0.6

TABLE 7.3

2-3 July observed and corrected concentration O_2 and TCO_2 *in situ* (μmol/kg, mean +/- 1 S.E.)

TABLE 7.3

2-3 July Oxygen and Total Carbon Dioxide concentration

Observed and corrected concentration in situ (µmol/kg)

4 m depth

Time / Date	1845 2/7	2200 2/7	0030 3/7	0300 3/7	0600 3/7	0900 3/7
Oxygen observed	336.6 +/- 0.1	336.4 +/- 0.1	333.2 +/- 0.4	332.1 +/- 0.2	330.5 +/- 0.4	332.3 +/- 0.1
Oxygen corrected	336.6 +/- 0.1	338.1 +/- 0.2	333.9 +/- 0.5	332.9 +/- 0.4	332.3 +/- 0.6	333.1 +/- 0.2
TCO_2 observed	1319.2 +/- 0.3	1321.8 +/- 0.3	1323.9 +/- 1.1	1325.8 +/- 1.0	1326.3 +/- 1.0	1327.5 +/- 0.4
TCO_2 corrected	1319.2 +/- 0.3	1320.7 +/- 0.6	1323.4 +/- 1.2	1325.3 +/- 1.9	1325.6 +/- 1.7	1327.7 +/- 1.5

TABLE 7.4

7 July observed oxygen concentration
In situ (μmol/kg, mean +/- 1 S.E.)

TABLE 7.4

7 July observed oxygen concentration in situ (µmol/kg)

Time/ Date	1030 7/7	1140 7/7	1350 7/7	1545 7/7	1825 7/7	2125 7/7	0245 8/7
Depth (m)							
2 m	342.5 +/- 0.8		347.0 +/- 0.4		364.7 +/- 0.5	355.3 +/- 0.4	341.9 +/- 0.2
3 m	342.7 +/- 0.6		347.4 +/- 0.9	357.8 +/- 1.0	360.4 +/- 0.2	355.7 +/- 0.1	339.4 +/- 0.2
4 m	340.2 +/- 0.1		346.7 +/- 0.4		359.0 +/- 0.2	355.5 +/- 0.5	338.8 +/- 0.2

TABLE 7.5

7 July observed TCO_2 concentration
In situ (μmol/kg, mean +/- 1 S.E.)

TABLE 7.5

7 July observed TCO_2 concentration in situ (μmol/kg)

Time/ Date	1030 7/7	1140 7/7	1350 7/7	1545 7/7	1825 7/7	2125 7/7	0215 8/7
Depth (m)							
2 m	1288.9 +/- 0.5	1286.4 +/- 1.2	1281.0 +/- 0.2	1275.7 +/- 0.7	1270.8 +/- 0.5	1272.2 +/- 0.1	1289.6 +/- 0.5
3 m	1286.8 +/- 1.7	1287.5 +/- 1.2	1281.0 +/- 0.2	1275.1 +/- 0.7	1273.4 +/- 0.2	1277.1 +/- 0.3	1287.8 +/- 0.4
4 m	1293.2 +/- 0.5	1291.2 +/- 0.1	1285.8 +/- 0.5	1279.5 +/- 0.3	1279.5 +/- 0.9	1280.1 +/- 0.4	

TABLE 7.6

7 July observed and corrected concentration O_2 and TCO_2 *in situ* (μmol/kg, mean +/- 1 S.E.)

TABLE 7.6

7-8 July Oxygen and Total Carbon Dioxide concentration

Observed and corrected concentration in situ (μmol/kg)

3 m depth

Time/ Date	1030 7/7	1140 7/7	1350 7/7	1545 7/7	1825 7/7	2125 7/7	0230 8/7
Oxygen observed	342.7 +/- 0.6		347.4 +/- 0.9	357.8 +/- 1.0	360.4 +/- 0.2	355.7 +/- 0.1	339.4 +/- 0.2
Oxygen corrected	342.7 +/- 0.6		348.7 +/- 1.4		359.6 +/- 1.3	355.0 +/- 0.4	338.6 +/- 0.5
TCO_2 observed	1286.8 +/- 1.7	1287.5 +/- 1.2	1281.0 +/- 0.2	1275.1 +/- 0.7	1273.4 +/- 0.2	1277.1 +/- 0.3	1287.8 +/- 0.4
TCO_2 corrected	1286.8 +/- 1.7	1286.2 +/- 2.7	1278.1 +/- 3.0	1272.0 +/- 2.1	1271.4 +/- 1.1	1276.8 +/- 0.5	

TABLE 7.7

2-3 July observed and corrected
molar ratios +/- 1 S.E.
(night-time measurements)

TABLE 7.7

2-3 July observed and corrected molar ratios taken during a night-time period

Time	1845-2200	2200-0030	0030-0300	0300-0600	0600-0900	1845-0600	1845-0300	1845-0000
Observed	(13.1)	0.79 +/- 0.447	(1.44)	(0.35)	(-0.68)	1.17 +/- 0.428	1.45 +/- 0.326	1.50 +/- 0.370
corrected	-0.99 +/- 0.358	0.75 +/- 0.580	(5.29)	(0.72)	(-1.82)	(8.55)	(-14.0)	1.96 +/- 0.706

( ) = A ratio where the standard deviation is close to or greater than the mean for either gas flux, hence error bars for this quotient cannot be calculated.

TABLE 7.8

In vitro comparison of O_2 and TCO_2

TABLE 7.8

Comparison of *in vitro* measurements

Details	Oxygen flux (µmol/kg h)	CO_2 flux (-µmol/kg h)	PQ or RQ	Chlorophyll (µg/l)
7/7/86				
GP	2.24 +/- 0.08	1.91 +/- 0.08	PQ = 1.17 +/- 0.065	
NP	1.87 +/- 0.08	0.85 +/- 0.08		7.8
Resp.	0.37 +/- 0.08	1.06 +/- 0.04	RQ = 2.87 +/- 0.567	
8-9/7/86				
(GP	0.23 +/- 0.02	0.16 +/- 0.03)		
NP	- 0.92 +/- 0.04	- 0.92 +/- 0.04		11.5
Resp.	1.15 +/- 0.04	1.07 +/- 0.04	RQ = 0.93 +/- 0.048	
9/7/86				
GP	2.28 +/- 0.02	2.12 +/- 0.08*	PQ = 1.08 +/- 0.042	
NP	1.56 +/- 0.02	1.02 +/- 0.05*		8.9
Resp.	0.73 +/- 0.02	1.10 +/- 0.07*	RQ = 1.51 +/- 0.104	
9-10/7/86				
(GP	0.23 +/- 0.03	0.23 +/- 0.05)		
NP	- 0.75 +/- 0.03	- 0.76 +/- 0.04		8.5
Resp.	0.99 +/- 0.03	1.10 +/- 0.07	RQ = 1.11 +/- 0.078	
10/7/86				
GP	1.43 +/- 0.06	1.44 +/- 0.06	PQ = 0.99 +/- 0.059	
NP	0.95 +/- 0.07	1.08 +/- 0.06		7.4
Resp.	0.49 +/- 0.07	0.36 +/- 0.06	RQ = 0.74 +/- 0.161	

Details	Oxygen flux (µmol/kg h)	CO_2 flux (-µmol/kg h)	PQ or RQ	Chlorophyll (µg/l)
10-11/7/86				
(GP	0.24 +/- 0.02	0.18 +/- 0.03)		
NP	- 0.56 +/- 0.03	- 0.24 +/- 0.04		7.7
Resp.	0.79 +/- 0.03	0.41 +/- 0.03	RQ = 0.52 +/- 0.043	
11/7/86				
GP	1.66 +/- 0.04	1.56 +/- 0.05	PQ = 1.06 +/- 0.043	
NP	0.94 +/- 0.05	0.59 +/- 0.05		8.1
Resp.	0.71 +/- 0.03	0.96 +/- 0.06	RQ = 1.35 +/- 0.102	

* = Light and dark bottles fixed after incubation finished and concentration obtained corrected for volume change.

Original data is tabulated in the appendix.

TABLE 7.9

Comparison of net community activity as estimated by *in situ* and *in vitro* measurements of O_2 and TCO_2.

TABLE 7.9

Comparison of net community activity

In situ and in vitro measurements of TCO_2 and O_2 (µmol/kg h)

Details	Day		Night	
	Oxygen (µmol/kg h)	TCO_2 (µmol/kg h)	Oxygen (µmol/kg h)	TCO_2 (µmol/kg h)
7/7/86				
In situ	2.24 +/- 0.08	1.69 +/- 0.20		
In vitro	1.87 +/- 0.08	0.85 +/- 0.08		
8-9/7/86				
In situ			- 1.81 +/- 0.03	- 1.35 +/- 0.06
In vitro			- 0.92 +/- 0.04	- 0.92 +/- 0.04
9/7/86				
In situ	1.92 +/- 0.03	1.39 +/- 0.07		
In vitro	1.56 +/- 0.02	1.02 +/- 0.05*		
9-10/7/86				
In situ			- 1.04 +/- 0.03	- 1.58 +/- 0.07
In vitro			- 0.75 +/- 0.03	- 0.76 +/- 0.04

Details	Day		Night	
	Oxygen (µmol/kg h)	TCO_2 (µmol/kg h)	Oxygen (µmol/kg h)	TCO_2 (µmol/kg h)
10/7/86				
In situ	0.50 +/- 0.03	1.23 +/- 0.03		
In vitro	0.95 +/- 0.07	1.08 +/- 0.06		
10-11/7/86				
In situ			- 0.58 +/- 0.05	- 0.31 +/- 0.06
In vitro			- 0.56 +/- 0.03	- 0.24 +/- 0.04
11/7/86				
In situ	0.56 +/- 0.06	0.40 +/- 0.04		
In vitro	0.94 +/- 0.05	0.59 +/- 0.05		

* = Light and dark bottles for incubation, fixed and corrected for volume change.

TABLE 7.10

Observed and corrected molar ratios as determined from *in situ* measurements of O_2 and TCO_2.

TABLE 7.10

Observed and corrected molar ratios calculated from *in situ* measurements (3 m depth)

Date/Time	Observed	Corrected
Day **7/7/86**	1.33 +/- 0.178	0.80 +/- 0.159
Night **7/7/86**	0.76 +/- 0.157	0.63 +/- 0.099
Night **8-9/7/86**	0.75 +/- 0.035	(- 0.27)
Day **9/7/86**	1.38 +/- 0.068	1.01 +/- 0.073
Night **9-10/7/86**	1.52 +/- 0.076	(4.79)
Day **10/7/86**	0.41 +/- 0.034	0.72 +/- 0.070
Night **10-11/7/86**	0.54 +/- 0.114	(0.22)
Day **11/7/86**	1.43 +/- 0.197	1.39 +/- 0.310

( ) = A ratio where the standard deviation is close to or greater than the mean for either gas flux, hence precision cannot be calculated for this ratio.

CHAPTER 8

MESOCOSM EXPERIMENT, LOCH EWE, SCOTLAND

The following section deals with results obtained during a series of experimental measurements undertaken in a mesocosm situated in a sea-loch at LochEwe, Scotland. Measurements were made from the twelfth of August through to the twenty-sixth of August 1987.

8.1 Chlorophyll measurements

Throughout the experimental period, intermittant fluorescence profiles were recorded using the Chelsea Instruments Aquatracka. These profiles indicated a surface maximum with a secondary sub-surface maximum at approximately 1 - 2.5 m depth, of roughly 10 mg Chl a m^{-3}. An attempt was made to calibrate the profiles by sampling frequently discrete water samples taken from the bag, using the Niskin water sampler. Chlorophyll concentrations recorded throughout the experimental period are detailed in the data appendix for Scotland. Unfortunately insufficient discrete samples were obtained to permit an accurate calibration, nevertheless relative profiles did show that the chlorophyll levels were higher inside the bag than outside.

8.2 Irradiance Measurements

Irradiance profiles were taken at regular intervals inside and outside the bag. The intention being to monitor any adverse effects of the mesocosm on the light field.

Quanta measurements within the bag suggested a compensation depth (1% of surface light) at approximately 10m which was much reduced to that outside the enclosure (15-20m) (Figs 8.1 and 8.2).

The exponential decrease in the light field both inside and outside the bag is given for two different profiles taken during the course of the experiment. It is apparent that irradiance diminishes at a faster rate in the bag, this could be due to the effect of the bag material reducing angular irradiance entering the bag through the walls or the increased concentration of phytoplankton in the bag. The latter explanation is more plausible as a comparison of light measurements in another enclosure (see Chapter 7), using a black sheet around the sides of a bag indicated that little light entering through the walls into the bag. The majority of light enters through the surface into the mesocosm. Profiles of K_d (attenuation coefficient for downwelling light) within the bag are more irregular than outside suggesting that the walls are providing some degree of internal scattering or shading. An alternative explanation is that upwelling is grossly enhanced within the bag. The ratio of upwelling to downwelling irradiance is termed the irradiance reflectance,

$$R = E_d / E_u$$

However, in the bag, R only accounts for a fraction of the downwelling light ; 2-6 % and outside 1-2 % Thus the bag walls appear to be providing the greatest error with a quantity of sideways scattered and internally reflected light. The bag is reducing the internal irradiance levels by a ratio of 1 - 1.7 over one irradiance profile.

Solar irradiance was recorded during the experimental period as a series of two hourly totals. The original data in units of gcal.cm^{-2} is detailed in the data appendix for Scotland along with corrected data adjusted for use by phytoplankton and recalculated in units of quanta x 10^{15} cm^{-2}.sec^{-1}.

8.3 Wind speed measurements Estimation of gas exchange rates

In order to budget the relative fluxes of O_2 and TCO_2 within the bag, two potential interfering factors need to be accounted for. The effect of physical mixing within the bag will be discussed in greater detail later in this chapter. The second factor is the exchange of gases between the sea and the atmosphere.

It is not possible in this study to make a complete correction for gas exchange due to the limited set of wind measurements, however, approximate calculations are feasible in order to establish the scale of the effect.

Carbon dioxide equilibrates with the atmosphere 10 times more slowly than oxygen (Broecker and Peng 1982). Since the greatest effect will therefore be seen with oxygen, the initial calculations will be made for this gas.

In the absence of an available, direct method for measuring the mass transfer coefficient, wind velocity is commonly used to estimate boundary layer thickness and so exchange rates.

Wind speed was recorded on average twice a day whilst on the raft, prior to sampling in the bag. With these values it is possible to calculate a gas exchange coefficient (K). This coefficient is then used to predict the rate of gaseous exchange at the air/sea interface over a certain time period.

Appendix 4 contains details and a worked example for the calculation of a gas exchange coefficient and rate for oxygen at a particular time and depth.

CALCULATION

Gas transfer can be summarised by the two following equations :

$$F = K [P_{atm(g)} - P_{w(g)}] \quad (1)$$

$$K = D . \alpha . h^{-1} \quad (2)$$

where

$P_{atm(g)}$ = Partial pressure of the specific gas in the atmosphere. (units = atm)

$P_{w(g)}$ = Partial pressure of the specific gas in the water. (units = atm)

K = Gas exchange coefficient (units = mol m^{-2} hr^{-1} atm^{-1})

F = Gas flux (units = mol m^{-2} hr^{-1})

D = Molecular diffusivity (units = m^2 s^{-1})

α = Solubility (units = mol m^{-3} atm^{-1})

h = Surface film thickness (units = m)

where equation (1) is derived from Ficks First Law of Diffusion.

The first method for calculating gas exchange utilises the relationship of K being a square function of wind speed (Tijssen and Eijgenraam 1982).

The second is the exponential relationship between h and wind speed given by Smith (1985). An example of the worked calculation of gas exchange is given in Appendix 4 using the approach of both Tijssen and Eijgenraam (1982) and Smith (1985). For one single given wind speed as used in the calculation a six fold difference in the rate of gas exchange occuring over a particular time period is observed between the two different approaches.

Table 8.1 contains calculated atmospheric loss due to air/sea exchange based on individual values of K and also averaged wind speed and K values for a preceding twelve hour period, following the approach of Tijssen and Eijgenraam (1982). It should be noted that the main sources of error in these estimates of gas exchange are the infrequency of wind speed measurements and that the diurnal change in supersaturation over the time period is not corrected for. It is possible to quantify the relative importance of these two errors.

<u>The effect of changing wind speed</u>
(after Tijssen and Eijgenraam 1982)

If $W = 45\ km.h^{-1}$ $K = 0.5625\ m.h^{-1}$

If $W = 5\ km.h^{-1}$ $K = 0.0070\ m.h^{-1}$

This shows that an eighty-fold difference exists between calculated gas exchange coefficients when the two extreme recorded wind speeds during the experimental period are used in the calculations.

The effect of diurnal change in supersaturation

An observed change of 28% in supersaturation was recorded from 22/08 0600h to 22/08 1800h. Using an average K value of 0.1 $m.h^{-1}$

0600h Flux = 6.53 mmol m^{-2} hr^{-1}
1800h Flux = 12.7 mmol m^{-2} hr^{-1}

It is apparent that errors in wind speed are larger than those from ignoring the diurnal curve in supersaturation. Flux calculations from the bag can be made using a mean wind speed taken from the the previous 12 hours (Table 8.1). However, this is frequently done by using only three values which is not adequate, a more satisfactory practise would be have access to continuous wind profiles, unfortunately not available at LochEwe.

The above estimates of error associated with wind measurements can be recalculated using the method suggested by Smith (1985).

Wind speed

If W = 45 km/h K = 0.173 mol m^{-2} hr^{-1}

If W = 5 km/h K = 0.016 mol m^{-2} hr^{-1}

Use of the exponential fit as described by Smith (1985) leads to an eleven fold difference in the value of the gas exchange coefficient using the maximum and minimum wind speed measured. Alternately, use of the squared function as described by Tijssen on the data provides an eighty fold difference. This is a good indication of the importance of the brief storm when using a squared function to relate exchange to wind speed.

When using the squared function it is advisable to have access to continuous records, a small data set can provide extremely misleading estimates of gas exchange.

In conclusion, two approaches are used in the calculation of gas exchange rates. Use of the squared function as described by Tijssen provides higher estimated rates but a thorough application is limited by the sensitivity of the approach to a small number of wind speed measurements.

Taking an average flux, there is approximately 10 mmoles m^{-2} h^{-1} being lost from the first one metre to the atmosphere. Fluxes observed at three metres for oxygen approximate at one mmole m^{-3} h^{-1}. This implies that the air/sea exchange is not minimal, however sufficient wind speed data does not exist to enable to quantify the effect adequately. Coupled with this is the conclusion drawn from the temperature and dye diffusion measurements described later in the section. These indicate a complicated mixing regime within the bag and would prevent extrapolation of a surface exchange to a depth within the bag by use of a singular diffusion coefficient.

8.4 Temperature Measurements

Temperature measurements are made within the bag with three main objectives.

1) First, to establish the similarity of temperature structure and hence physical characteristics within and without the bag.

A series of temperature profiles taken inside the enclosure using the Chelsea Instruments Aquatracka indicated a shallow wind-mixed layer depth of 1m followed by a weakly stratified region down to 15m.

Within the bag a continual, weak thermocline persisted from 2 to 3 m. Exterior to the bag a weak thermocline was present at approximately 7 m. Clearly, there were dissimilarities between the inside and outside environments.

2) Second, a time series of temperature was needed in order to establish a region of comparative stability to facilitate the decision over which depths were to be sampled in following the chemical flux.

Figure 8.3 is such a time series with temperatures taken every 2 hours from the thermistor chain data (data in the Appendix) for the time period 25/8 2200 h through to 26/8 0600 h. Convective nocturnal cooling is apparent at the surface. The limit to which convective cooling can penetrate depends on the external air temperature and intensity of salt stratification. Figure 8.4 is an enlarged view of Figure 8.3 giving a more detailed view and once again indicating this convective mixing to 2 m depth.

Figures 8.5, 8.6 and 8.7 show further temperature changes as recorded by the thermistor chain. In these plots hourly values are used starting at 1200 h 25/8. One channel was placed at the surface whilst the remaining ten are at one metre intervals down to 10 m depth. The effects of mixing the bag at thirty six hours into the time series is evident. The series of temperature profiles shows that prior to mixing, the effect of surface heating penetrates down to below three metres depth, though nocturnal convection and mixing was limited to two metres depth. No obvious stable region was apparent after examination of these profiles (Figs 8.6 and 8.7) and as fluxes below six metres were too small to follow with our methods, it was decided that a series of depths should be sampled from 1 - 6 m for maximum coverage.

3) The third aim of recording temperature changes within the mesocosm is to allow the calculation of eddy diffusivity coefficients. These coefficients are calculated under the previously described one-dimensional vertical diffusion model applied to the water column (see Chapter 7, Appendix 1, Appendix 2). The coefficients can then be applied to *in situ* observation of oxygen and TCO_2 gradients and fluxes in order to correct for physical mixing (Appendix 2).

Hourly eddy diffusion coefficients (K_z) were calculated using the thermistor data obtained (an example of this calculation is given in Appendix 1). The continuous temperature profiling permitted a greater number of coefficients to be calculated compared to the Swedish experiment. The coefficients are given in Table 8.3, the surface channel has been ignored in the calculations due to the irregular nature of the profile obtained. This suggests that the thermistor had been exposed to air occassionally due to the action of waves on the surface water in the bag.

Coefficients calculated in the region of the thermocline (3-4 m) should be most reliable as they are in an area where vertical advection is at a minimum and are also beneath the depth of nocturnal convection. However the coefficients are frequently negative and a large range is represented throughout the whole period (Table 8.4).

These results are very similar to those obtained in the Swedish experiment (Chapter 7, section 7.2), in that case, it was assumed to be due to a unrepresentative and insufficient series of temperature measurements. This argument cannot be sustained in this case, a much larger number have been obtained here using the continuous profiles recorded by the thermistor chain, but still with similar results.

This evidence strongly suggests that a simple one dimensional vertical diffusive model for a mesocosm is not adequate or even a useful simplification as suggested by Steele et al (1977).

8.5 Rhodamine dye experiment

An alternative method for estimating the coefficients is by use of a tracer such as a dye. Hesslein and Quay (1973) describe the method and assumptions behind this approach.

A known amount of dye was added at 1416 h on 27/8/87 to the surface of the bag. A total of four profiles were made in the bag following addition of the dye. The last profile was repeated on a different more sensitive channel all five profiles are shown giving the distribution of the dye following addition at the surface (Figures 8.8 to 8.12). The dye profiles indicate a progressive movement down the bag by the dye, though not completely smooth or regular. No obvious anomalies are present as observed during a dye addition by Steele et al (1977) in the same mesocosm although a stepping is evident. This stepping is mirrored by the corresponding temperature profiles for the time period following the dye addition (Figure 8.13). The stepping is a gradual reversion of the temperature distribution to that prior to mixing.

Eddy diffusion coefficients can be calculated using a similar approach to that used with the temperature profiles. The results are similar to those obtained by temperature in that they do not support the simple one dimensional model due again to the irregularity of the size and sign of the coefficient (Table 8.4).

A mass balance of the dye from the observed concentrations can be made (Table 8.5) and the deficits observed suggests that horizontal advection is present in the bag and that combined with the nature of the coefficients determined both by temperature and dye distribution, the physics of the bag cannot be adequately described in terms of vertical Fickian diffusion alone.

8.6 Chemical measurements of O_2 and TCO_2

Chemical measurements taken during the experiment can be separated into three sections.

The first section consists of an initial series of six hourly *in situ* measurements and corresponding *in vitro* incubations starting at 1800 h 12/08/87 through to 1745 h 14/08/87. Observed *in vitro* and *in situ* concentrations are detailed in the data Appendix for Scotland.

The second section followed mixing of the bag. A series of *in situ* measurements and *in vitro* incubations were undertaken at twelve hour intervals. This began at 1700 h 18/08/87 through until 0615 h 20/08/87. Observed *in vitro* and *in situ* concentrations are detailed in the data Appendix for Scotland.

Following another attempt at mixing the bag the third experimental period was undertaken. A series of *in situ* measurements and *in vitro* incubations were undertaken at twelve hour intervals. This began at 1800 h 21/08/87 through to 0600 h 24/08/87. Observed *in vitro* and *in situ* concentrations are detailed in the data Appendix for Scotland.

1) First sampling period.

The in situ measurements for both O_2 and TCO_2 are shown in Figures 8.14 and 8.15. The expected diurnal curve is not at all evident and the observed changes difficult to explain satisfactorily. A series of depth profiles were then initiated to allow a closer examination of the change of gas concentration with depth in the bag. These indicated an intense gradient in the bag for both gases and the surface being highly supersaturated with respect to oxygen. A change of approximately 50 μmol/kg in oxygen occurred over a depth of five metres. This strong spatial gradient meant that the sampling technique used could be inadequate under those conditions.

The main supposition, and indeed advantage, with sampling in situ within a mesocosm is the ability to sample the same water mass at the same depth consistently. Such a gradient would mean that any slight error in depth sampled, or water movement up and down in the bag by say, tidal forcing could produce a change in gas concentration that would aliase any diel changes occurring within the bag.

Following examination of the data obtained in situ it was decided to mix the bag and attempt to reduce the gradients observed in concentrations of these two gases. It was apparent that in order to establish the biological signal present in the bag, the strong physio-chemical gradients would have to be greatly reduced.

Prior and subsequent to mixing, oxygen profiles were taken to follow the progression and distribution of supersaturation of the gas with depth. The enclosure was mixed twice and the measurements taken after each mixing episode plotted in Figure 8.16. The figure shows that the gradient was reasonably dispersed with a slight drop in the percentage supersaturation.

Combined with measurements being made *in situ*, two *in vitro* incubations were carried out. The estimated rates of production and respiration from both incubations are detailed in Table 8.6 along with all other *in vitro* incubations carried out during the entire experimental period. The first incubation indicates a drop in oxygen in the dark not matched with a rise in TCO_2. The second has an unexpected drop in oxygen in the light accompanied by a low level of precision. The corresponding TCO_2 incubation indicates a drop in TCO_2 in both the light and dark. These results are difficult to explain satisfactorily. The unusual features of the *in vitro* incubations cannot be explained by the same reasoning offered for the unexpected *in situ* changes.

In addition to production rates it is possible to calculate appropriate PQs and RQs for each incubation. These quotients along with the observed molar ratios for the *in situ* measurements are given in Table 8.7. Although from the nature of the profiles already discussed, realistic molar ratios are not expected they are included for the sake of completeness. It is apparent that neither the *in vitro* or *in situ* measurements are as expected.

Following the mixing of the bag another series of *in situ* measurements and *in vitro* incubations were undertaken every 12 hours.

2) Second sampling period.

The appropriate *in situ* concentrations are shown in Figures 8.17 and 8.18.

Oxygen concentrations (Fig. 8.17) exhibit a diurnal rhythmn however observed TCO_2 changes (Fig. 8.18) show some unusual features. The drop in TCO_2 at 1m during the second night period may be explained by the proximity to the surface and involve either air/sea exchange or the effects of night-time convection.

However the same effect is not observed in the oxygen which equilibrates more rapidly than TCO_2 and should be affected to the same extent in nocturnal mixing. The magnitude of the changes observed at 6m is larger than all other depths. The large drop in TCO_2 from 0615 to 1830 19/08/87 is suprising as there will be reduced irradiance at 6m compared to the other depths, fluorescence profiles indicated the chlorophyll maximum to occur above six metres. In addition, no corresponding rise is observed during the following night period. One explanation is that the bag was not fully mixed to that depth. The gradient can be seen to increase relatively below 4m for TCO_2 and so errors discussed previously for the first sampling period could be responsible, namely an error in the sampling depth.

Photosynthetic and respiratory quotients for in vitro incubations and the molar ratios associated with the water column measurements are given in Table 8.8 as a mean value along with one standard error.The respiratory quotient for incubation 5 is unusually high due to a large observed rise in carbon dioxide not matched by a corresponding depletion of oxygen.

Estimated production and respiration rates from the in vitro incubations carried out during this period are given in Table 8.6 along with all other in vitro incubations carried out during the entire experimental period.

Following the above series of measurements, the bag was mixed once more and six consecutive twelve hourly in situ measurements were made along with two in vitro incubations set up in conjunction with the last three in situ data points, this represents the third and last sampling period.

3) Third sampling period

The results for observed *in situ* concentrations and data from the two incubations are given in the data appendix for Scotland. Figures 8.19 and 8.20 represent observed *in situ* changes for both gases. Figure 8.21 is an expanded graph of Figure 8.20 showing the observed *in situ* concentrations of TCO_2 for the 4, 5 and 6 m depths. These three depths have been expanded upon as four and five metres are the only depths sampled during this period that produce an expected diurnal signal for TCO_2.

A diurnal signal is observed for oxygen concentrations *in situ* down to four metres (Figure 8.19). At 5m an increase is observed during the first daytime period but a decrease in the second. At 6m no daytime increase is observed but a gradual drop in oxygen concentration observed throughout the whole sampling period. Examination of the solar energy records for this time period (Data Appendix - Loch Ewe) shows that the first daytime period received more light than the the second. A compensation depth of 5-6 m is apparent.

The corresponding measurements of TCO_2 are not complementary or consistent with those described of oxygen for the first three metres or the six metres depth. It is apparent (Figure 8.21) that only at 4 and 5 metres depth is a complementary series of fluxes observed.

Photosynthetic and respiratory quotients for *in vitro* measurements and molar ratios for *in situ* fluxes are arranged in Table 8.9. The mean ratios are given plus one standard error. Due to the unusual concentrations observed in the TCO_2 profiles several of the quotients are either negative or extremely high. Estimated rates of production and respiration for the two incubations are detailed in Table 8.6 along with all other *in vitro* incubations taken throughout the entire experimental period.

Correction for physical processes

It is possible to correct observed data to take account of vertical diffusion using a value of Kz (0.2 m^2/h) taken from the literature. Figures 8.22 and 8.23 show both observed and corrected data points for the 3 m depth for oxygen and carbon dioxide. Figure 8.24 contains observed and corrected data for carbon dioxide at the 5 m depth. All observed data has been recalculated using a Kz value of 0.2 m^2/h.

A worked example for the correction of observed data is detailed in Appendix 2. All three corrected or calculated profiles are significantly different. This is the opposite result to the correction of profiles obtained during the Swedish bag experiment (see Chapter 7), however it still does not alter any of the unusual quotients or relative fluxes of the two gases since in this experiment.

In fact the diffusion correction to the 5 m profile for TCO_2 alters the observed diurnal rhythmn and replaces it with a general decrease throughout the period.

Photosynthetic and respiratory quotients for in vitro measurements and molar ratios for in situ fluxes are given in Table 8.9. The mean ratios are given along with one standard error. Due to the unusual concentrations observed in the TCO_2 profiles several of the quotients are either negative or extremely high. Estimated rates of production and respiration for the two in vitro incubations are given in Table 8.6.

8.7 Summary

Previous observations made within a mesocosm (Chapter seven) demonstrated a strong relationship between TCO_2 and oxygen flux both *in situ* and *in vitro*. Attempts to correct the *in situ* measurements for physical mixing and air/sea exchange were hampered by a lack of appropriate data.

Within the current experiment, wind speed data was obtained however continuous wind speed records were not available. A reasonable correction was not possible considering the sparse wind speed data and so was not attempted with the *in situ* fluxes.

Continuous temperature profiles were obtained and a series of eddy diffusion coefficients calculated under the assumptions of a simple vertical diffusion model. In addition a dye experiment was undertaken to provide alternative estimates of the mixing coefficients. Both the temperature and dye observations suggest that the model was too simplistic and did not adequately represent the mixing processes occurring within the bag. A correction to the observed fluxes was therefore not possible.

Measurements made within the Swedish mesocosm showed a diurnal rhythmn for both oxygen and TCO_2. This was not always observed from *in situ* measurements made within the Scottish mesocosm. A number of unusual features were observed both *in situ* and *in vitro*.

Examination of Table 8.6 allows a comparison of all productivity and respiration rates as estimated from *in vitro* incubations during the experiment by both gases. Few similarities exist between the two approaches in either GP, NP or respiration rates. The range of photosynthetic and respiratory quotients is unusally large. Respiratory quotients range from -56.7 to 5.13 with the three PQ values being -1.37, 1.33 and 1.44.

This range is much greater than that observed during work in the Swedish bag (see Chapter seven), also no negative quotients were observed *in vitro* during that experiment.

A comparison of *in situ* and *in vitro* estimates of net community activity by both techniques (Table 8.10) also indicates extensive dissimilarities. This is a direct result of the anomalies mentioned previous regarding the unusual *in vitro* incubations observed, plus the *in situ* rates. Observed molar ratios during the daytime range from -2.98 through to 1.60, the range for the night-time molar ratios is larger -5.82 to 10.15.

FIGURE 8.1

Irradiance profiles for inside
and outside the mesocosm.
(Surface to fourteen metres)

FIGURE 8.2

Irradiance profiles for inside
and outside the mesocosm.
(Surface to twelve metres)

Fig. 8.1

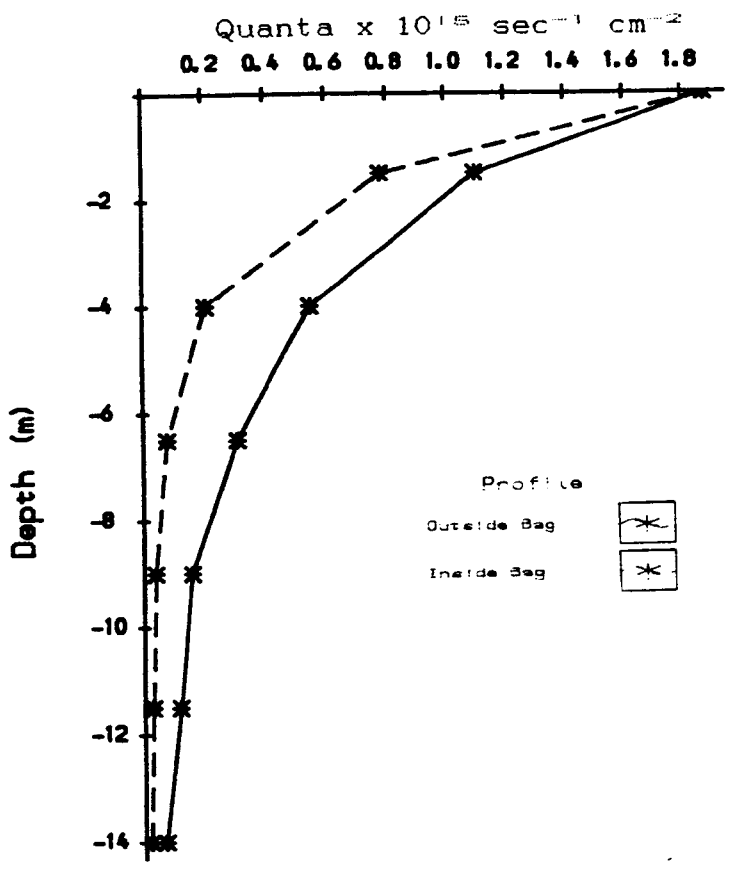

Quanta x 10¹⁵ sec⁻¹ cm⁻²
0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8
Depth (m)
-2
-4
-6
-8
-10
-12
-14
Profile
Outside Bag
Inside Bag

Fig. 8.2

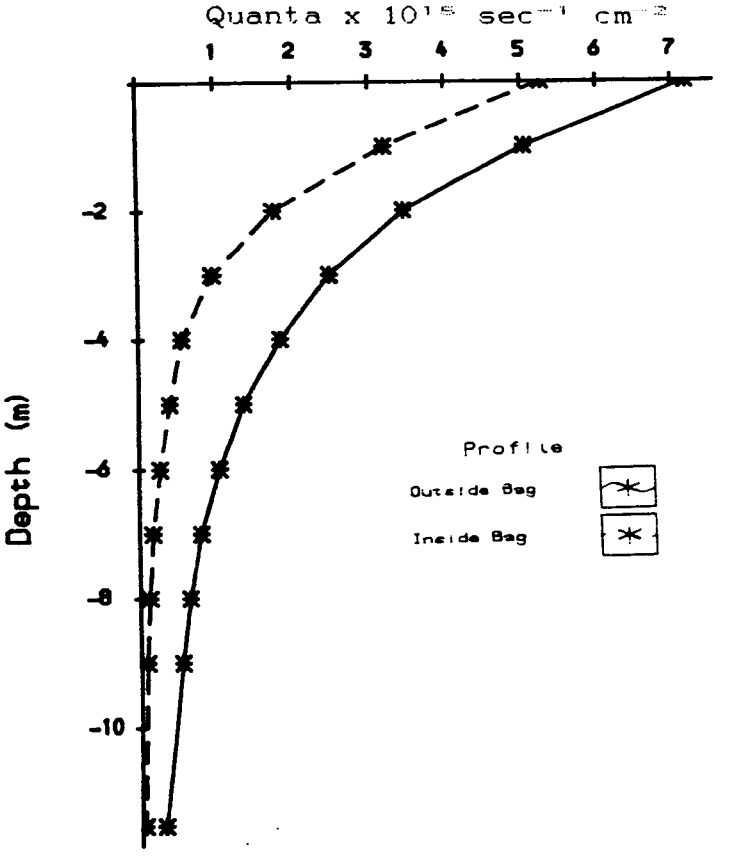

Quanta x 10¹⁵ sec⁻¹ cm⁻²
1 2 3 4 5 6 7
Depth (m)
-2
-4
-6
-8
-10
Profile
Outside Bag
Inside Bag

FIGURE 8.3

Time series of two hourly temperature profiles
(25/8/86 2200 h to 26/8/86 0600 h)

FIGURE 8.4

Figure 8.3 expanded
(Surface to three metres)

Fig. 8.3

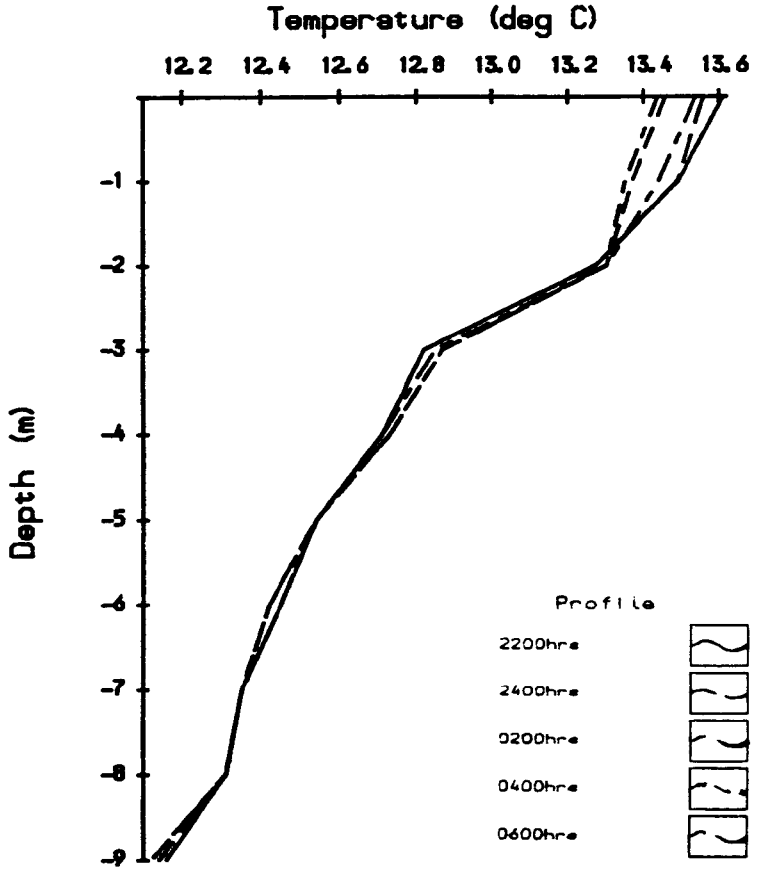

Temperature (deg C)
12.2
12.4
12.6
12.8
13.0
13.2
13.4
13.6
Depth (m)
-1
-2
-3
-4
-5
-6
-7
-8
-9
Profile
2200hrs
2400hrs
0200hrs
0400hrs
0600hrs

Fig. 8.4

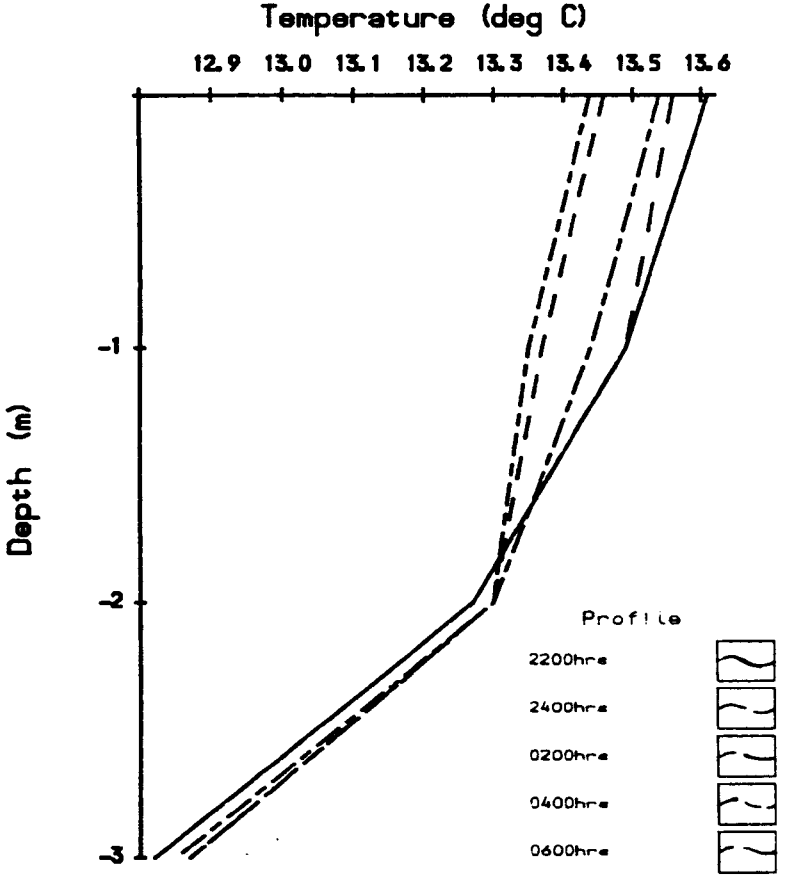

Temperature (deg C)
12.9
13.0
13.1
13.2
13.3
13.4
13.5
13.6
Depth (m)
-1
-2
-3
Profile
2200hrs
2400hrs
0200hrs
0400hrs
0600hrs

FIGURE 8.5

Temperature profiles taken using thermistor
(One to ten metres)
Hourly values from 1200 h 25/8/87 to 28/8/87

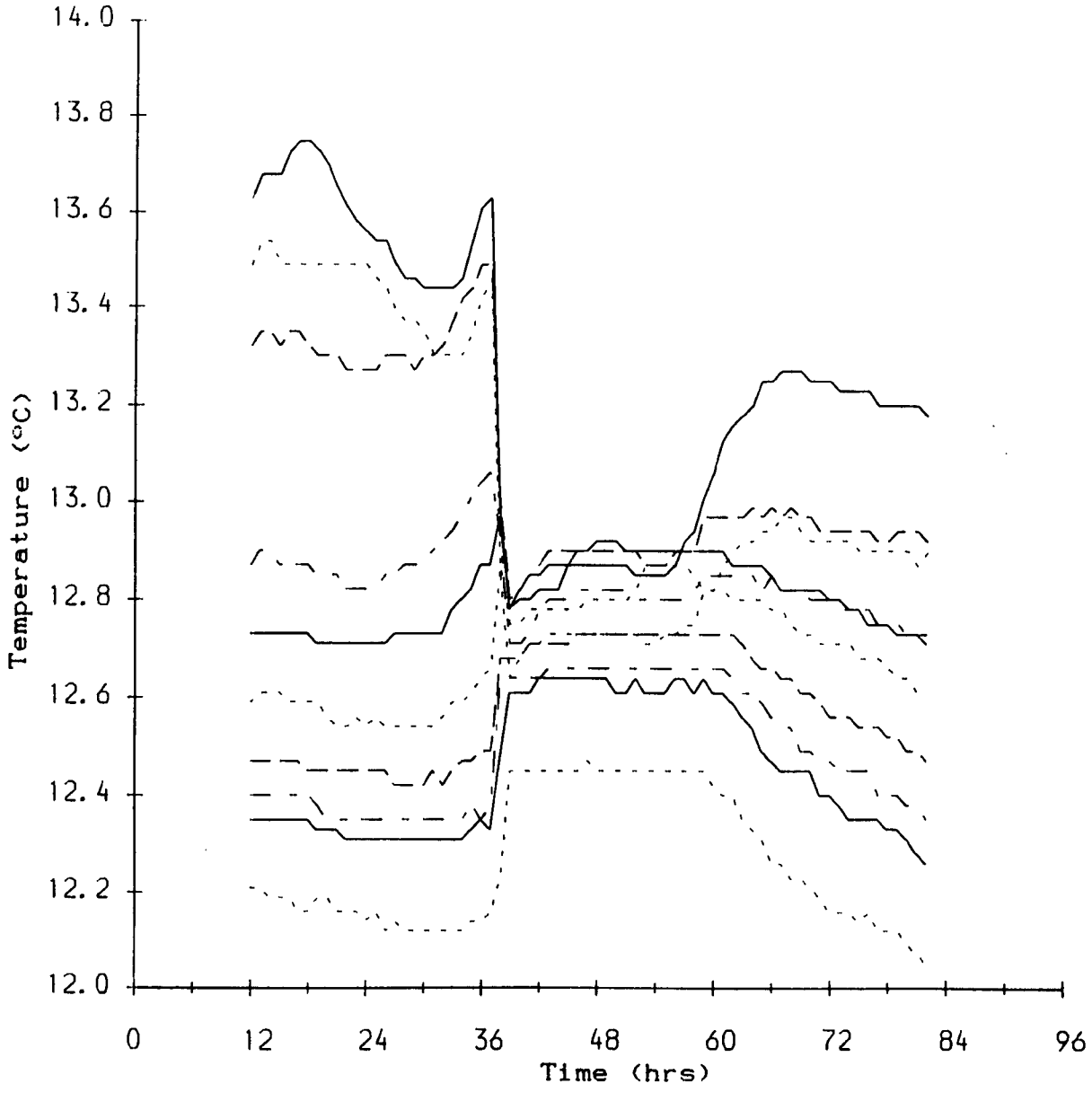

14.0
13.8
13.6
13.4
13.2
13.0
12.8
12.6
12.4
12.2
12.0
Temperature (°C)
0
12
24
36
48
60
72
84
96
Time (hrs)

Fig. 8.5

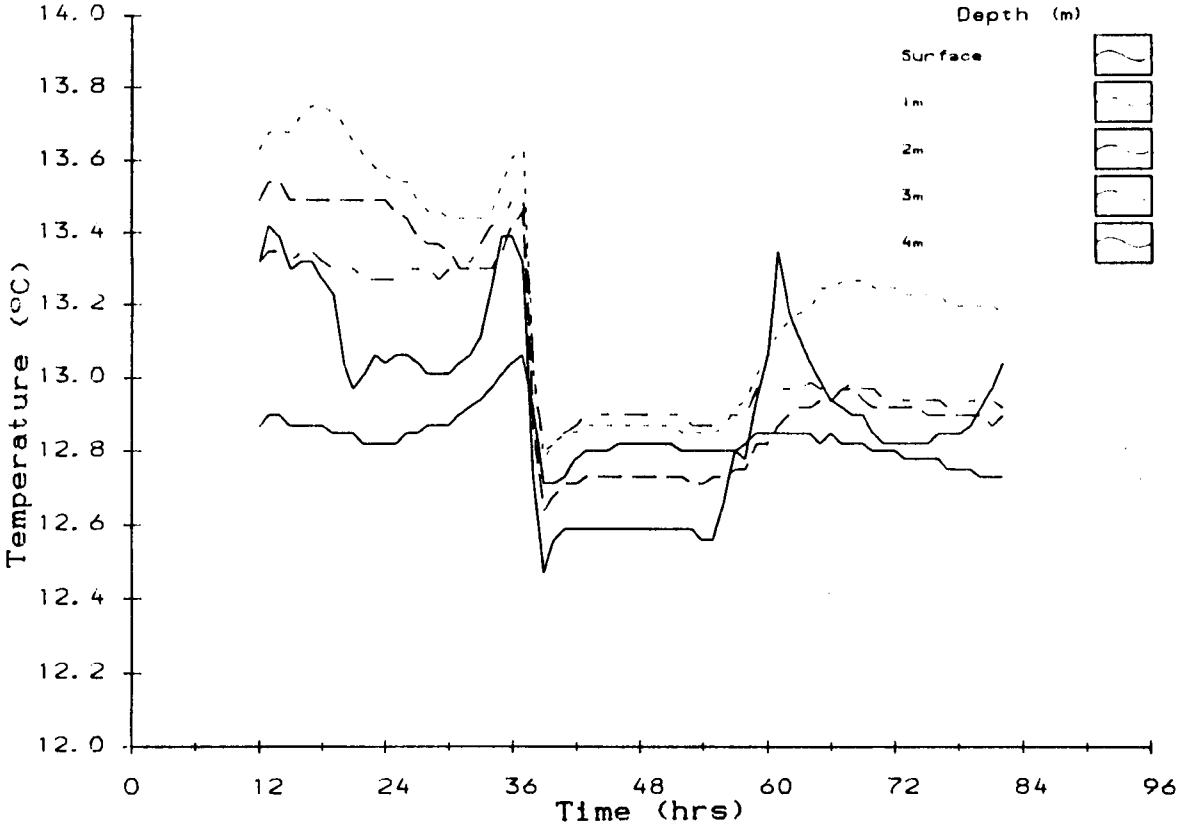
FIGURE 8.6

Temperature profiles taken using thermistor
(Surface to ten metres)
Hourly values from 1200 h 25/8/87 to 28/8/87

FIGURE 8.7

Temperature profiles taken using thermistor
(Five to ten metres)
Hourly values from 1200 h 25/8/87 to 28/8/87

Fig. 8.6


Depth (m)
Surface
1m
2m
3m
4m
Temperature (°C)
14.0
13.8
13.6
13.4
13.2
13.0
12.8
12.6
12.4
12.2
12.0
0
12
24
36
48
60
72
84
96
Time (hrs)

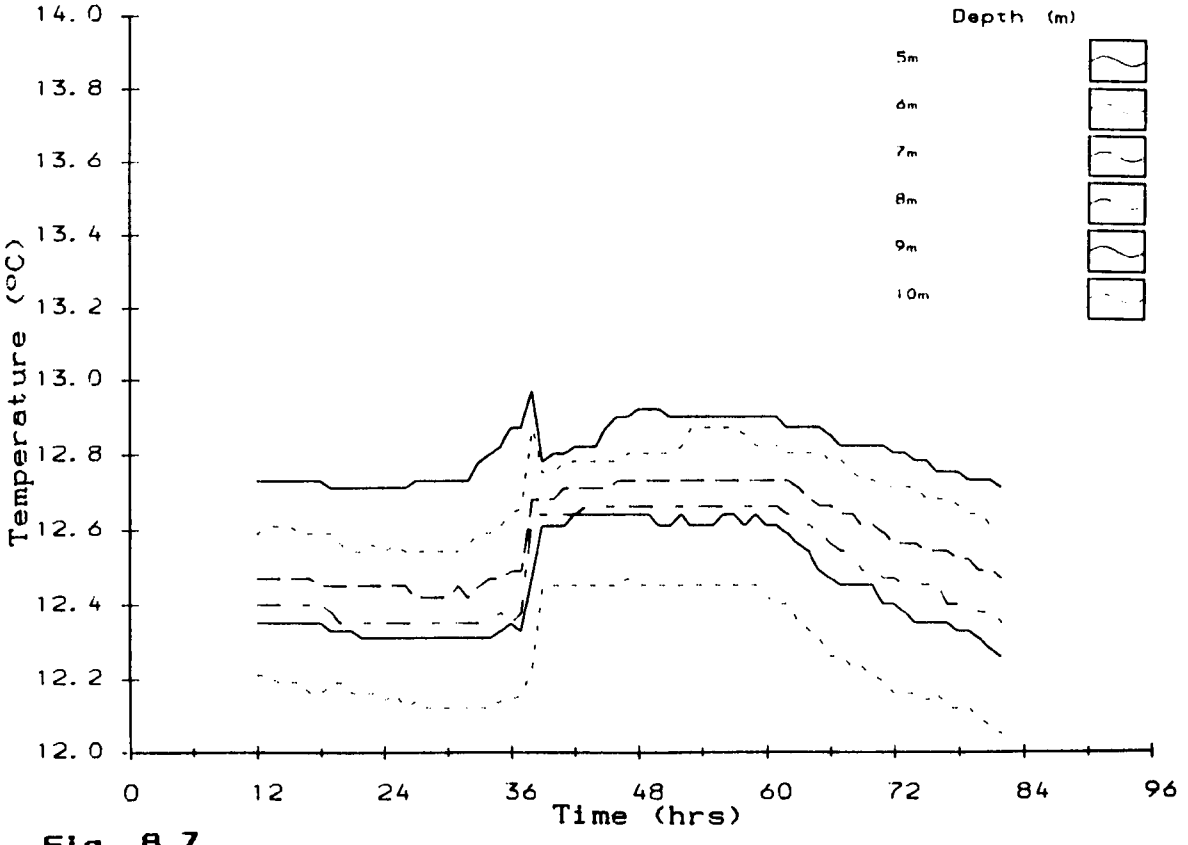

Depth (m)
5m
6m
7m
8m
9m
10m
Temperature (°C)
14.0
13.8
13.6
13.4
13.2
13.0
12.8
12.6
12.4
12.2
12.0
0
12
24
36
48
60
72
84
96
Time (hrs)

Fig. 8.7

FIGURE 8.8

Dye profile 1
Time from release 00:12 (HH:MM)

FIGURE 8.9

Dye profile 2
Time from release 01:13 (HH:MM)

FIGURE 8.8

Dye Profile 1

Time from release 00:12 (HH:MM)

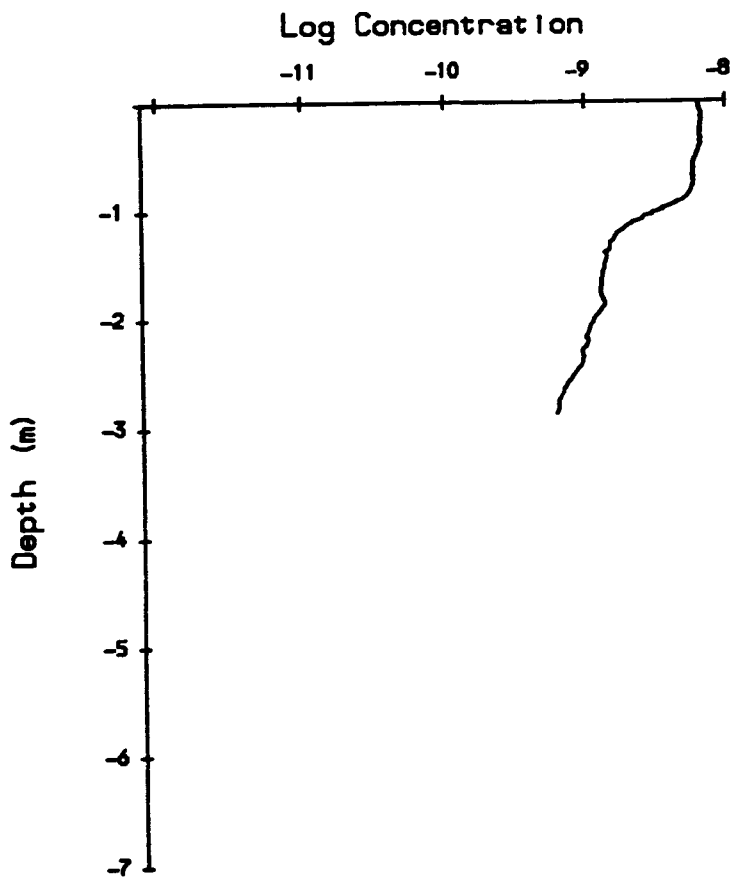


FIGURE 8.9

Dye Profile 2

Time from release 01:13 (HH:MM)

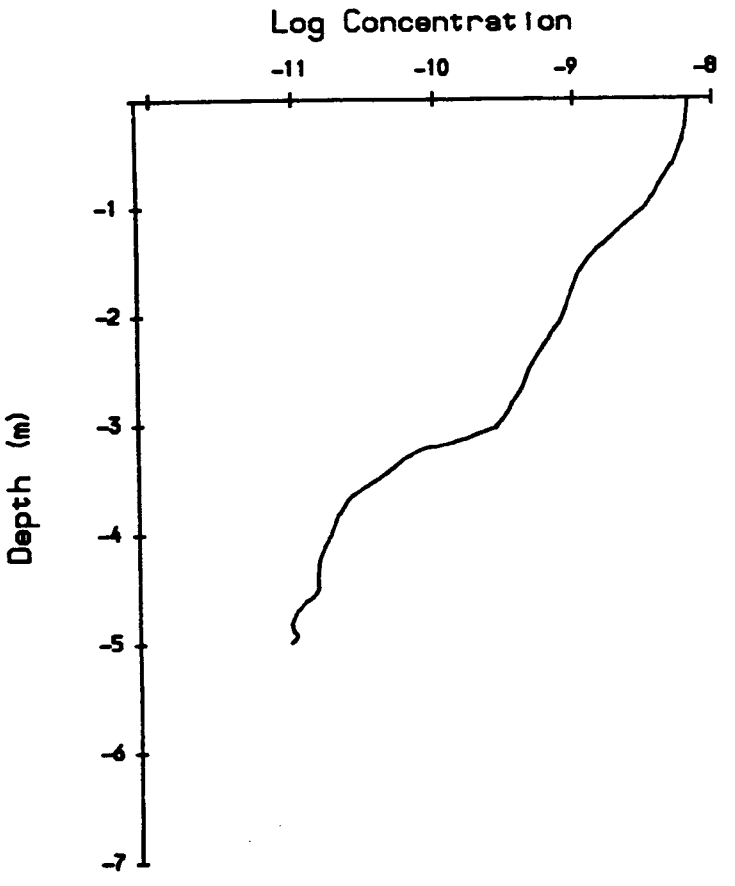


FIGURE 8.10

Dye profile 3
Time from release 04:20 (HH:MM)

FIGURE 8.11

Dye profile 4
Time from release 19:04 (HH:MM)

FIGURE 8.10

Dye Profile 3

Time from release 04:20 (HH:MM)

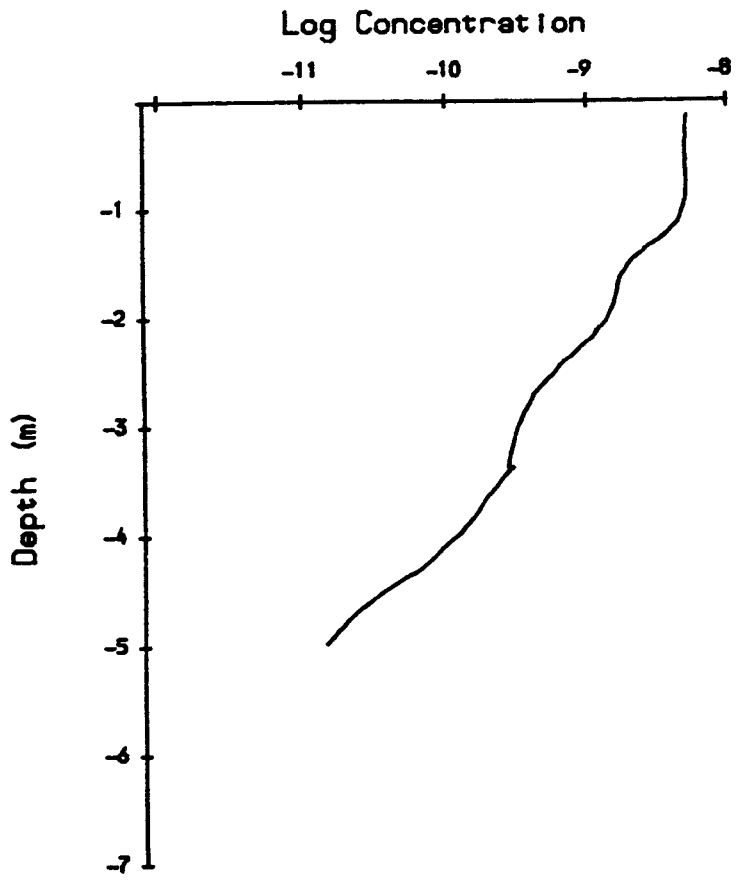


FIGURE 8.11

Dye Profile 4

Time from release 19:04 (HH:MM)

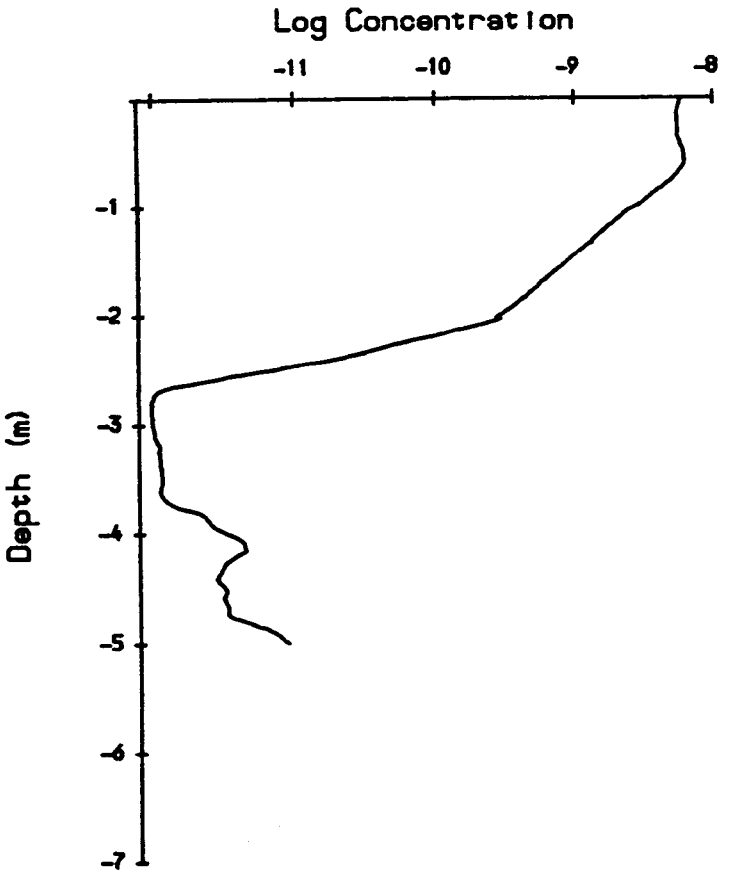


FIGURE 8.12

Dye profile 5
Time from release 19:23 (HH:MM)

FIGURE 8.12

Dye Profile 5

Time from release 19:23 (HH:MM)

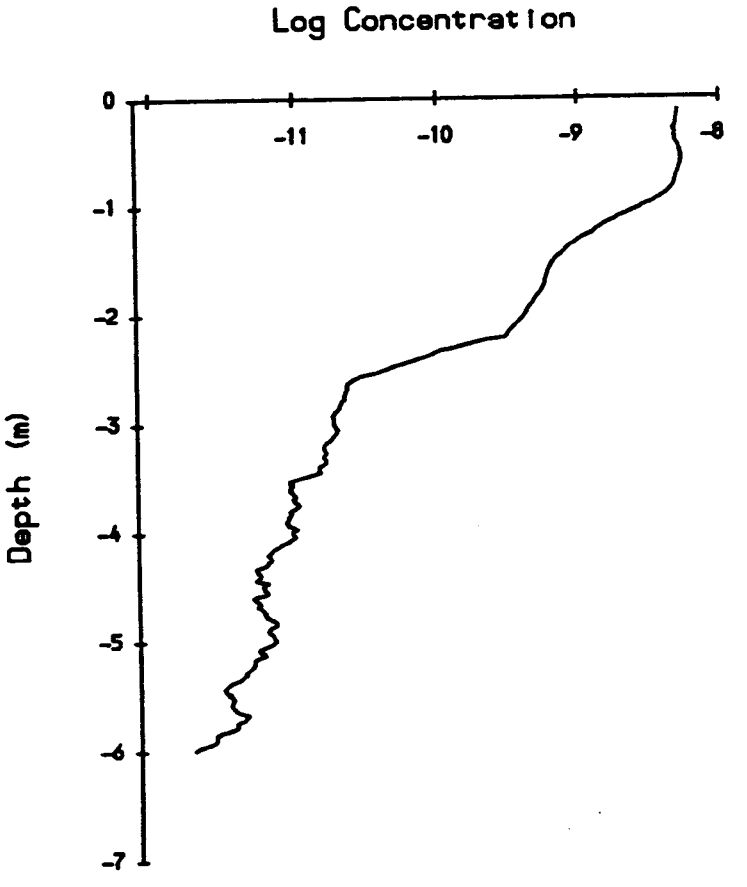


FIGURE 8.13

Temperature profiles taken using thermistor
(One to six metres)
Profiles observed whilst dye in bag.

Fig. 8.13

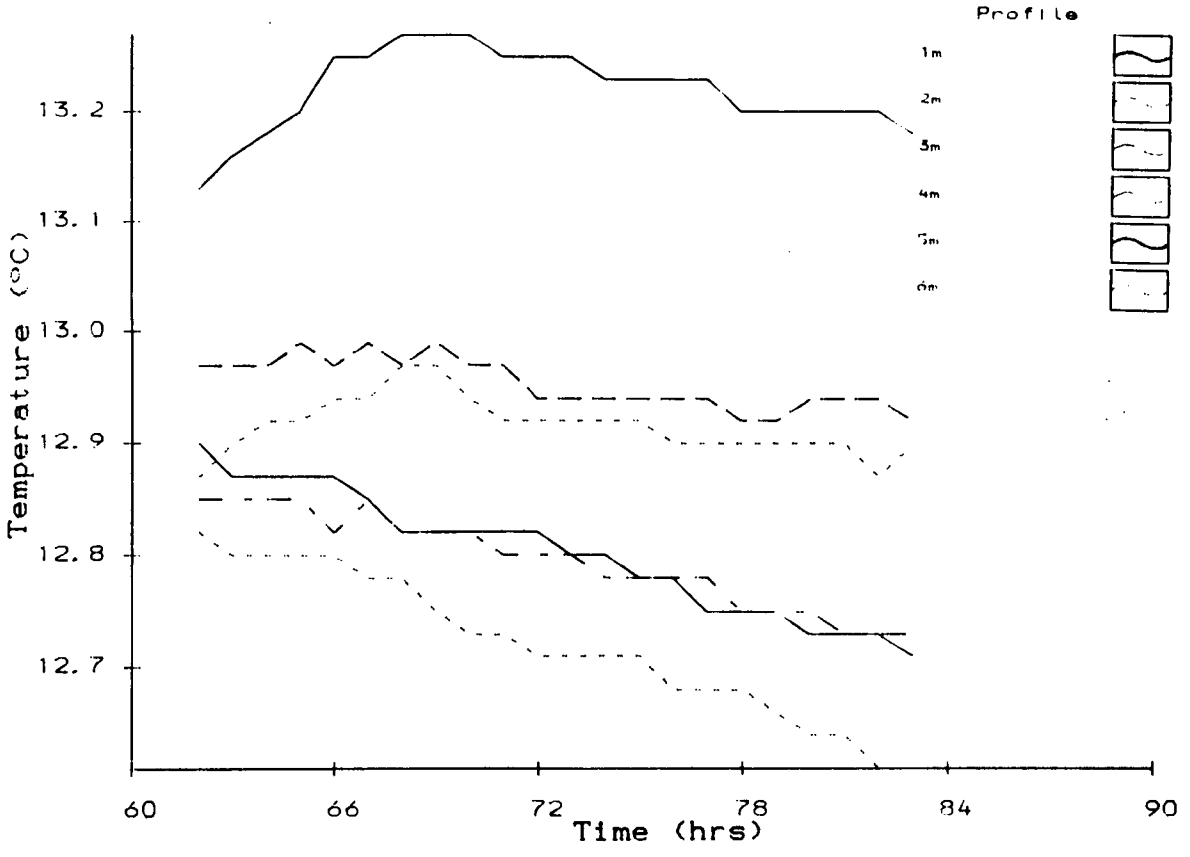

Profile
1m
2m
3m
4m
5m
6m
13.2
13.1
13.0
12.9
12.8
12.7
Temperature (°C)
60
66
72
78
84
90
Time (hrs)

FIGURE 8.14

Observed *in situ* oxygen concentrations
at depths 1m, 3m, 4m and 5m.
(12/8/87 1800 h to 14/8/87 1745 h)

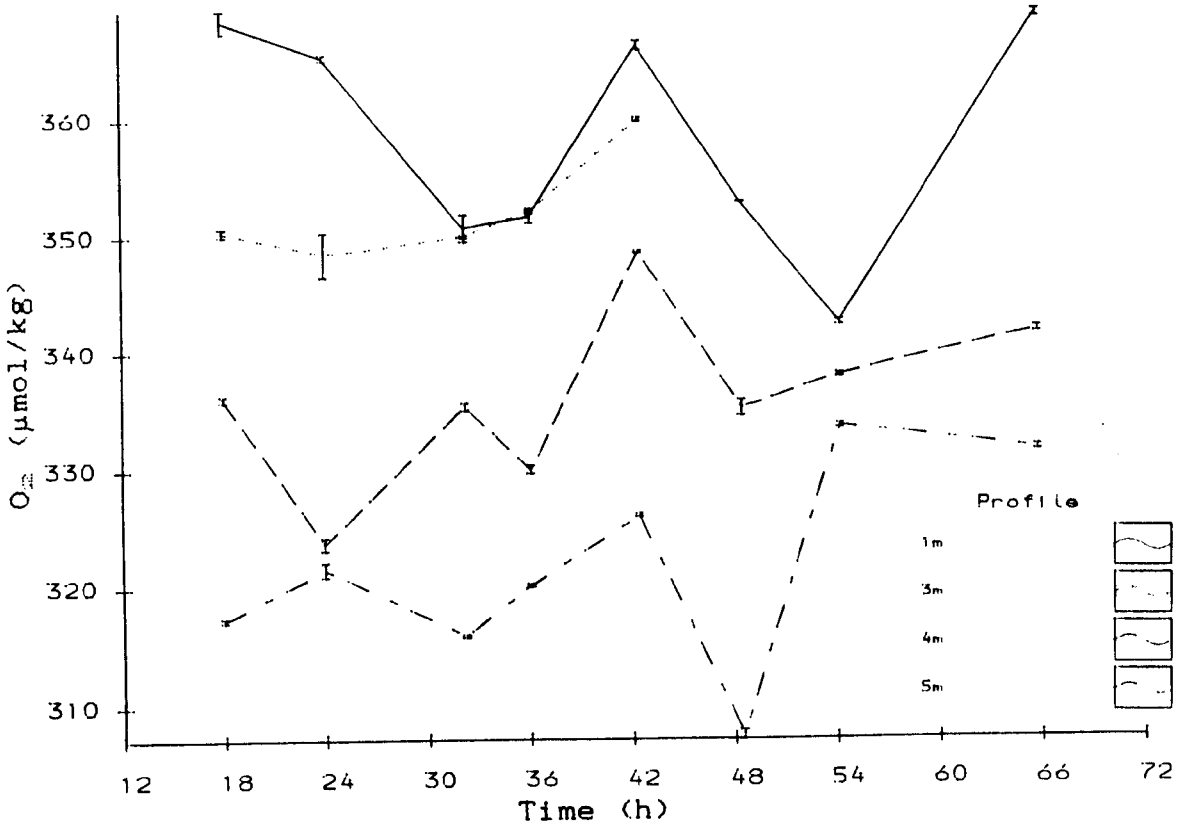
Note :
Molar scale on Y axis not equivalent in Fig. 8.15

FIGURE 8.15

Observed *in situ* TCO_2 concentrations
at depths 1m, 3m, 4m and 5m.
(12/8/87 1800 h to 14/8/87 1745 h)

Note :
Molar scale on Y axis not equivalent in Fig. 8.14

Fig. 8.14



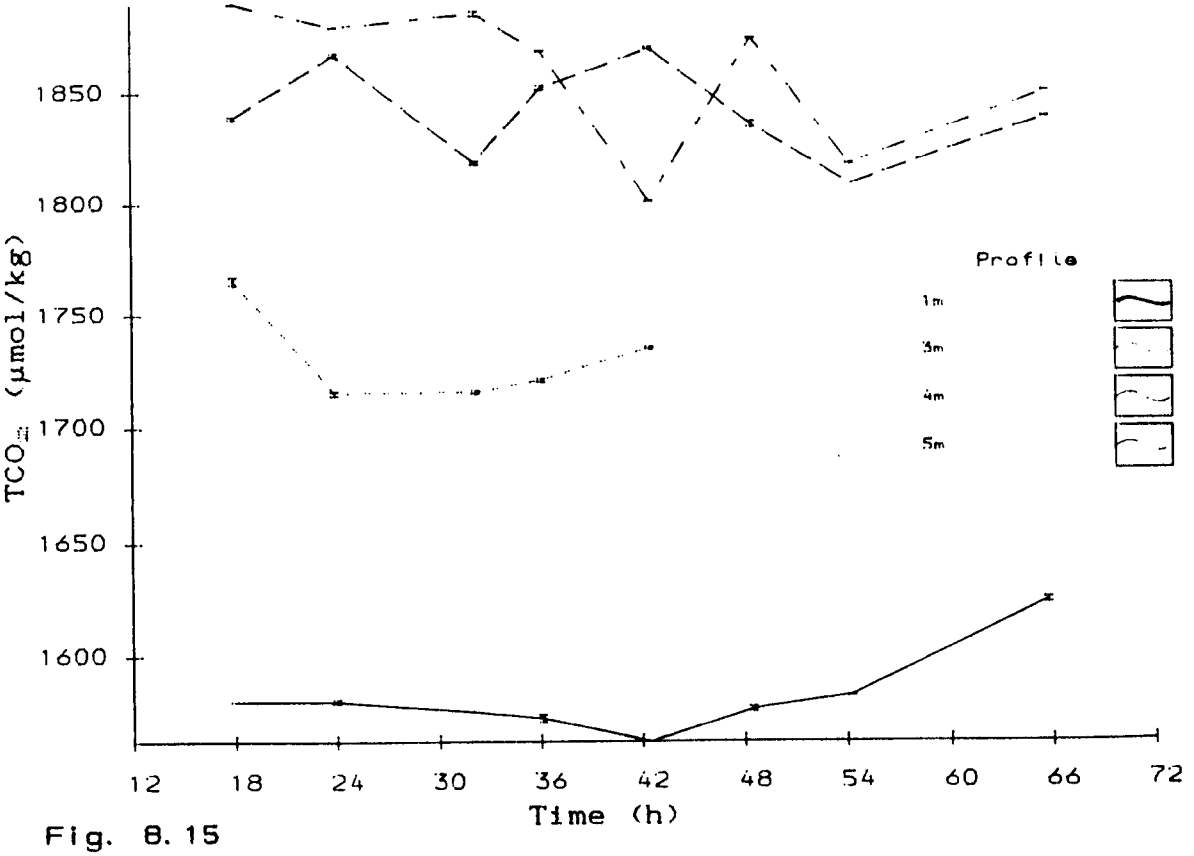
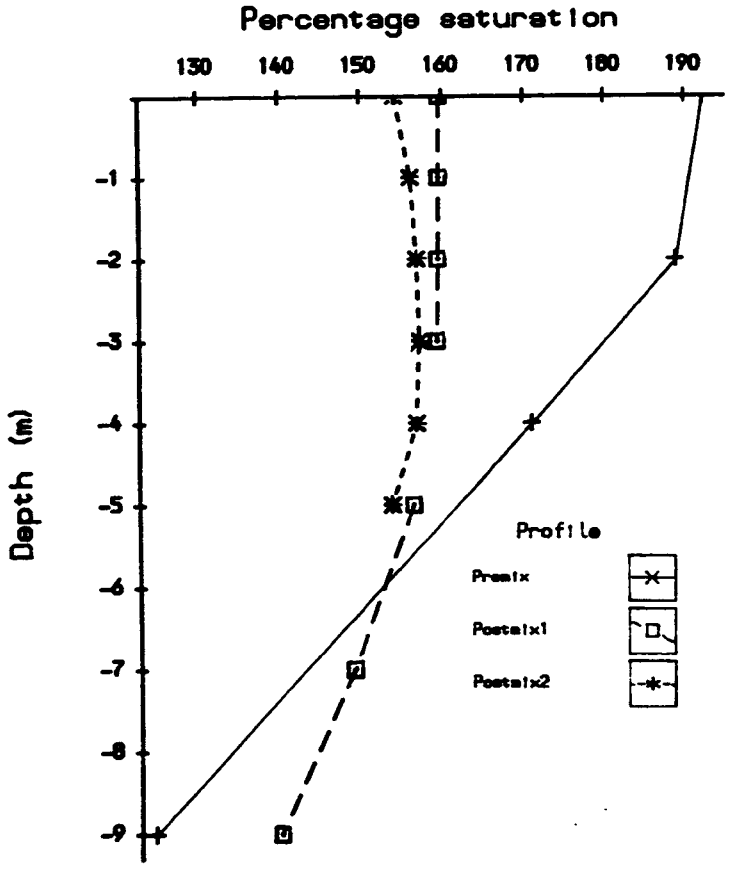


Fig. 8.15

FIGURE 8.16

Recorded percentage saturation
prior and then subsequent to mixing.
(Surface to nine metres)

Fig. 8.16


Percentage saturation
130
140
150
160
170
180
190
Depth (m)
-1
-2
-3
-4
-5
-6
-7
-8
-9
Profile
Premix
Postmix1
Postmix2

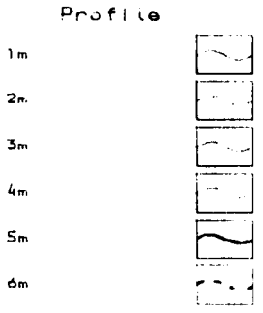


FIGURE 8.17

Observed in situ oxygen concentrations
at depths one to six metres .
(18/8/87 1700 h to 20/8/87 0615 h)

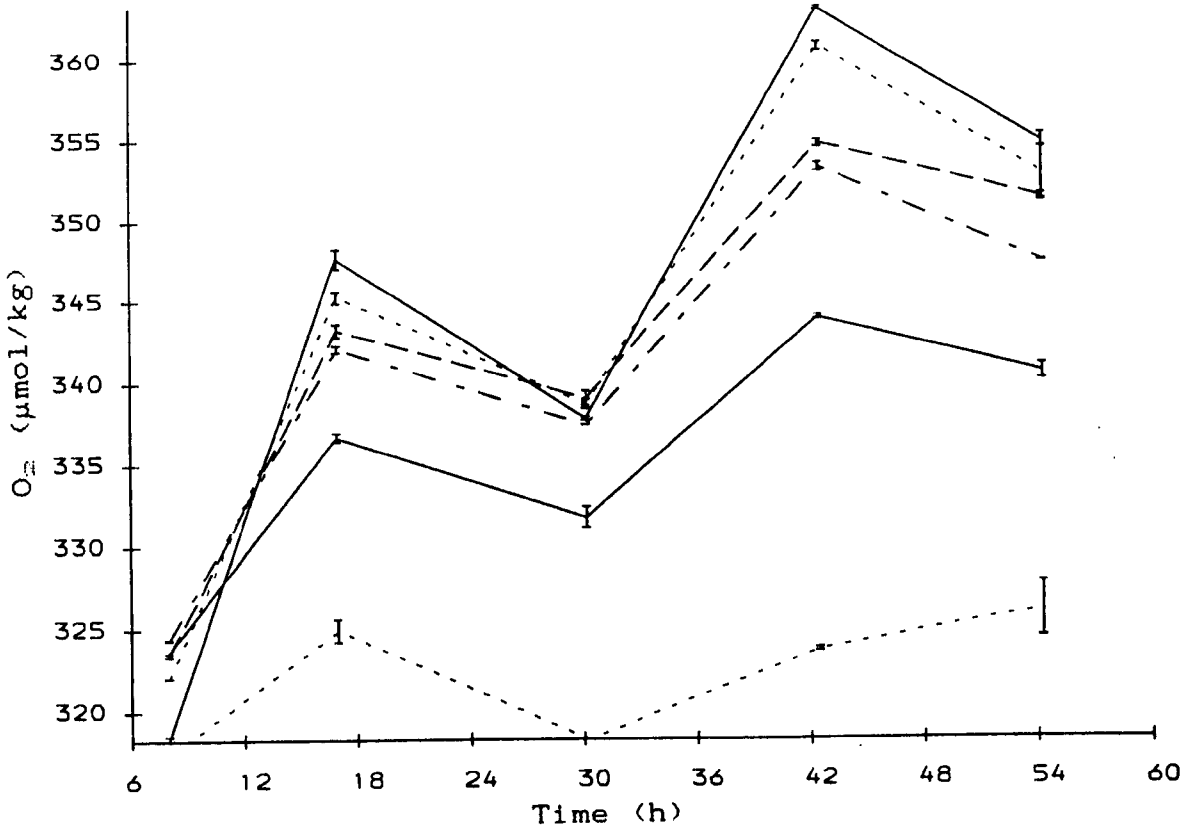
Note :
Molar scale on Y axis not equivalent in Fig. 8.18

FIGURE 8.18

Observed in situ TCO_2 concentrations
at depths one to six metres.
(18/8/87 1800 h to 20/8/87 0615 h)

Note :
Molar scale on Y axis not equivalent in Fig. 8.17

Fig. 8.17



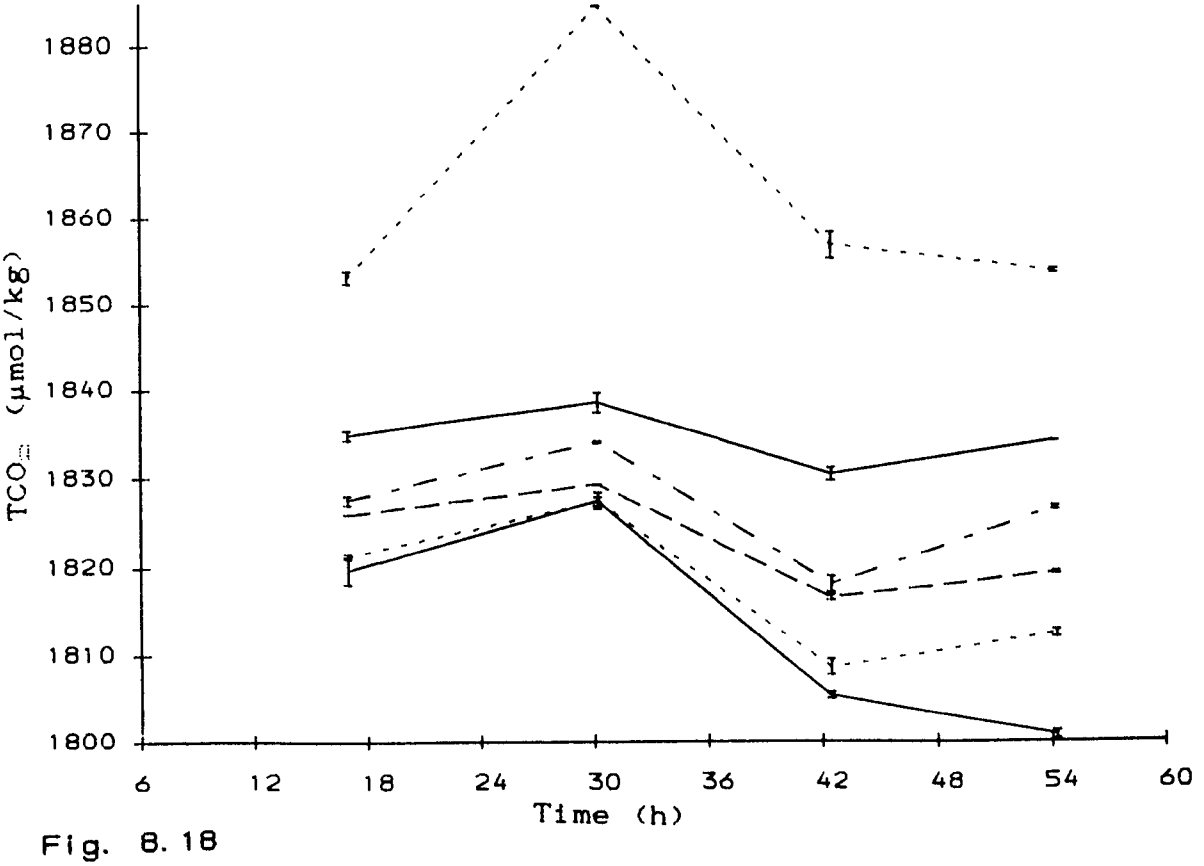


Fig. 8.18

FIGURE 8.19

Observed *in situ* oxygen concentrations
at depths one to six metres .
(21/8/87 1800 h to 24/8/87 0600 h)

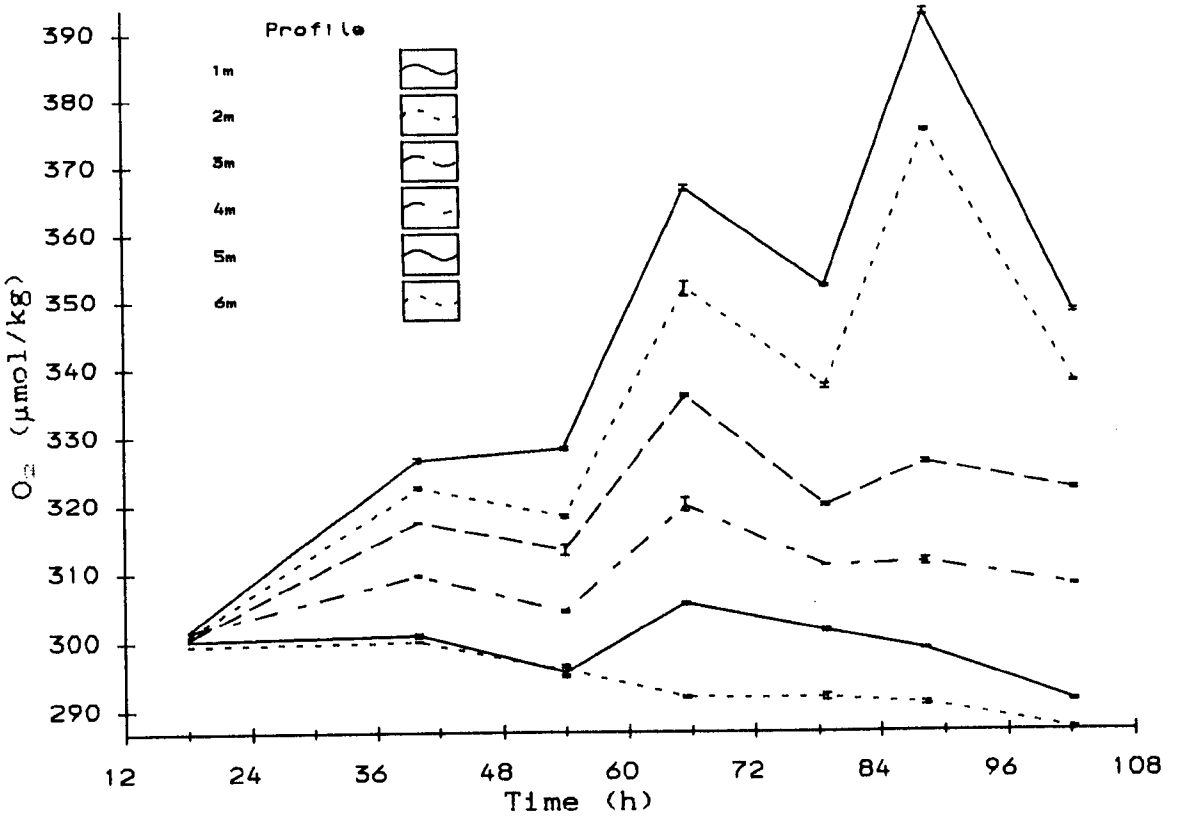
Note :
Molar scale on Y axis not equivalent in Fig. 8.20

FIGURE 8.20

Observed *in situ* TCO_2 concentrations
at depths one to six metres.
(21/8/87 1800 h to 24/8/87 0600 h)

Note :
Molar scale on Y axis not equivalent in Fig. 8.19

Fig. 8.19



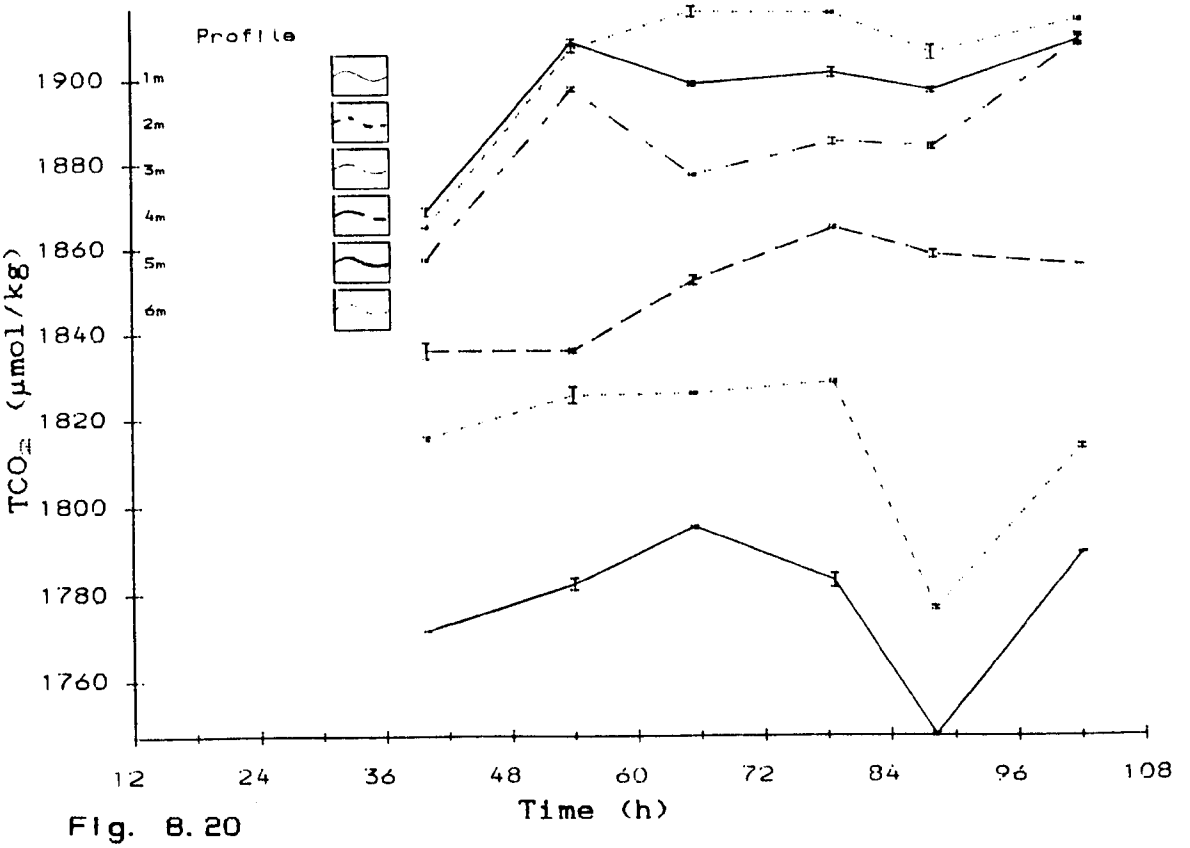


Fig. 8.20

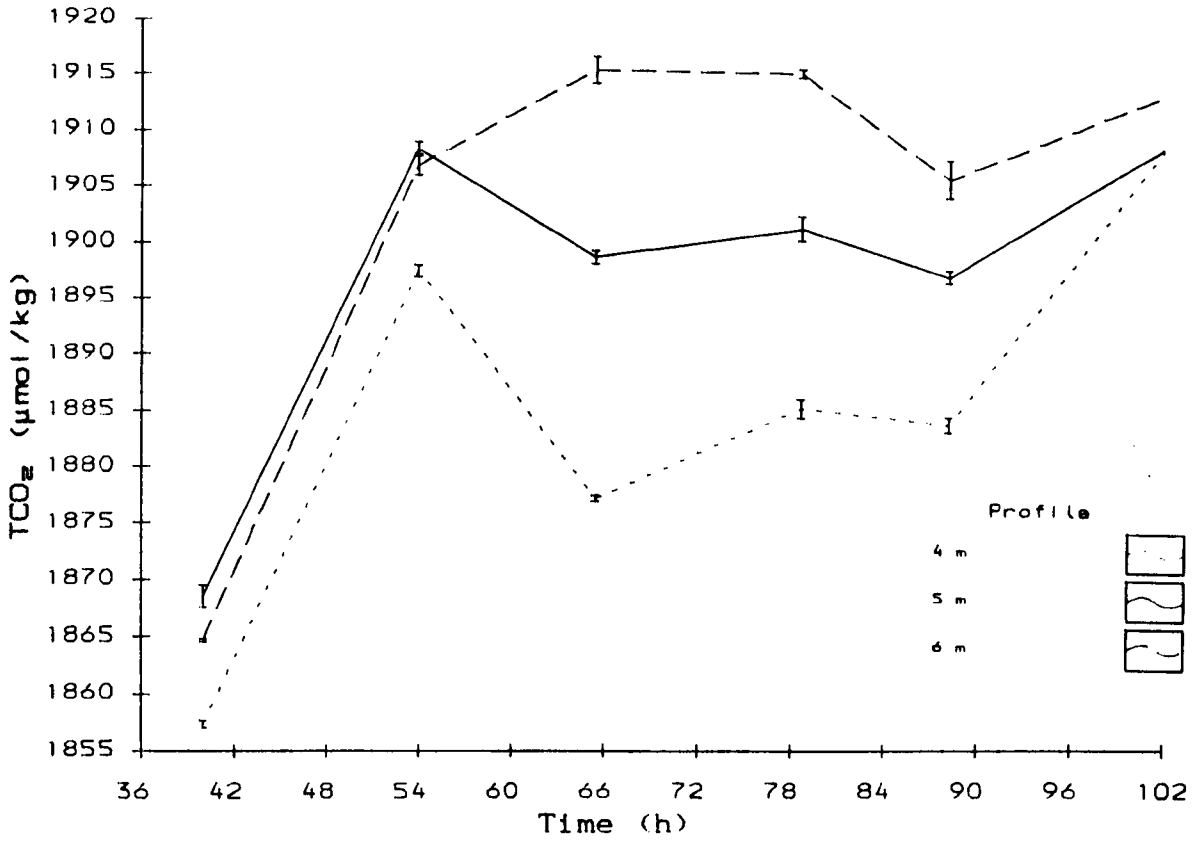
FIGURE 8.21

Observed *in situ* TCO_2 concentrations
at depths four to six metres .
(21/8/87 1800 h to 24/8/87 0600 h)

FIGURE 8.22

Observed and corrected profile of O_2
in situ concentration at 3 m depth
(21/8/87 1800 h to 24/8/87 0600 h)

Fig. 8.21



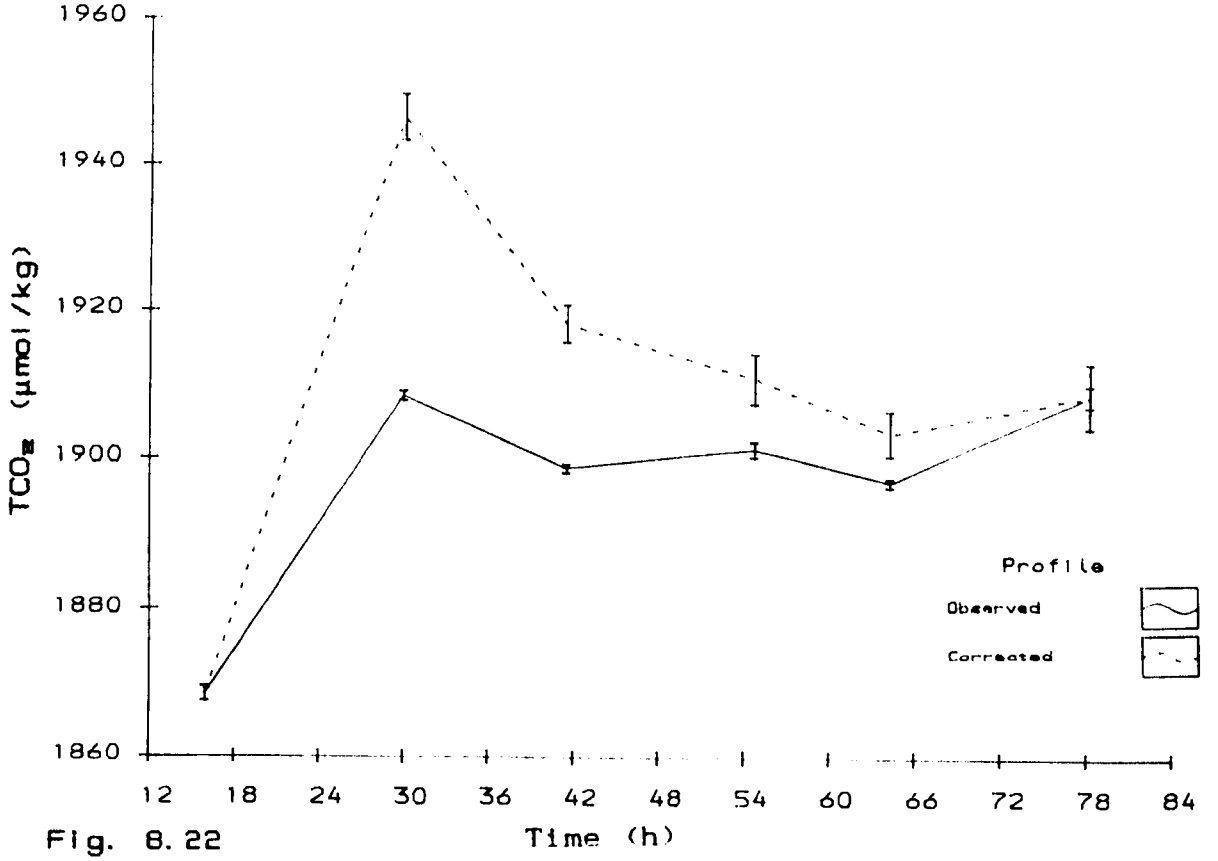


Fig. 8.22

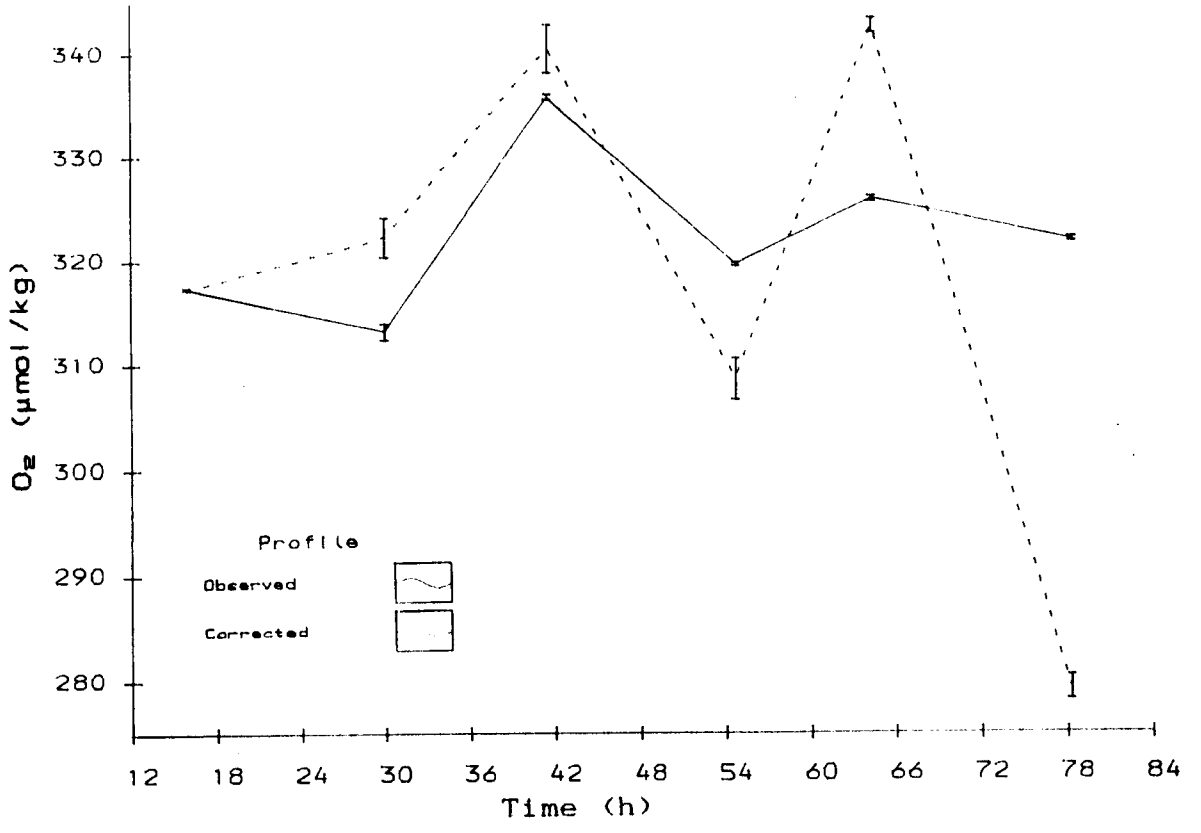
FIGURE 8.23

Observed and corrected profile of TCO_2 *in situ* concentration at 3 m depth (21/8/87 1800 h to 24/8/87 0600 h)

FIGURE 8.24

Observed and corrected profile of TCO_2 *in situ* concentration at 5 m depth (21/8/87 1800 h to 24/8/87 0600 h)

Fig. 8.23



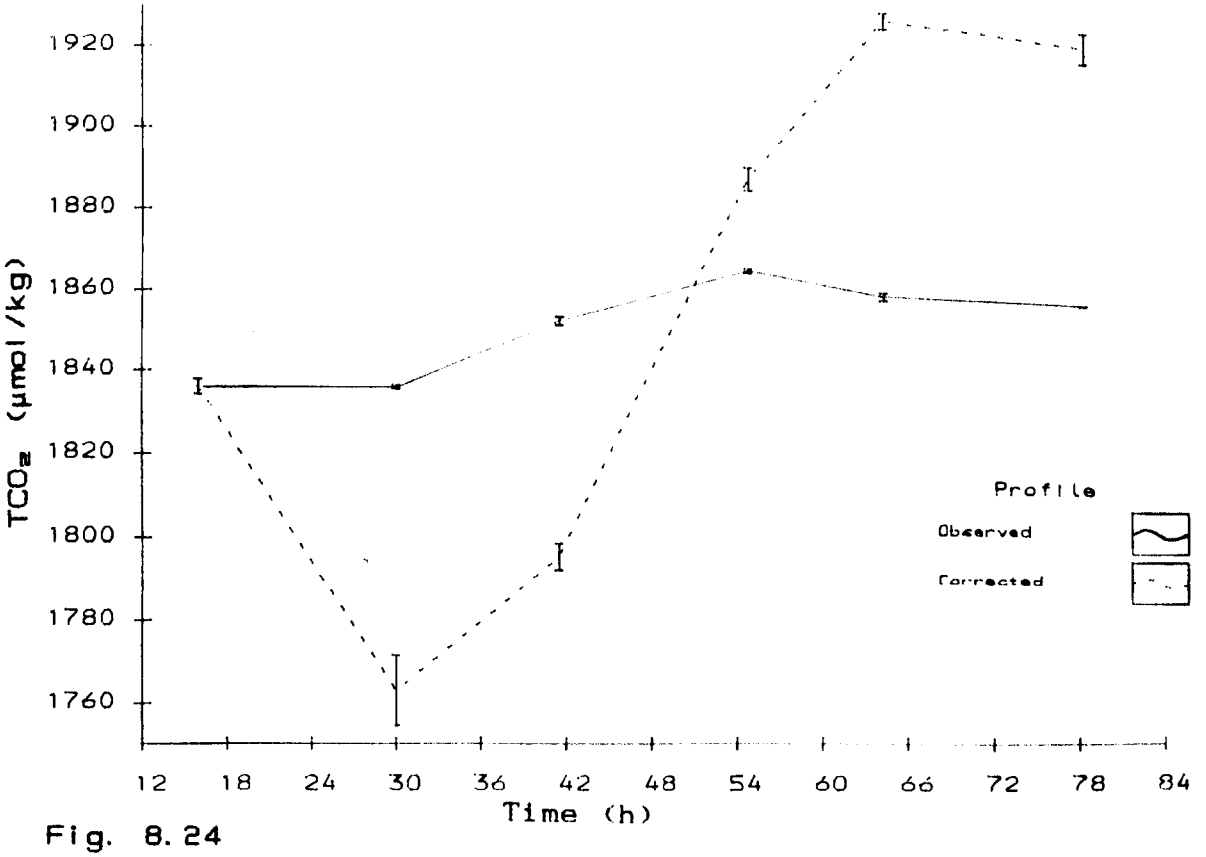


Fig. 8.24

TABLE 8.1

Calculated Atmospheric Loss for Oxygen
(after Tijssen and Eijgenraam 1982)

TABLE 8.1

Calculated Atmospheric Loss for Oxygen

Based on individual values of K (gas exchange coefficient) (calculated after Tijssen and Eijgenraam 1982)

Date	Time (h)	Oxygen Flux (mmoles $h.m^{-2}$)	Date	Time (h)	Oxygen Flux (mmoles $h.m^{-2}$)
12/08	1800	0	13/08	0000	0
13/08	0700	0.7 - 5.8	13/08	1200	23.7
13/08	1800	60.3	14/08	0600	0.6 - 2.2
14/08	1800	11.9	18/08	0700	1.6
18/08	1800	20.3 - 29.3	19/08	0600	0.8 - 3.0
19/08	1800	0	20/08	0600	0
21/08	1800	8.5 - 19.1	22/08	0600	0
22/08	1800	3.5 - 7.9	23/08	0600	0
23/08	1800	14.3 - 22.2	24/08	0600	0

Based on averaged values of K for the preceding 12 hours

Date	Time (h)	Oxygen Flux (mmoles) $h.m^{-2}$	Date	Time (h)	Oxygen Flux (mmoles) $h.m^{-2}$
12/08	1800	-	13/08	0000	0
13/08	0700	1.6	13/08	1200	7.6
13/08	1800	23.6	14/08	0600	16.9
14/08	1800	5.2	18/08	0700	1.7
18/08	1800	17.6	19/08	0600	12.3
19/08	1800	1.3	20/08	0600	0
21/08	1800	-	22/08	0600	7.9
22/08	1800	3.8	23/08	0600	2.9
23/08	1800	12.2	24/08	0600	7.8

TABLE 8.2

Gas Exchange Coefficients
calculated after Tijssen and Eijgenraam (1982)

TABLE 8.2

Gas Exchange Coefficient :- K ($m.h^{-1}$)

(calculated after Tijssen and Eijgenraam 1982)

Day	Time (h)	Wind ($Km.h^{-1}$)	(Wind Speed)^2 $m.sec^{-1}$	K ($m.h^{-1}$) x 10^{-2}
12/08	1800	0	0	0
13/08	0000	0	0	0
13/08	0700	5-15	1.93-17.39	0.70-6.26
13/08	1200	30	69.39	24.98
13/08	1800	45	156.25	56.25
14/08	0600	5-10	1.93-7.73	0.70-2.78
14/08	1800	20	30.91	11.13
18/08	0700	10	7.73	2.78
18/08	1800	25-30	48.16-69.39	17.34-24.98
19/08	0600	5-10	1.93-7.73	0.70-2.78
19/08	1800	0	0	0
20/08	0600	0	0	0
21/08	1800	20-30	30.91-69.39	11.13-24.98
22/08	0600	0	0	0
22/08	1800	10-15	7.73-17.39	2.78-6.26
23/08	0600	0	0	0
23/08	1800	20-25	30.91-48.16	11.13-17.34
24/08	0600	0	0	0

TABLE 8.3

Hourly Eddy diffusivity coefficients
calculated using thermistor temperature data
(25/8/87 1300 h - 26/8/87 1600 h)

TABLE 8.3

Eddy Diffusivity Coefficients
(calculated from thermistor data)

Units = cm^2/sec

Date Time (hrs)	Depth (m) 2m	Depth (m) 3m	Depth(m) 4m
25/8			
1300	*	*	0.15
1400	1.39	0.16	*
1500	*	*	*
1600	*	*	*
1700	0.00	0.12	*
1800	*	0.25	*
1900	0.00	0.11	*
2000	*	*	*
2100	0.00	0.16	*
2200	*	0.18	*
2300	*	*	*
0000	0.28	*	*
26/8			
0100	0.63	*	0.12
0200	2.43	*	0.13
0300	*	*	0.08
0400	*	0.12	0.10
0500	2.78	*	*
0600	*	*	0.14
0700	*	*	0.30
0800	*	*	0.26
0900	*	*	0.26
1000	0.25	*	0.35

Date Time (hrs)	Depth (m) 2m	Depth (m) 3m	Depth(m) 4m
26/8			
1100	0.60	*	0.41
1200	0.59	*	0.25
Bag mixed			
1300	*	1.45	*
1400	*	3.83	*
1500	*	1.06	*
1600	0.35	*	0.14

* indicates a negative coefficient obtained.

TABLE 8.4

Eddy diffusivity coefficients
calculated from dye diffusion measurements
for Profiles 2 and 3.

TABLE 8.4

Eddy Diffusivity Coefficients
(calculated from dye measurements)

Units = cm^2/sec

Depth	Profile 2	Profile 3
1m	0.568	0.004
1.5m	4.31	-0.009
2m	1.49	0.08
2.5m	-3.42	-0.03
3.0m	-	-0.05
3.5m	-	0.02
4.0m	-	-0.013

TABLE 8.5

Observed dye concentration
for Profiles 1 to 5.

TABLE 8.5

Dye Concentration in Profiles 1-5

Units = g dye/g seawater x 10^{-11}

Depth (m)	Profile 1	Profile 2	Profile 3	Profile 4	Profile 5
0.5	627.0	569.0	507.0	621.0	529.0
1.0	353.0	313.0	486.0	279.0	283.0
1.5	134.0	124.0	196.0	65.8	67.1
2.0	112.0	82.3	138.0	28.6	40.5
2.5	85.5	47.3	58.7	0.7	4.3
3.0	-	28.3	32.4	0.1	1.8
3.5	-	3.8	24.8	0.1	0.9
4.0	-	1.8	11.9	0.3	0.9
4.5	-	1.5	3.6	0.3	0.6
Total	1311.50	1171.01	1458.35	996.00	928.19
Time from dye release	00:12	01:13	04:20	19:04	19:23

TABLE 8.6

In vitro comparison of O_2 and TCO_2

TABLE 8.6

Comparison of *in vitro* measurements

Details	Oxygen flux (µmol/kg h)	CO_2 flux (-µmol/kg h)	PQ or RQ
12-13/8/87			
(GP	0.09 +/- 0.04	0.08 +/- 0.07)	
NP	- 0.25 +/- 0.04	- 0.00 +/- 0.09	
Resp.	0.34 +/- 0.02	0.08 +/- 0.07	RQ = (0.24)
13/8/87			
GP	- 0.47 +/- 0.17	0.01 +/- 0.17	PQ = -1.37 +/- 0.303
NP	- 1.42 +/- 0.05	1.31 +/- 0.04	
Resp.	0.95 +/- 0.17	1.30 +/- 0.17	RQ = (-56.7)
18-19/8/87			
(GP	0.14 +/- 0.02	0.12 +/- 0.04)	
NP	- 0.26 +/- 0.04	- 0.43 +/- 0.06	
Resp.	0.40 +/- 0.04	0.56 +/- 0.05	RQ = 1.40 +/- 0.189
19/8/87			
GP	1.47 +/- 0.05	1.02 +/- 0.12	PQ = 1.44 +/- 0.177
NP	0.95 +/- 0.05	0.19 +/- 0.13	
Resp.	0.52 +/- 0.03	0.82 +/- 0.06	RQ = 1.58 +/- 0.147
19-20/8/87			
(GP	0.22 +/- 0.04	0.06 +/- 0.07)	
NP	0.14 +/- 0.05	- 0.35 +/- 0.11	
Resp.	0.08 +/- 0.05	0.41 +/- 0.09	RQ = (5.13)

Details	Oxygen flux (μmol/kg h)	CO_2 flux (-μmol/kg h)	PQ or RQ
23/8/87			
GP	1.88 +/- 0.14	1.41 +/- 0.12	PQ = 1.33 +/- 0.151
NP	0.83 +/- 0.12	0.51 +/- 0.16	
Resp.	1.05 +/- 0.09	0.90 +/- 0.15	RQ = 0.86 +/- 0.161
23-24/8/87			
(GP	0.17 +/- 0.02	0.12 +/- 0.05)	
NP	- 0.86 +/- 0.02	- 0.77 +/- 0.03	
Resp.	1.03 +/- 0.01	0.89 +/- 0.05	RQ = 0.86 +/- 0.046

Original data for <u>in vitro</u> fluxes is given in the appendix.

( ) = A ratio where the standard deviation is close to or greater than the mean for either gas flux, hence error bars cannot be calculated for this ratio

TABLE 8.7

Observed molar ratios as determined from *in situ* measurements of O_2 and TCO_2. Photosynthetic and respiratory quotients from *in vitro* incubations.
(12/8/87 1800 h to 14/8/87 0615 h)

TABLE 8.7

Observed molar ratios from in situ measurements

Depth (m)	Night Insitu 1-3 12/08/87-13/08/87 1800-0815 h	Day Insitu 3-5 13/08/87-13/08/87 0815-1830 h	Night Insitu 5-7 13/08/87-14/08/87 1830-0615 h
1m	-0.28 +/- 0.025	1.21 +/- 0.097	0.86 +/- 0.018
3m	(-119.86)	-0.50 +/- 0.030	No data
4m	(-26.13)	-0.26 +/- 0.009	-5.82 +/- 0.104
5m	-3.20 +/- 0.938	0.12 +/- 0.003	-2.15 +/- 0.096

Observed Photosynthetic & Respiratory Quotients

In vitro Incubations

Depth (m)	Incubation 1 Night	Incubation 2 Day
3m	RQ (0.24)	RQ (-56.7)
		PQ -1.37 +/- 0.303

Original data for both in situ and in vitro fluxes is given in the data appendix.

( ) = A ratio where the standard deviation is close to or greater than the mean for either gas flux, hence error bars for this quotient cannot be calculated (see Appendix 3)

TABLE 8.8

Observed molar ratios as determined from *in situ* measurements of O_2 and TCO_2. Photosynthetic and respiratory quotients from *in vitro* incubations.
(18/8/87 1700 h to 20/8/87 0615 h)

TABLE 8.8

Observed molar ratios from in situ measurements

Depth (m)	Night Insitu 9-10 18/08/87-19/08/87 1700-0615 h	Day Insitu 10-11 19/08/87-19/08/87 0615-1830 h	Night Insitu 11-12 19/08/87-20/08/87 1830-0615 h
1m	0.79 +/- 0.191	1.16 +/- 0.055	-0.55 +/- 0.087
2m	0.93 +/- 0.108	1.19 +/- 0.071	0.49 +/- 0.164
3m	0.82 +/- 0.120	1.23 +/- 0.052	0.87 +/- 0.130
4m	1.39 +/- 0.124	0.99 +/- 0.059	1.47 +/- 0.178
5m	0.75 +/- 0.285	1.50 +/- 0.273	1.13 +/- 0.279
6m	4.72 +/- 0.508	0.20 +/- 0.010	1.25 +/- 1.113

Observed Photosynthetic & Respiratory Quotients

In vitro Incubations

Depth (m)	Incubation 3 Night	Incubation 4 Day	Incubation 5 Night
3m	RQ 1.40 +/- 0.189	RQ 1.58 +/- 0.147 PQ 1.44 +/- 0.177	RQ (5.13)

Original data for both in situ and in vitro fluxes are detailed in the appendix.

( ) = A ratio where the standard deviation is close to or greater than the mean for either gas flux, hence error bars cannot be calculated for this ratio.

TABLE 8.9

Observed molar ratios as determined from *in situ* measurements of O_2 and TCO_2. Photosynthetic and respiratory quotients from *in vitro* incubations. (21/8/87 1600 h to 24/8/87 0615 h)

TABLE 8.9

Observed molar ratios from in situ measurements

Depth (m)	Night Insitu 13-14 21/08/87-22/08/87 1600-0600 h	Day Insitu 14-15 22/08/87-22/08/87 0600-1730 h	Night Insitu 15-16 22/08/87-23/08/87 1730-0645 h
1m	6.90 +/- 1.070	-2.98 +/- 0.343	0.85 +/- 0.124
2m	2.31 +/- 0.493	(-91.14)	0.18 +/- 0.029
3m	(0.01)	-1.39 +/- 0.058	1.38 +/- 0.174
4m	7.54 +/- 0.344	0.76 +/- 0.047	0.90 +/- 0.126
5m	7.25 +/- 1.026	1.03 +/- 0.124	0.64 +/- 0.314
6m	10.15 +/- 2.013	0.46 +/- 0.126	(3.70)

Depth (m)	Day Insitu 16-17 23/08/87-23/08/87 0645-1615 h	Night Insitu 17-18 23/08/87-24/08/87 1615h-0615 h
1m	1.16 +/- 0.056	0.94 +/- 0.017
2m	0.74 +/- 0.011	0.98 +/- 0.019
3m	0.96 +/- 0.151	-0.59 +/- 0.353
4m	(0.27)	7.64 +/- 1.230
5m	-0.62 +/- 0.187	1.54 +/- 0.201
6m	-0.10 +/- 0.056	2.04 +/- 0.123

Observed Photosynthetic and Respiratory Quotients
In vitro Incubations

Depth (m)	Incubation 7 Day	Incubation 8 Night
3m	RQ 0.86 +/- 0.161 PQ 1.33 +/- 0.151	RQ 0.86 +/- 0.049

Original data for both in situ and in vitro fluxes are detailed in the appendix.

( ) = A ratio where the standard deviation is close to or greater than the mean for either gas flux, hence error bars for this quotient cannot be calculated (see Appendix 3)

TABLE 8.10

Comparison of net community activity as estimated by *in situ* and *in vitro* measurements of O_2 and TCO_2.

TABLE 8.10

Comparison of net community activity
In situ and in vitro measurements of TCO_2 and O_2

Details	Night		Day	
	Oxygen (μmol/kg h)	TCO_2 (-μmol/kg h)	Oxygen (μmol/kg h)	TCO_2 (-μmol/kg h)
12-13/8/87				
In situ	- 0.26 +/- 0.03	1.45 +/- 0.07		
In vitro	- 0.25 +/- 0.04	- 0.00 +/- 0.09		
13/8/87				
In situ			1.29 +/- 0.04	- 5.05 +/- 0.10
In vitro			- 1.42 +/- 0.05	1.31 +/- 0.04
18-19/8/87				
In situ	- 0.32 +/- 0.05	- 0.26 +/- 0.00		
In vitro	- 0.26 +/- 0.04	- 0.43 +/- 0.06		
19/8/87				
In situ			1.29 +/- 0.04	1.05 +/- 0.01
In vitro			0.95 +/- 0.05	0.19 +/- 0.13

Details	Night		Day	
	Oxygen (µmol/kg h)	TCO_2 (-µmol/kg h)	Oxygen (µmol/kg h)	TCO_2 (-µmol/kg h)
19-20/8/87				
In situ	- 0.29 +/- 0.03	- 0.25 +/- 0.03		
In vitro	0.14 +/- 0.05	- 0.35 +/- 0.11		
23/8/87				
In situ			0.66 +/- 0.04	0.69 +/- 0.10
In vitro			0.83 +/- 0.12	0.51 +/- 0.16
23-24/8/87				
In situ	- 0.29 +/- 0.03	0.17 +/- 0.10		
In vitro	- 0.86 +/- 0.02	- 0.77 +/- 0.03		

Original data for both in situ and in vitro fluxes are detailed in the appendix.

CHAPTER 9

Results of Challenger Cruise 16/87

9.1 Introduction

The original intention of the cruise was to determine both pH and TCO_2 of the surface waters in the area of the N.E.Atlantic covered by the ships track. The two system variables, pH and TCO_2 were to be used to calculate pCO_2 levels for the surface waters.

TCO_2 measurements were my responsibility whilst Plymouth Marine Laboratory (Dr. M. Whitfield) were to provide pH determinations. Coupled with surface measurements it was intended that a series of sub-surface profiles of pCO_2 should also be collected. Observed surface distribution was to be linked with a combination of physical (Arctic and Sub Arctic fronts) and biological factors (coccolithophore blooms). Water column measurements would have helped identify the North Atlantic Bottom Water (NABW) and from this water a possible rate of anthropogenic carbon dioxide removal could be estimated in relation to previous calculations stemming from the 1981 TTO expedition.

Unfortunately the pH system did not function adequately on board whilst the ship was alongside and so a last minute decision was taken to have a number of water bottles delivered to the ship so that water samples could be preserved for alkalinity determination later on shore at PML. Additional bottles were flown out halfway through the cruise to join the ship during the exchange of personnel at the Faroe Islands.

Unfortunately, instructions to the ship regarding the preservation of the samples coupled with the type of bottle (polyethylene) meant that the alkalinity samples could not be successfully analysed. A thorough description of the approaches used to determine the alkalinity is given in the Methods section (chapter six).

A conventional pH meter and combination ROSS electrode (Orion, MSE, Surrey) from U.C.N.W. were taken on the cruise, the original intention being to provide a back-up for the PML system. This system was linked to a continous logging unit and employed throughout the first half of the cruise. However, continual drifting of the electrode potential meant that despite frequent calibrations the results are not reliable.

Malfunctioning of the pH system coupled with incorrect preservation of the alkalinity samples has meant that TCO_2 determinations are the only carbon system variable available from the cruise for examination and further interpretation.

It is convenient to separate the two different type of sampling, water column profiling and surface mapping, for purposes of results presentation.

9.2 Discrete Water Column Measurements from CTD Bottle Casts

Water samples for TCO_2 determinations were taken at 20 of the total 28 CTD stations profiled during the cruise. For each of these stations, up to 12 sampling depths were selected according to the main gradients observed on the downcast, of dissolved oxygen, chlorophyll fluorescence and light transmission.

An oxygen electrode provided continuous profiles of dissolved oxygen, also discrete samples were taken on each cast for calibration purposes. All oxygen concentrations supplied by Dr Purdie and Mr Parkes of Southampton University are discrete oxygen values. O_2 electrodes are notoriously fickle instruments and matching discrete sampling with the measurements for TCO_2 avoided potential errors.

All sub-surface profiles are given in Figures 9.1 to 9.19. For each station oxygen (μmoles/kg), TCO_2 (μmoles/kg), chlorophyll (mg/m^3) are represented on one plot, temperature and salinity on the other for comparison.

9.3 Comparison of Challenger 16/87 and TTO 1981 data

Absolute values of both TCO_2 and O_2 concentrations recorded during the cruise show remarkable similarity with those recorded during the TTO study in July 1981. Figure 9.20 shows the station positions of the TTO expedition in the area. Due to other demands on the ships time only two of the stations were adequately matched with stations on this cruise, a third being reasonably close. Table 9.1 has details of the comparable stations. TCO_2 was obtained with a gas extraction procedure followed by a coulometric end-point during this cruise. TCO_2 was calculated from a potentiometric alkalinity determination during the TTO expedition.

Recent papers by Bradshaw and Brewer (1988,1988) observed a large discrepancy between manometric and potentiometric estimates of TCO_2 during the TTO study (see Chapter 5). The TCO_2 determined during this cruise is expected to be compatible to the manometric estimates as described by Bradshaw and Brewer, however, in this instance there does not appear to be the large disrepancy (up to 20 µmol/kg) noticed by them in the surface waters (ie less than 1000 metres).

9.4 Observation of the presence of NABW

Ellett et al (1983) observed the movement of Norwegian Deep Water passing through the Faroe Shetland Channel where some of it spills over the Wyville Thomson Ridge and passes down the shelf by a variety of routes, including the Rockall Trough, to the shelf edge and over to the abyssal plain. The pCO_2 of this water mass is of great interest as it is a part of the North Atlantic Deep Water which is proposed to be one of the main sinks for atmospheric carbon dioxide.

Three stations: 20, 21 and 23 were positioned in order to observe the deep water and so hopefully determine pCO_2 levels within the water mass. Neither of the three stations gave an indication of deep water flow from the temperature, salinity measurements, however the last depth sampled for both Stations 20 and 21 may have been too shallow to be certain to include the feature if present.

The conclusions drawn from the temperature and salinity data was reinforced by oxygen determinations.

The deep oxygen minimum layer was recorded at all stations south of latitude 60° N plus Station 13 to the north. (Parkes MSc Thesis 1988 Southampton University).

Stations to the north of the Wyville Thomson Ridge had no deep oxygen minimum layer related to that observed in the Rockall Trough, though once again the stations may have been too shallow to observe the minimum.

9.5 Sub-surface contouring along three transects

Contouring of sub-surface oxygen, TCO_2, temperature and salinity data has been carried out along three transects. These are drawn between Stations 10, 5 and 4 (transect a), Stations 9, 12, 14, 21 and 20 (transect c) and 18, 17, 15, 14, 25 and 24 (transect b). The position of the transects taken are shown for reference in Figure 9.21.

The contour diagram for Stations 10 to 4 of oxygen and TCO_2 is given in Figure 9.22, the corresponding temperature and salinity diagram shown in Figure 9.23. The water depth for the stations is marked on the diagrams and linked up in order to a first order approximation of the bottom topography.

Figure 9.23 indicates a weak salinity front occurring between Stations 5 and 10 with evidence of upwelling occurring between 500-700 m on the corresponding oxygen profile (Figure 9.22).

Figure 9.24 has the transect for Stations 18 to 25 of oxygen and TCO_2, corresponding temperature and salinity given in Figure 9.25. A strong front is apparent on both the temperature and salinity profiles (Figure 9.25) just north of Station 17. This is matched by a stark discontinuation in the oxygen levels, rising sharply just north of the front (Figure 9.24). Levels of TCO_2 just continue to rise gently. This is presumed to be evidence of the Arctic front which has been observed at this position for this time of the year.

Stations 9 to 20 are represented in Figure 9.26 for both oxygen and TCO_2, temperature and salinity in Figure 9.27. No particular features are apparent in these transects.

9.6 Surface Measurements - General Trends

On examination of the data obtained, it is apparent that three distinct areas were mapped during the cruise.

i) Rockall

This comprises the majority of the cruise from port to port, but excluding data obtained north of the Faroes Bank/Channel (Figures 9.28, 9.29, 9.30).

ii) Faroe

All stations north of the Faroe Bank/Channel excluding data north of latitude 64°N (Figures 9.28, 9.29, 9.30)

iii) Front (Arctic)

This comprises nine sampling points north of latitude 64 N (Figures 9.28, 9.29, 9.30).

During statistical analysis of the surface data, the above sub-divisions are retained, the data sets are given in the data appendix for this cruise. For convenience, when the complete set of surface measurements are discussed, the data is referred to as the surface data.

Contouring is a useful means of representing surface values. A series of contour diagrams were produced using a computer assisted contouring package known as SURFACE II present on the VAX mainframe at U.C.N.W. A number of features are apparent from examination of the contour maps.

Figure 9.31 represents surface temperature noted at the time of sampling for discrete TCO_2 concentration, the position of individual data points are given by crosses for reference.

The bunching of contours at approximately 64° N and between 5-8°W is presumed to indicate the presence of the Arctic front. The Sub-Arctic front is poorly defined and not apparent in terms of surface temperature features.

Salinity (Figure 9.32) also confirms the presence of the Arctic front, plus a weak bunching of contours reflecting the Sub-Arctic front around 15°W and 58-59°N. The highest salinity values are apparent on crossing the Rockall Bank.

Attenuation (Figure 9.33) is taken from recorded transmission percentages. A couple of high values over 1.4 m^{-1} are observed, in addition to a generally raised attenuation profile close in to the Faroe Islands and extending out onto the Faroe Shelf.

Although chlorophyll fluorescence (Figure 9.34) indicates a compatible rise in surface chlorophyll close in to the Faroes, this is based on a single chlorophyll value of 5.3 mg/m^3. Surface chlorophyll is generally less than 1.5 mg/m^3.

Total carbon dioxide (Figure 9.35) is on first appearances a complicated surface picture, however several strong features are apparent. A drop in surface TCO_2 levels is apparent in the region north of Hatton Bank and bounded by Lousy Bank and the Icelandic Basin (see Figure 9.30 for geographical details), ie between Stations 12 and 14 (Figure 9.28). On crossing the channel between Lousy Bank and the Faroe shelf, TCO_2 levels increase to being greater than 2080 μmoles/kg and then a general decrease is seen on the Faroes shelf extending northwards towards the Arctic front.

Phytoplankton hauls on the Faroes shelf indicated a predominance of diatoms, whereas at Stations 5, 11-15 and 23-25 coccolithophores were most abundant.

Two surface contour maps are available to show the levels of dissolved oxygen in relation to the other variables.

These are reproduced courtesy of G. Parkes (Soton. University). Surface concentration (μmoles/kg) is given in Figure 9.36 and percentage saturation in Figure 9.37.

Both maps indicate a general increase in absolute and percentage saturation of oxygen in a NW direction towards the proposed location of the Sub-Arctic front. Most noticeable is the rise in surface oxygen in and around the Faroe Islands.

9.7 Precision of coulometric TCO_2 measurements

This cruise was the first time the system had been throughly tested under such varying and arduous conditions. Noise presumably due to the ships mains gave high blank readings and produced a low precision associated with some samples. A frequency histogram can be produced in order to show the variation in precision associated with different samples.

Figure 9.38 shows the range of standard errors and coefficient of variance associated with sample bottles taken from the CTD casts. All of these bottles were fixed using $HgCl_2$. A total of 123 bottles were preserved and the majority analysed to give three replicates.

Statistical analysis of the precision obtained shows the following ;

	C.V.%	S.E.(μmoles/kg)
Mean	0.08	0.94
Mode	0.04	0.70

Figure 9.39 shows similar variables associated with bottles taken from the non-toxic seawater supply and analysed to give surface values. These bottles were not fixed and a total of 99 samples analysed to give an average three replicates from each bottle.

Statistical analysis of the precision obtained shows the following ;

	C.V.%	S.E.(μmoles/kg)
Mean	0.07	0.87
Mode	0.07	0.80

9.8 Statistical analysis of surface data

For purposes of statistical analysis the surface measurements were divided into four data sets

a) Surface - all data (101 sampling points).

b) Rockall - excluding data points north of the Faroes Bank/Channel (75 sampling points).

c) Faroes - all points north of the Faroes Bank/Channel excluding data collected north of latitude 64^{0} (26 sampling points).

d) Front - nine sampling points north of latitude 64^{0}.

For all four data sets, the following variables were analysed.

i) Temperature
ii) Salinity
iii) Attenuation
iv) Chlorophyll
v) Total carbon dioxide

The most frequently used statistical test for correlation is the Pearson product-moment test which assumes normality when testing hypotheses about this correlation coefficient (R). For data that does not satisfy the normality assumption, another measure of the linear relationship between two variables is the non-parametric Spearman Rank correlation coefficient (Rs).

The efficiency of Rs compared to the Pearson R when testing for association in the population is 91%, if all of the assumptions for using the Pearson test are met.

Prior to deciding which correlation test was suitable it was necessary to test the data for normality using the Kolmogorov-Smirnov Goodness of Fit test, which is a non parametric test that indicates whether the sample represents a normal population. The results of the test are given in Table 9.2.

The nine sampling points in the frontal data set were not tested due the small size of the set.

In a total of four cases the test indicated that the data was not normally distributed.

1) Temperature - Surface data. A frequency histogram indicated a bi-modal distribution, the data was not transformed.
2) Attenuation - Surface data. This was successfully transformed by taking the reciprocal of attenuation.
3) Attenuation - Rockall data. This was successfully transformed by taking the reciprocal of attenuation.
4) TCO_2 - Rockall data. A frequency histogram of the data suggested a depressed distribution. A number of transformations were attempted in order to normalise the data, finally the data was left untransformed.

As a number of the variables were not normally distributed, a non-parametric test ranked correlation was performed on the data. The results of the non-parametric correlation are given in Tables 9.3 to 9.6.

9.8.1 Non-parametric correlation between variables

Surface data (Table 9.3)

Three strong sets of correlation are apparent. First, the two physical parameters, temperature and salinity are positively correlated. Second, TCO_2 is positively correlated to salinity, which is expected due to a presumed salinity/alkalinity relationship but not correlated to temperature. Third, the 'biological' variables, attenuation and chlorophyll are negatively correlated with TCO_2.

Rockall data (Table 9.4)

The correlations observed are similar to the complete surface data set, the same variables are correlated but generally with a stronger correlation. Salinity and TCO_2 positively correlated, attenuation, chlorophyll and TCO_2 all negatively correlated.

Faroes data (Table 9.5)

This smaller data set indicates substantially different correlated variables compared to the previous data sets. TCO_2 and salinity are not significantly correlated nor TCO_2 and temperature or TCO_2 and attenuation. All other pairs of variables are in general correlated with an additional strength.

Front data (Table 9.6)

Temperature and salinity are strongly correlated as is attenuation with both temperature and salinity. TCO_2 is more strongly correlated with temperature than salinity, the opposite of observations seen in the other data sets. No chlorophyll data is available.

9.8.2 Parametric correlation between variables

Pearson correlation coefficients can also be determined using the transformed variables where appropriate. The results of these correlations are given in Tables 9.7 to 9.10. When the parametric and non-parametric correlations are compared there are distinct differences observed, most importantly, these differences occur not only in the variables that were tested not normal but also those that initially were taken to be normally distributed from using the K-S test.

9.8.3. Principle Component Analysis

Multiple regression tests similar to those described above are helpful in suggesting where a relationship between two variables may exist. More useful would be to know which variables control, either alone or in combination, the variation observed in TCO_2 in the surface waters. Specifically, whether the variation is primarily aligned with biological or physical factors. With this in mind a test of principle components was applied to the surface data with the following goals,

1) To identify underlying factors that explain the correlations amongst a set of variables.
2) To determine the number of dimensions required to represent a set of variables.

The basis of any factor analysis is the parametric correlation coefficient. Generation of this coefficient must be rigorous and follow assumptions regarding that statistic.

Assumptions regarding the correlation coefficient

First, the correlation must be linear as it is a linear model used in the correlation determination. A random correlation is acceptable if non-linearity is demonstrated. Second, homogeneity of variance must be maintained within the sample population.

Examination of the parametric correlations obtained (Tables 9.7 - 9.10) suggested that several pairs of correlated variables did not demonstrate linearity. All pairs of variables were examined further to demonstrate randomness.

Random Correlation

By comparing the observed values of the dependent variables to the values predicted by the linear regression equation, it is possible to check how well the model of linear fit is with the data.

The difference between the observed and predicted variable is called the residual. The relative magnitudes of the residuals can be standardised by dividing the estimates through by their standard deviations. The resulting standardised residuals can be expressed in standard deviation units above or below the mean. A plot of the standardised residuals against predicted should show no relationship if the assumptions of linearity and homogeneity of variance are met.

Several pairs of variables did show a relationship.

Surface data	- TCO_2 / Attenuation
Faroes data	- Temperature / Chlorophyll
	- TCO_2 / Chlorophyll
Rockall data	- Temperature / 1/Attenuation
	Salinity / 1/Attenuation

Despite these pairs, the majority of the data did satisfy the requirements and a Principle Components analysis was carried out.

Results of the Principle Components Analysis

The results of the analysis are given in Tables 9.11 to 9.13. No PC analysis was carried out on the Frontal data due to the small number of sample points available.

Only eigenvalues of greater than one have any significance and are normally taken as the default values in any factor analysis However in both the Rockall and Surface data, a third factor has been included in the factor analysis for information.

With a factor analysis, factors between - 0.3 and + 0.3 are not used in the interpretation and can be ignored in any interpretation of the results.

Surface data (Table 9.11)

Realistically, only 1 factor is significant. This factor indicates that 53 % of variance observed can be explained using this factor. Interestingly, the factor links TCO_2 positively with the physical variables, temperature and salinity, and the value of these three will increase while the biological factors, attenuation and chlorophyll would drop.

Rockall data (Table 12)

Again, only one factor is significant and it explains up 57 % of the variation seen in the surface variables. This factor links TCO_2, temperature and salinity positively together once more, whilst attenuation and chlorophyll are negatively related.

Faroes data (Table 13)

Here two factors are significant though the third factor only accounts for 22 % of the observed variation. Factor 1 as in both the Surface and Rockall data is positively linked TCO_2, temperature and salinity along with negatively linked chlorophyll and attenuation. This factor only accounts for 57 % of the observed variation. The second factor combines temperature and salinity in a negative relationship with TCO_2. Both attenuation and chlorophyll are not significant in this factor.

Conclusions from the Principle Components Analysis

The initial basis for accepting the results of this PC test though relatively sound are not statistically as rigorous as hoped, therefore any observations must recognise that several pairs of variables did not satisfy the criteria.

In both the Surface and Rockall analysis only one factor was recognised by the test and this accounted for just over 50 % of the observed variation. This is minimal and suggests that a large amount of the variation observed cannot be explained by the factor analysis, this is perhaps not unexpected. An additional factor is recognised from the Faroes analysis, however this factor can account for only 20 % of the observed variation with the primary factor accounting for around 50 % once again.

In all three analyses the main factor is similar, it links TCO_2 in a positive relationship with temperature and salinity, negatively to chlorophyll and attenuation. This suggests that approximately 50 % of the observed variation is explained by a combination of all the variables, the remainder of the variation is not adequately explained by the factor analysis.

The Principle Components analysis does not provide any radical insight into the observed distributions of these variables.

It is apparent that the distributions observed are a complex result of a number of interacting processes and that insufficient data or variables are present in order to elucidate further the controls involved.

9.9 Summary

The initial intention of measurements of carbonate system on the Challenger cruise was to provide pCO_2 determinations as calculated from pH and TCO_2 measurements. Unfortunately only one variable, TCO_2 was reliably obtained.

The coulometric system proved to be sufficiently reliable and robust to allow extensive use with both fixed and unfixed samples. The system required frequent attention however, it maintained a good precision throughout the cruise.

Comparison with previous data obtained during the TTO expedition showed remarkable agreement for both oxygen and TCO_2.

Statistical analysis of TCO_2 using a non-parametric, ranked correlation technique indicated a negative relationship with both attenuation and chlorophyll. A positive relationship was observed with salinity, also a positive relationship between temperature and salinity. These general correlations were altered around the Faroe Islands and across the Arctic front.

FIGURES 9.1 - 9.19

SYMBOLS USED IN GRAPHS

Δ = Chlorophyll A (mg/m^3)

□ = Oxygen (micromol/kg)

\+ = Carbon Dioxide (micromol/kg)

* = Temperature (^oC)

◊ = Salinity (‰)

Figure 9.1 **STATION 1**

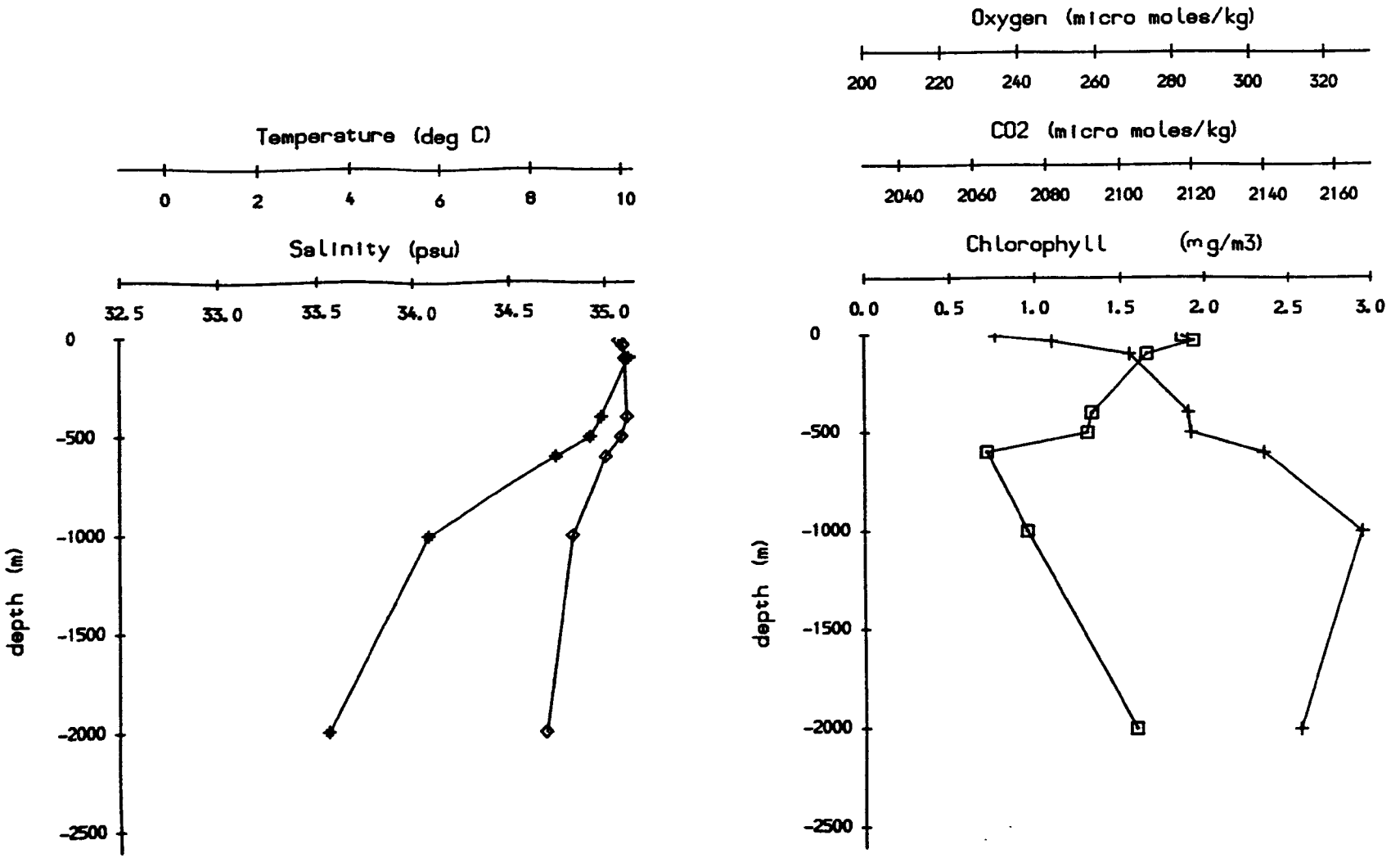


Figure 9.2 **STATION 4**

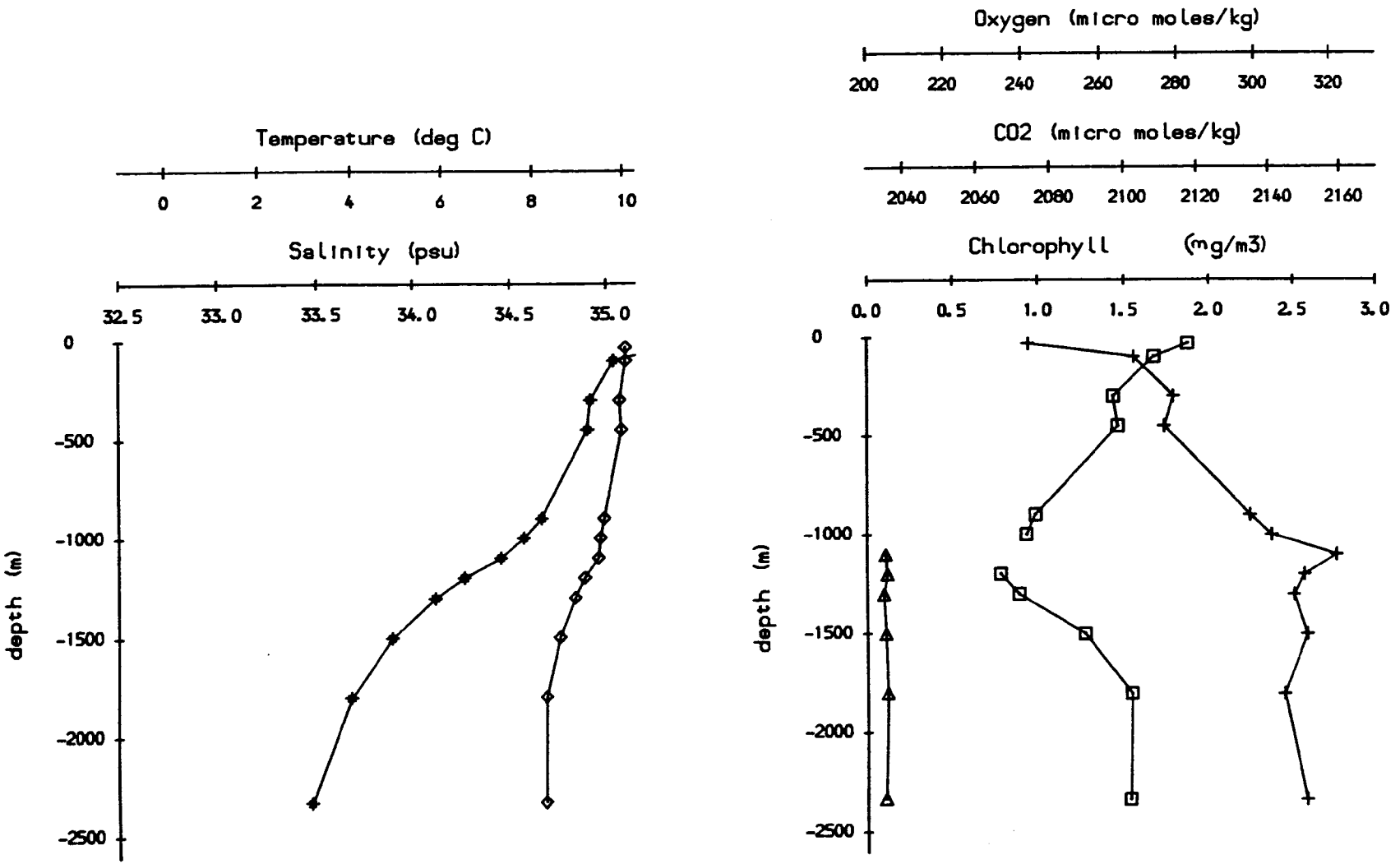


Figure 9.3 **STATION 5**

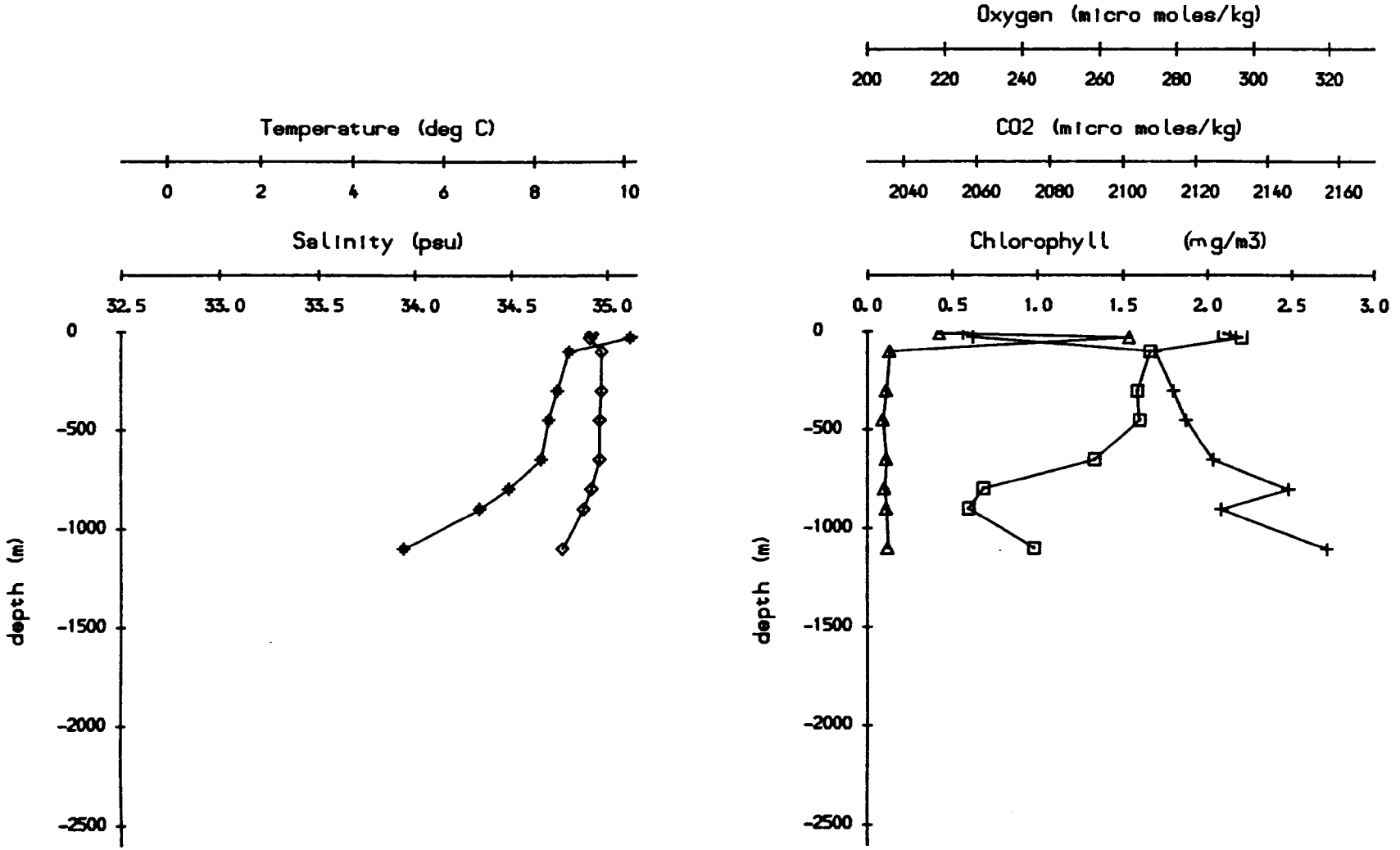


Figure 9.4 **STATION 6**

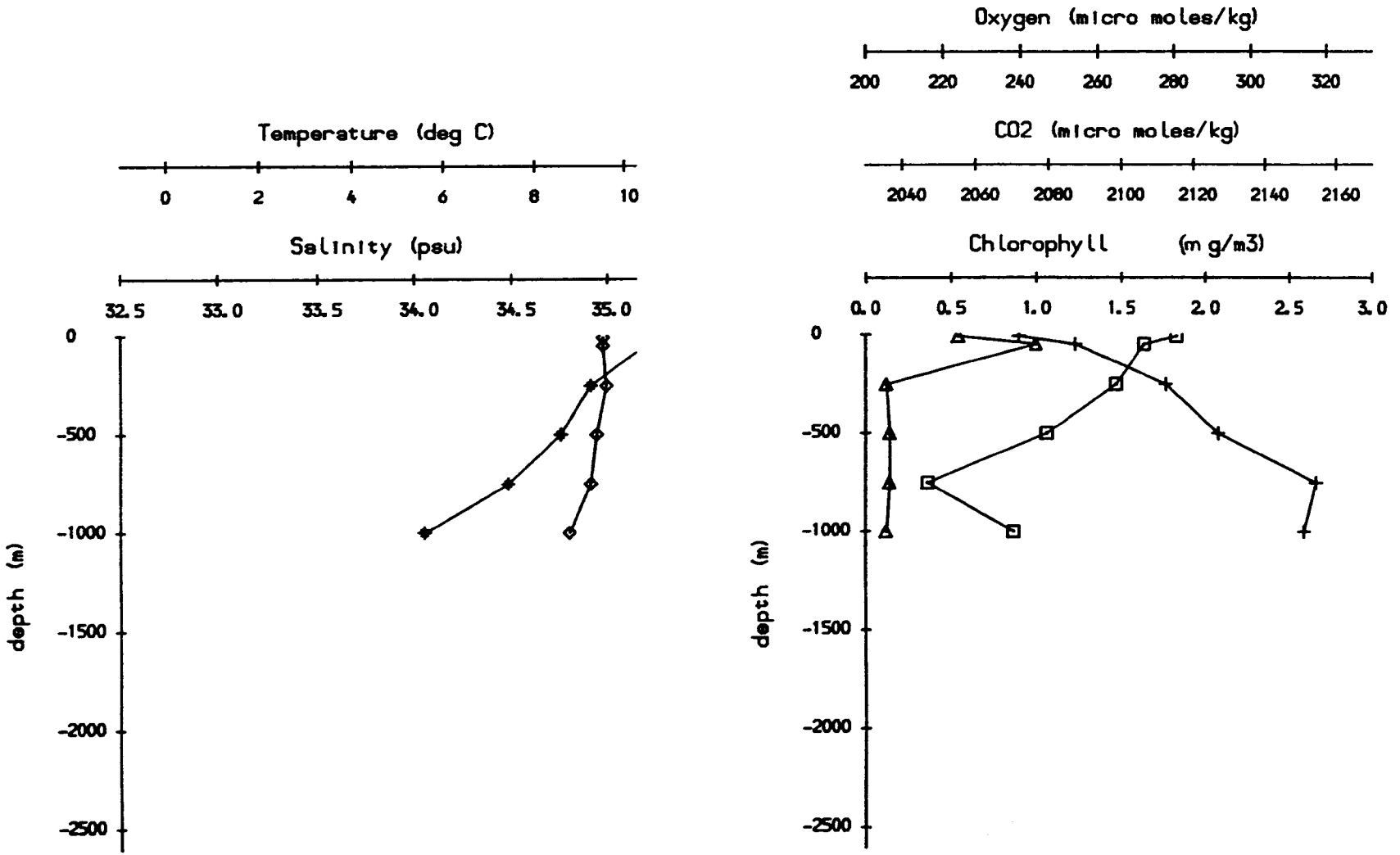


Figure 9.5 **STATION 8**

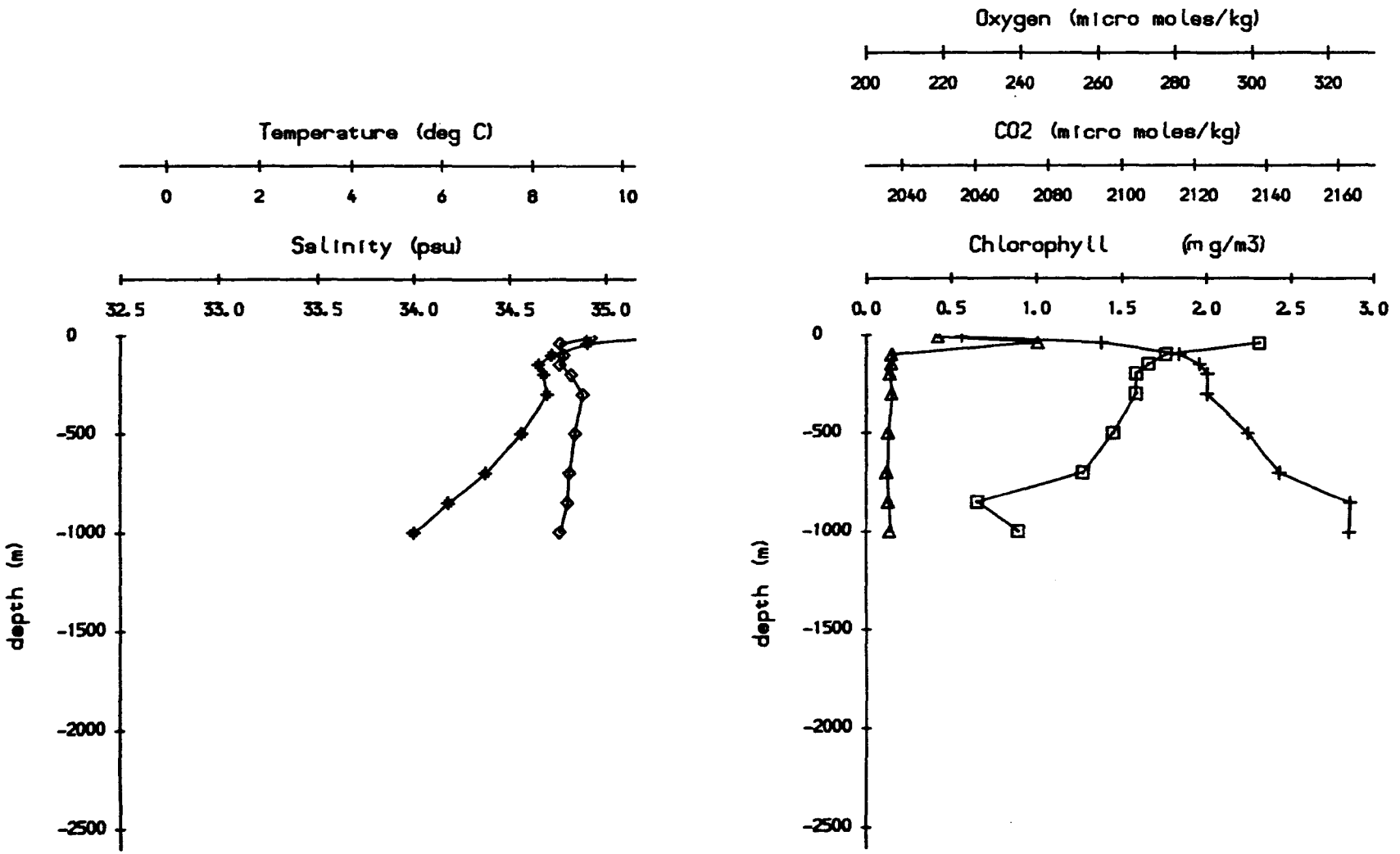


Figure 9.6 **STATION 9**

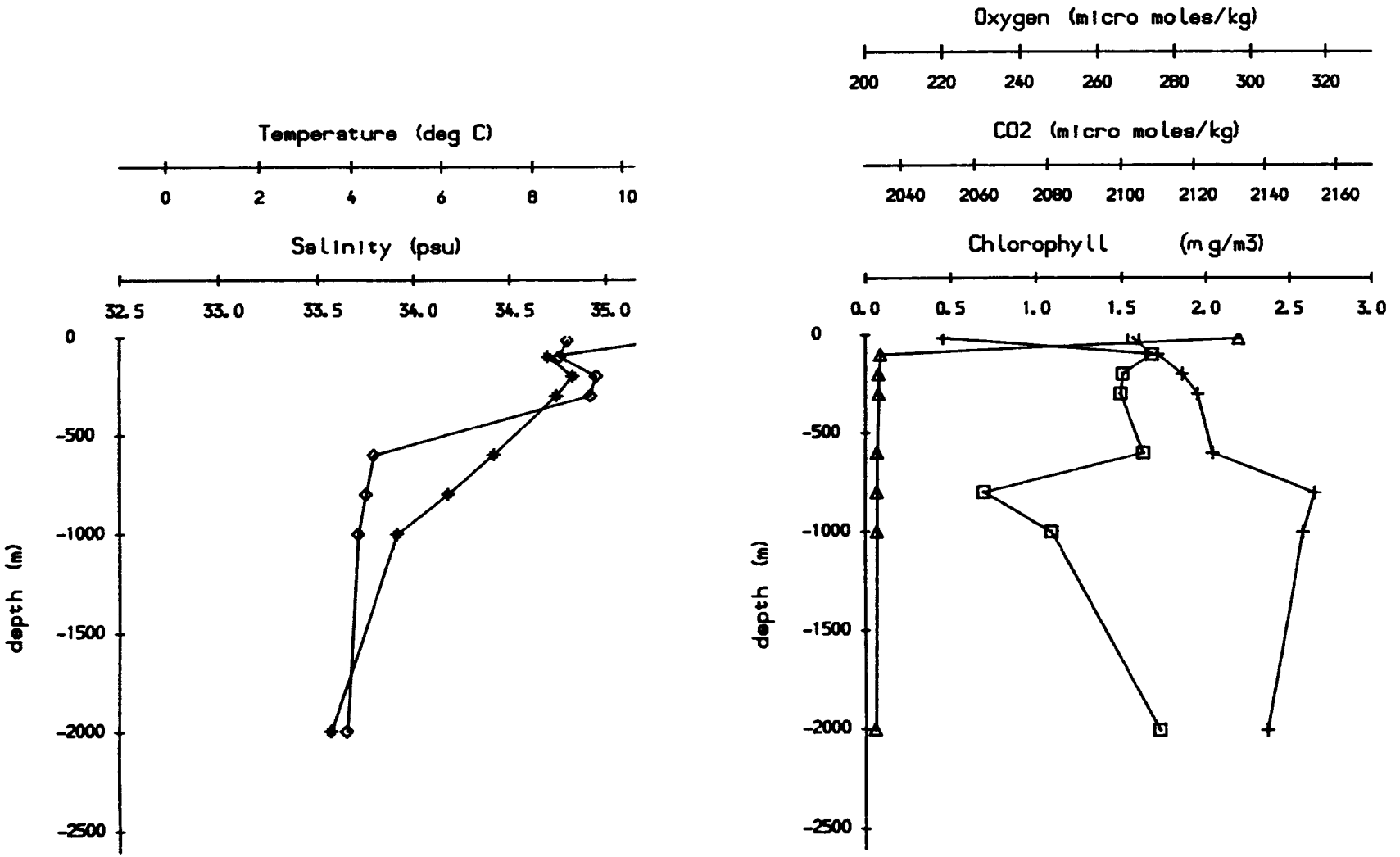


Figure 9.7 **STATION 11**

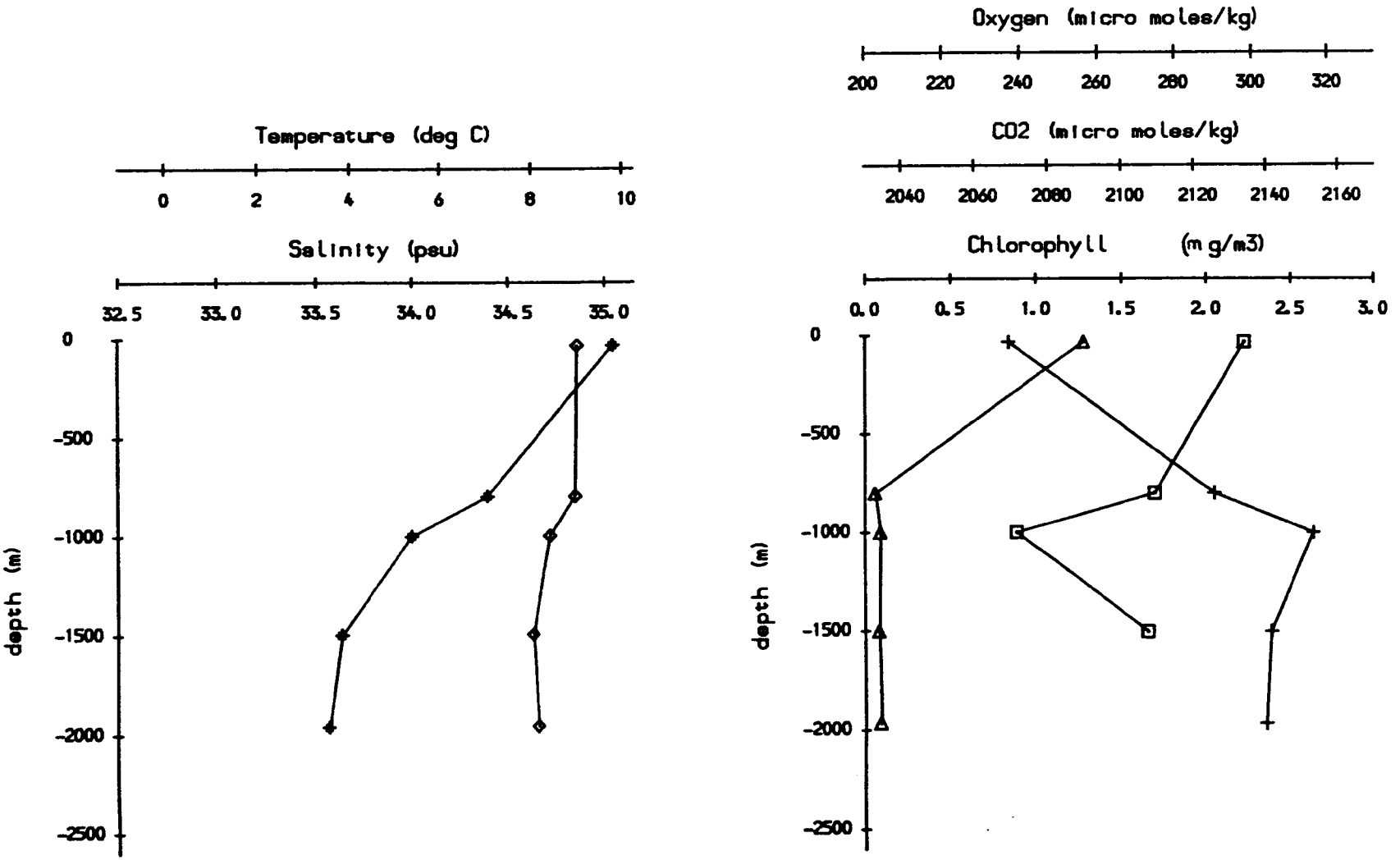


Figure 9.8 **STATION 12**

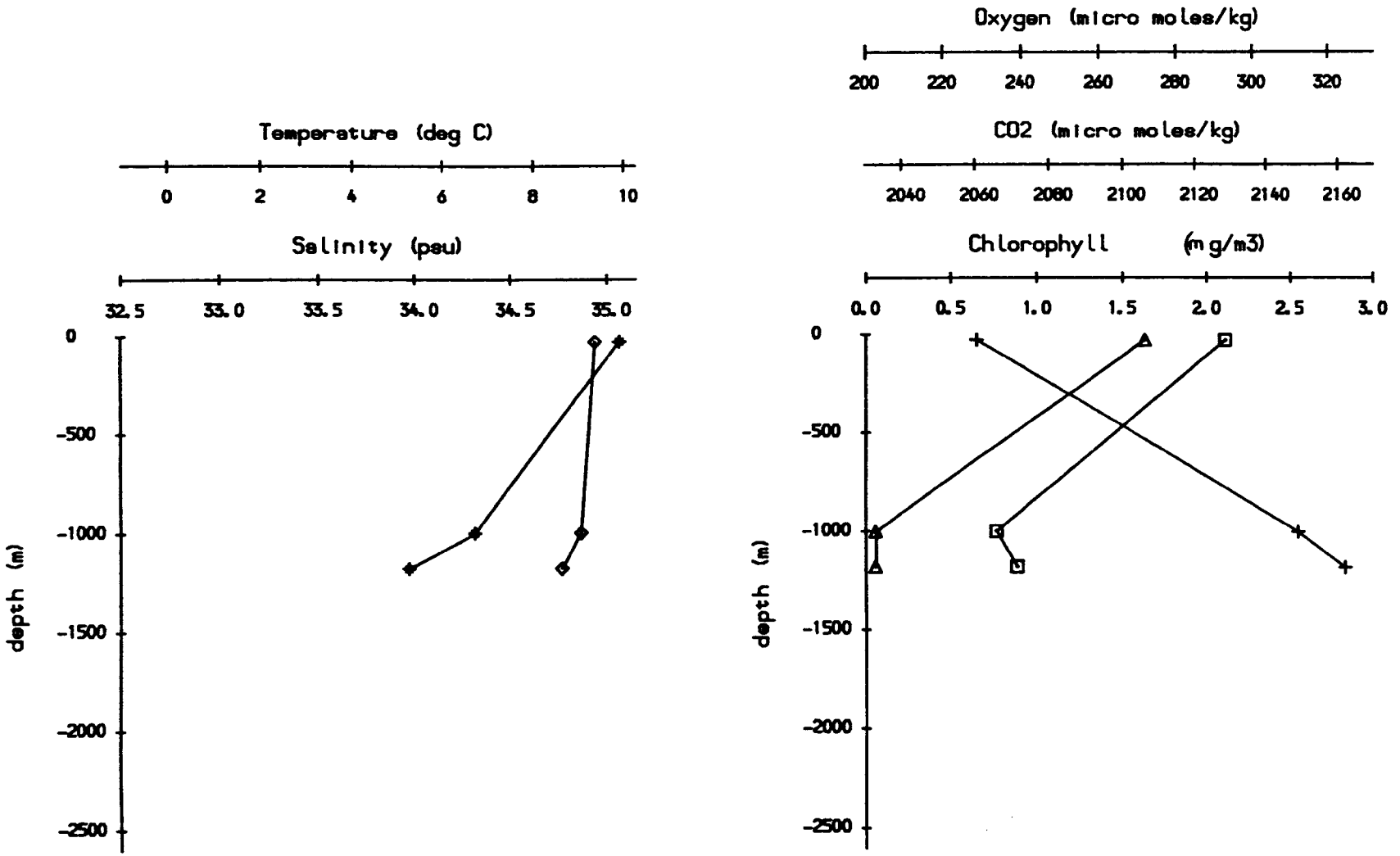


Figure 9.9 **STATION 14**

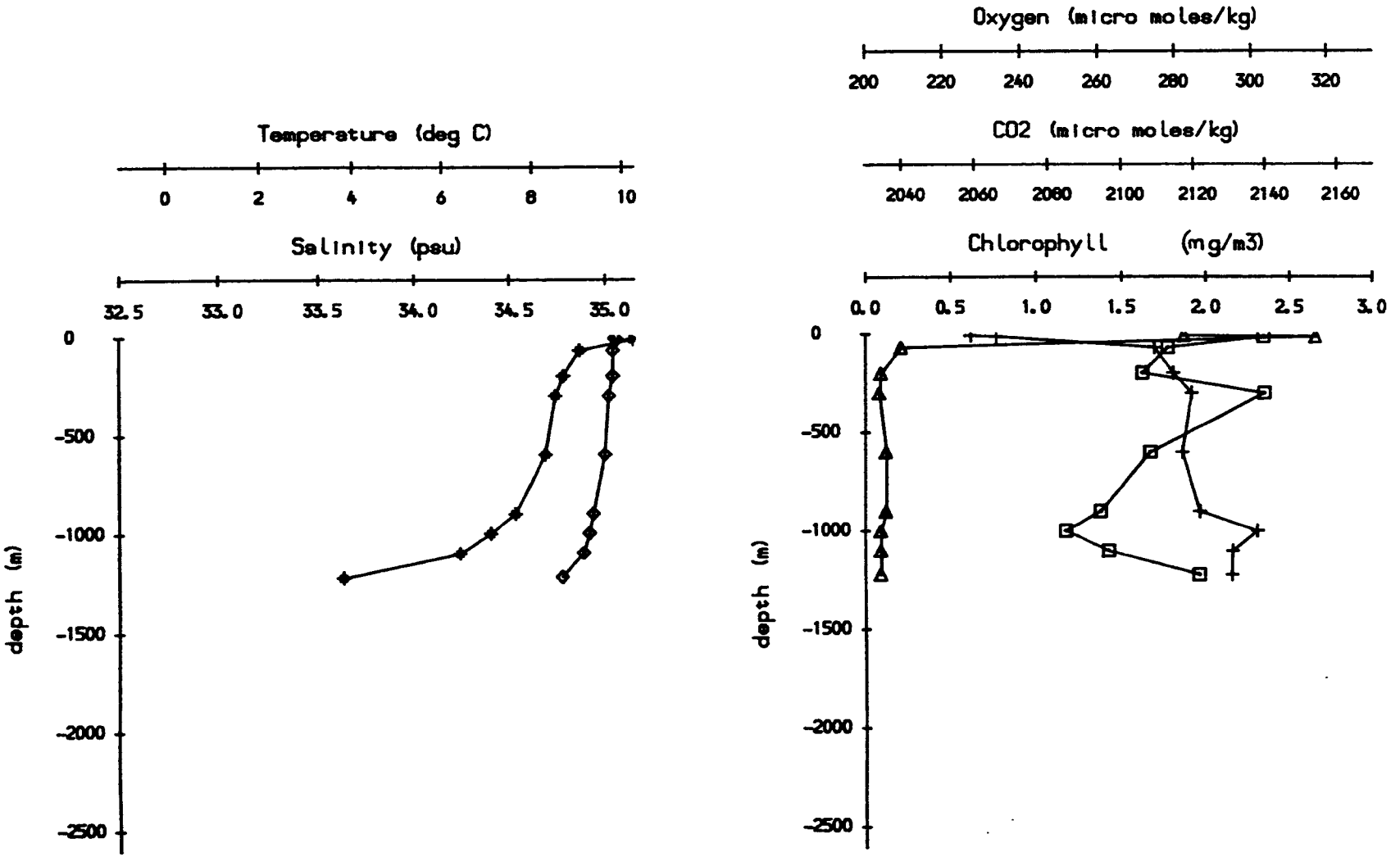


Figure 9.10 **STATION 15**

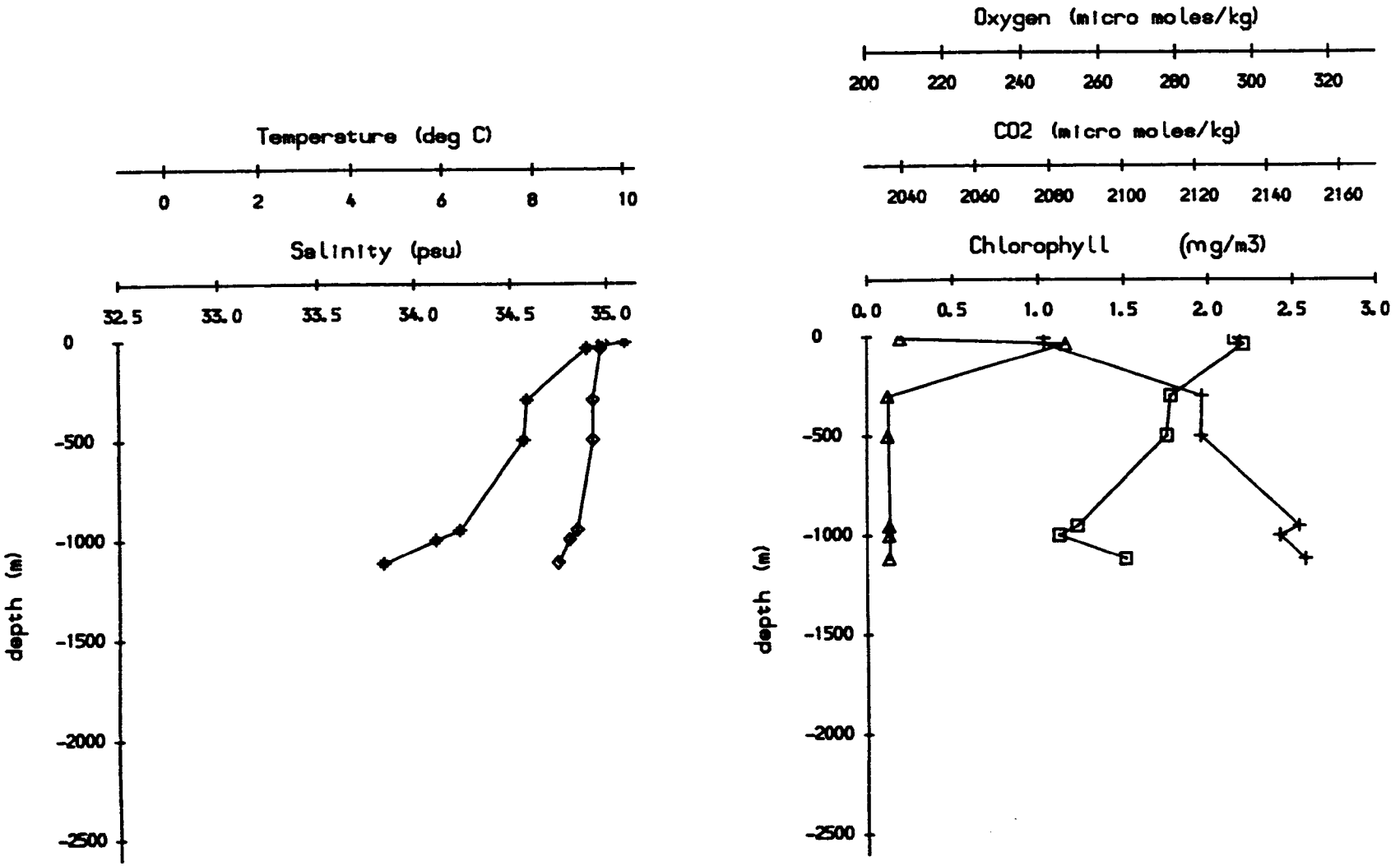
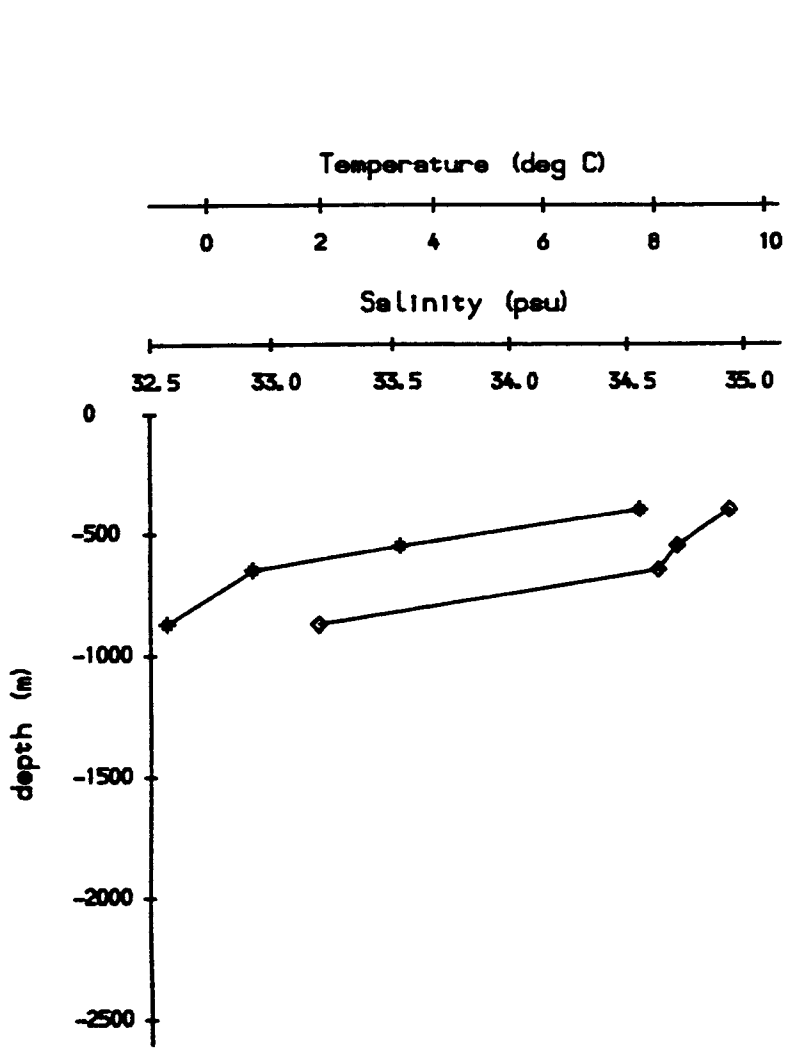


Figure 9.11 **STATION 16**



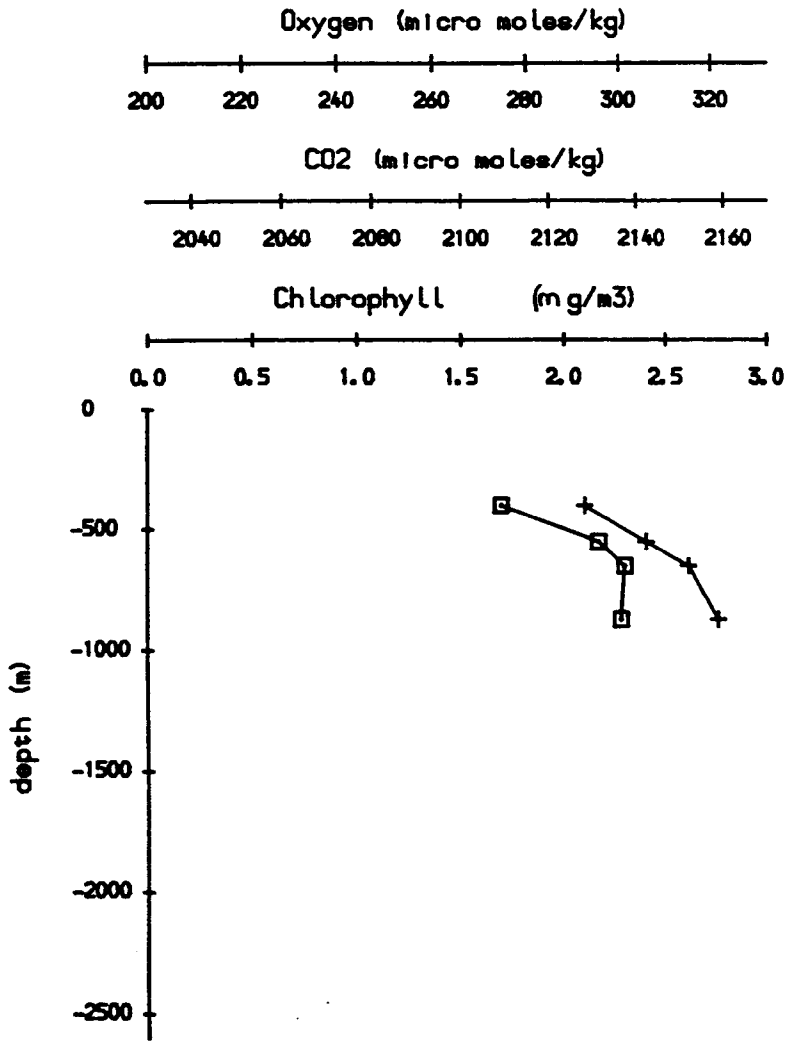


Figure 9.12 **STATION 17**

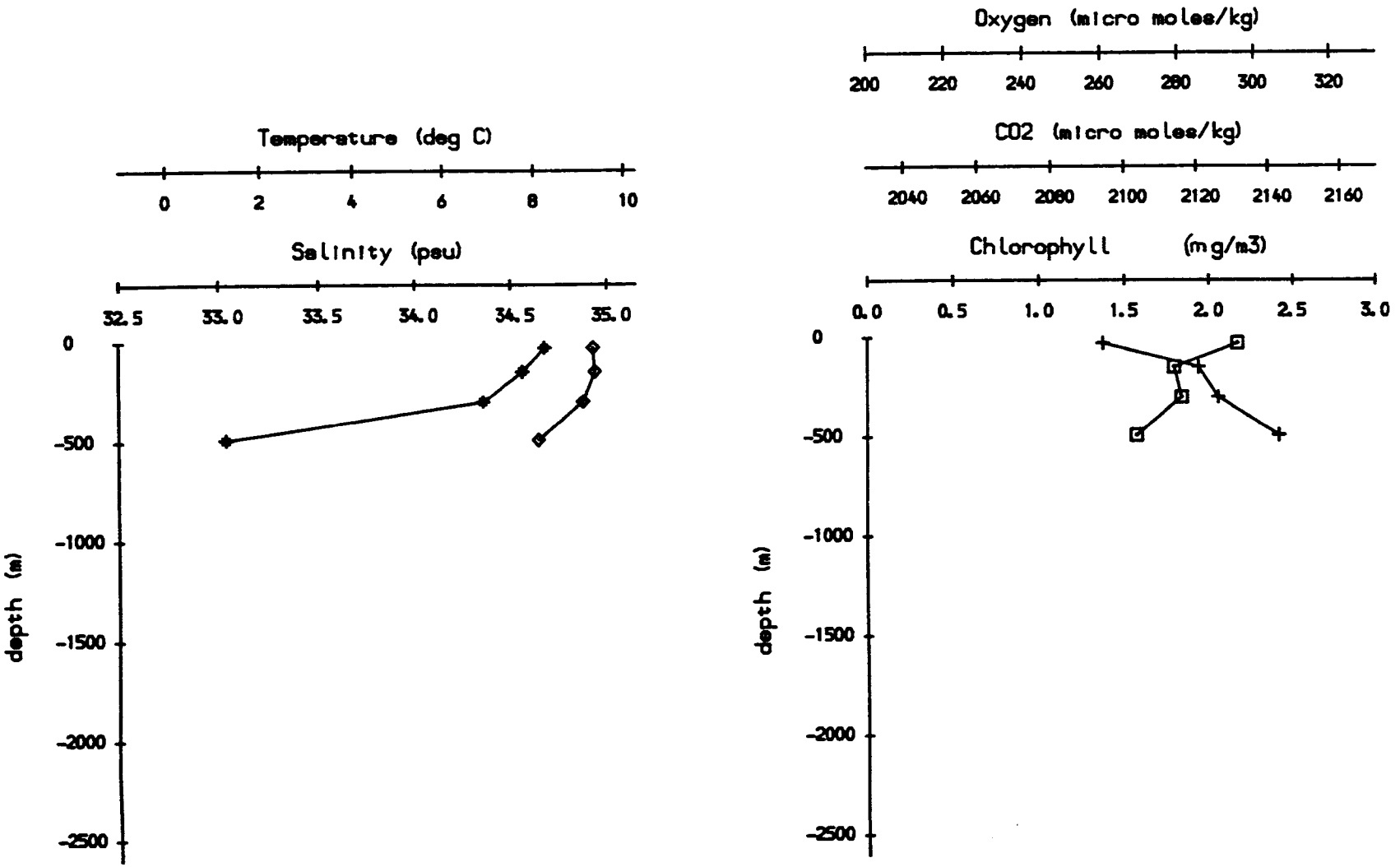


Figure 9.13 **STATION 18**

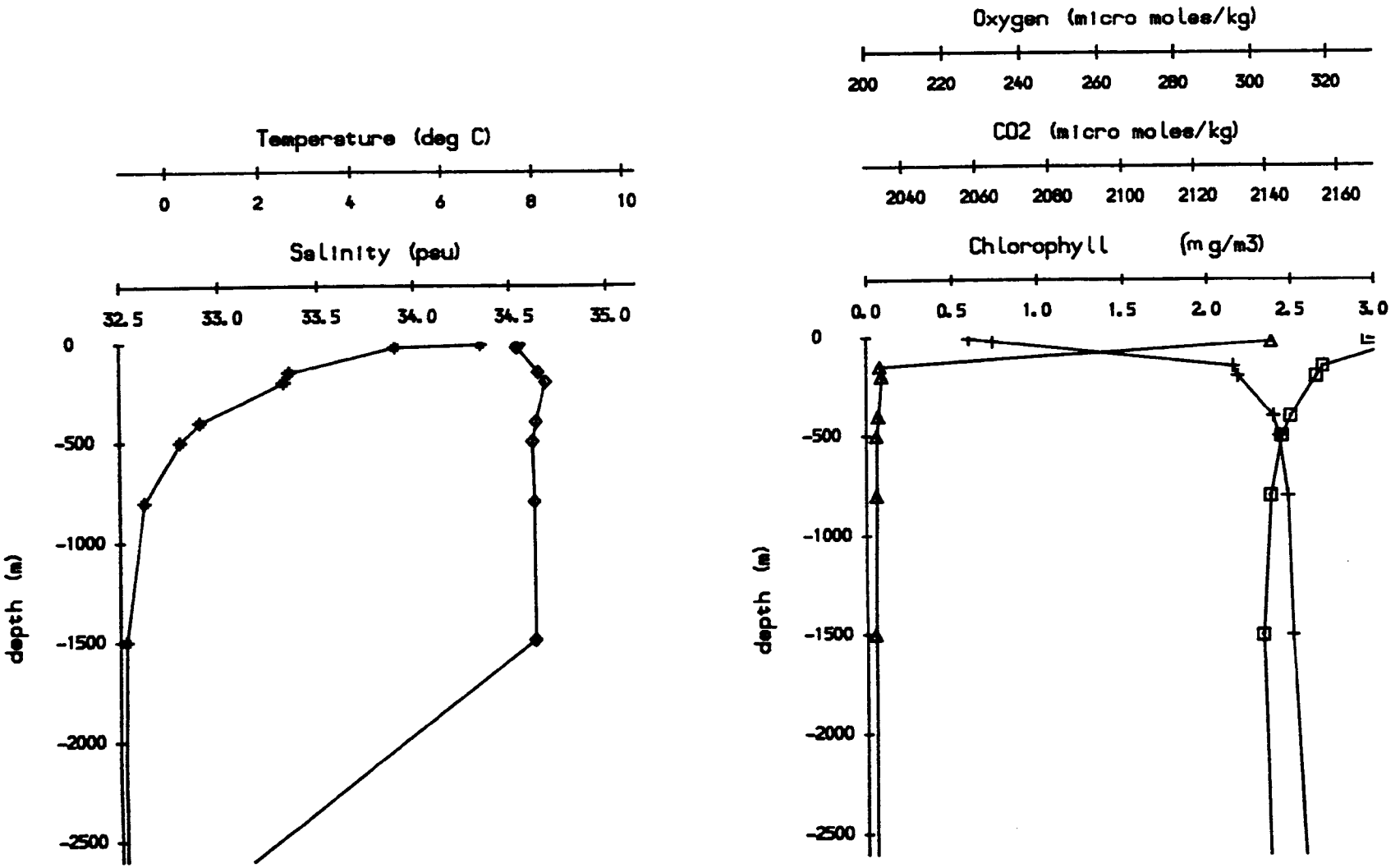


Figure 9.14 **STATION 19**

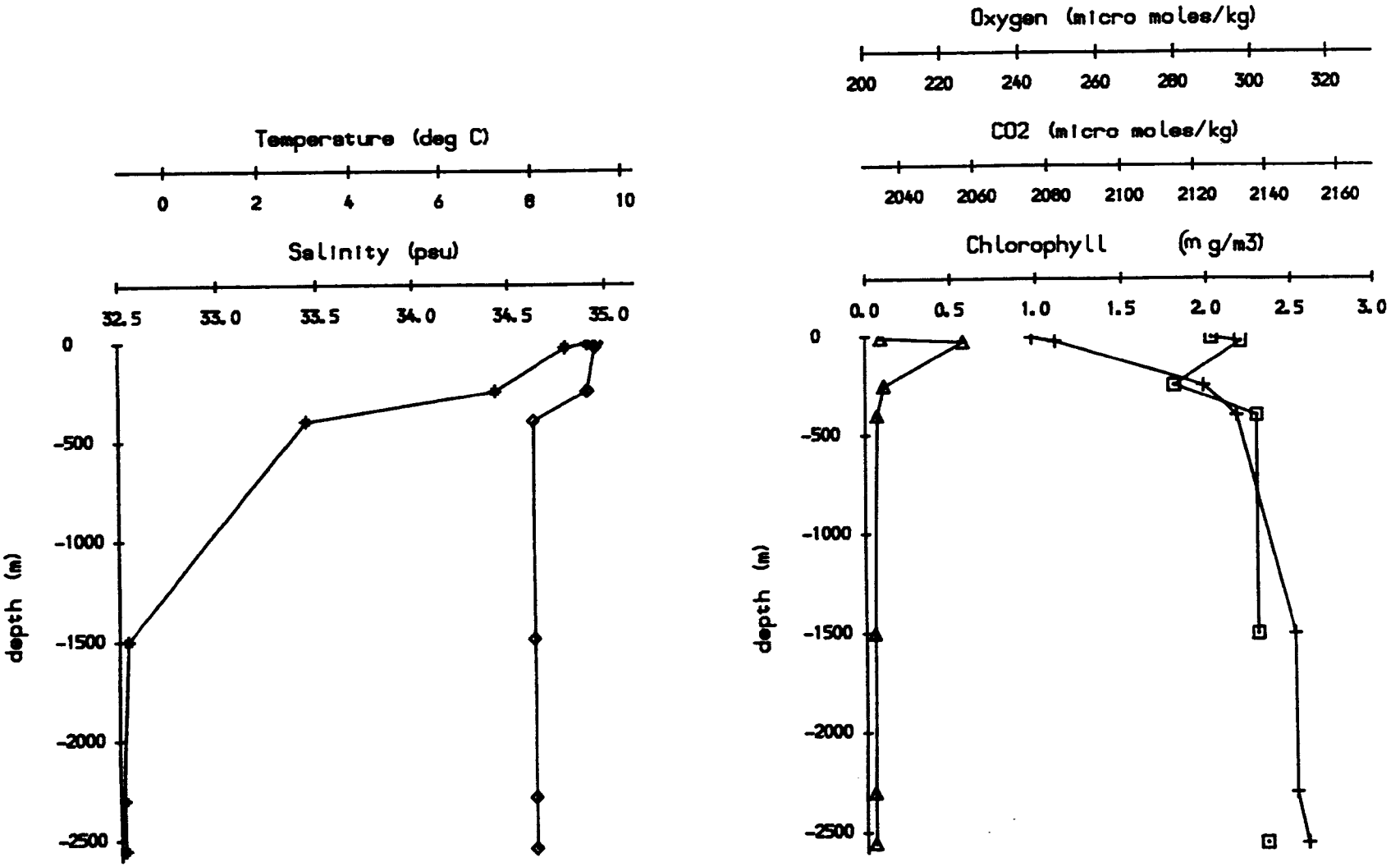


Figure 9.15 **STATION 20**

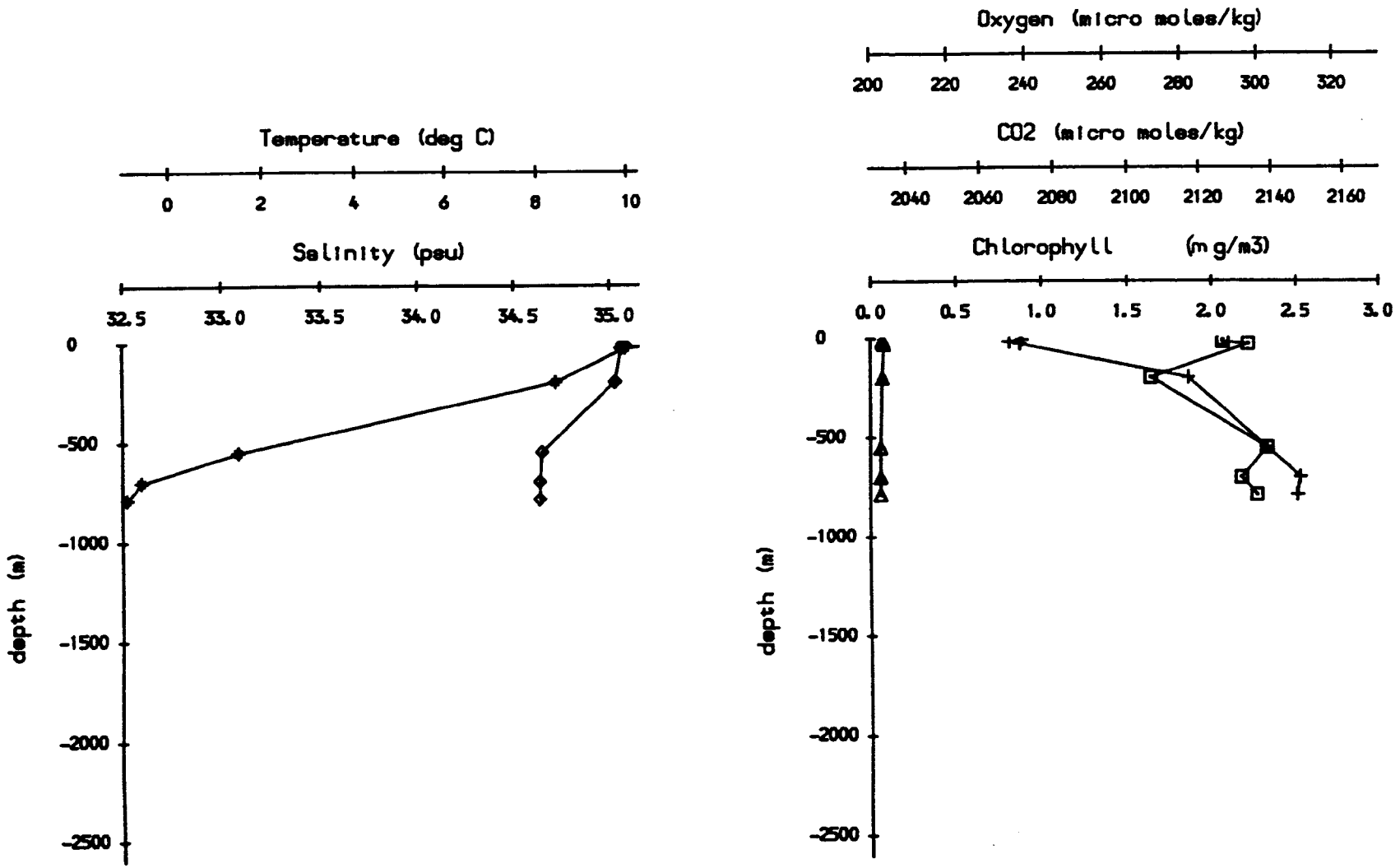


Figure 9.16 **STATION 21**

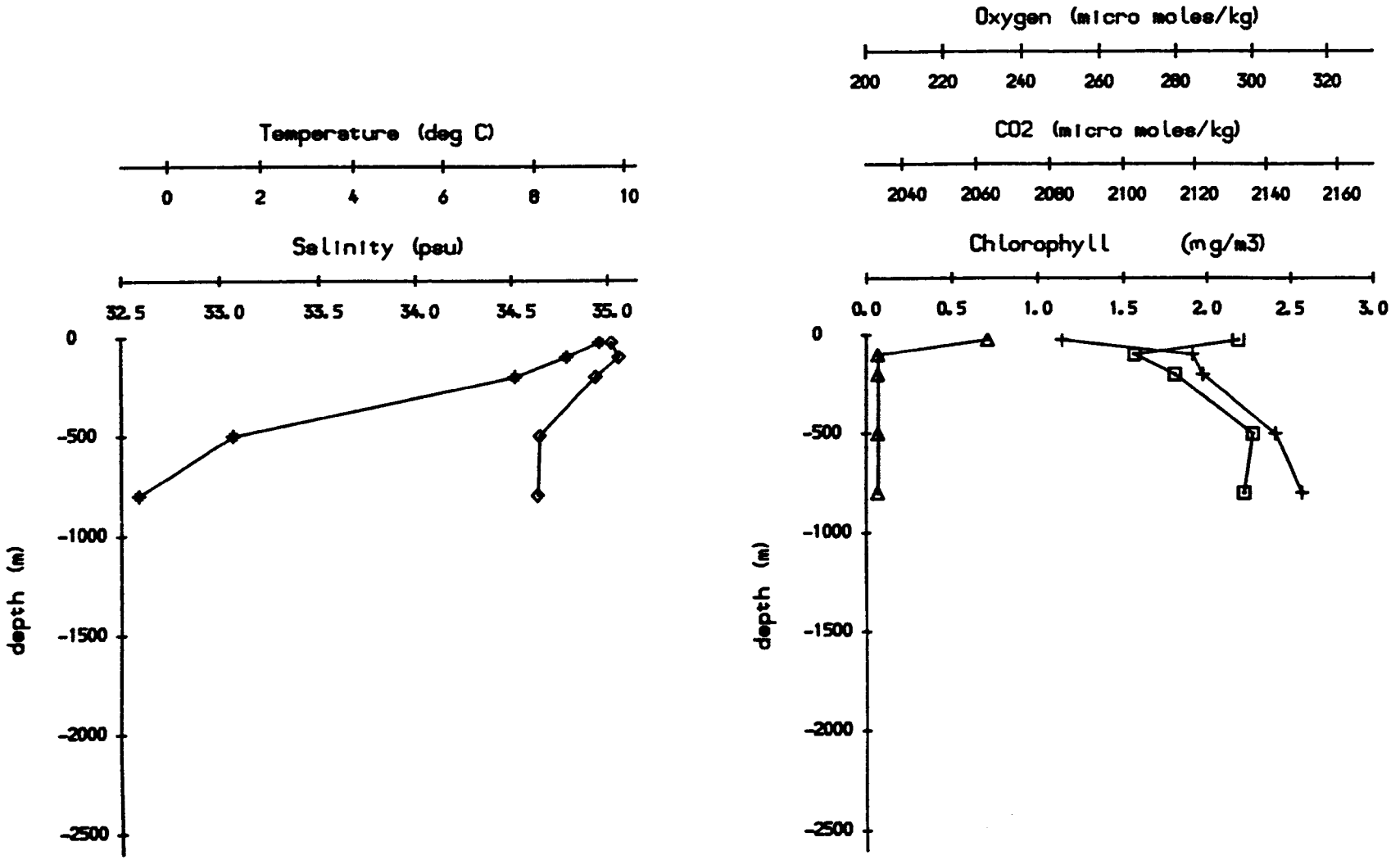


Figure 9.17 **STATION 23**

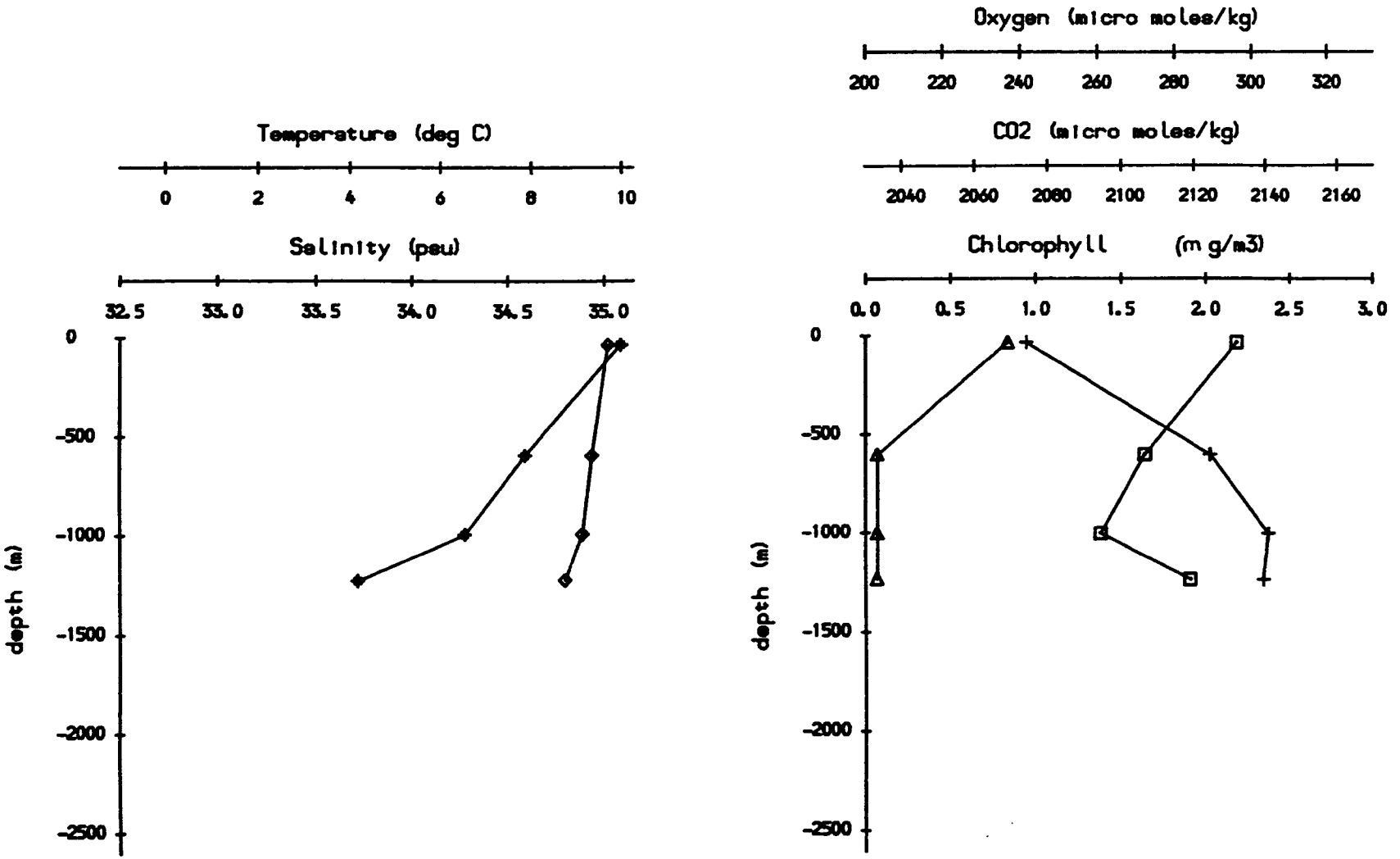
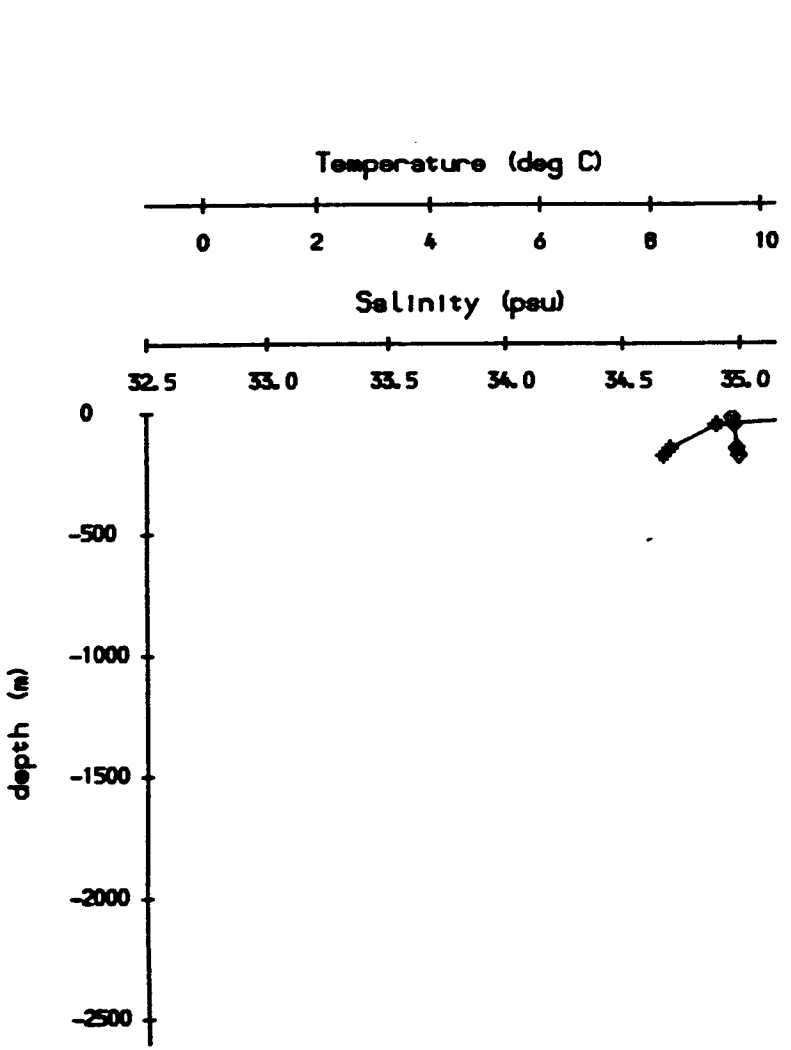


Figure 9.18 **STATION 24**



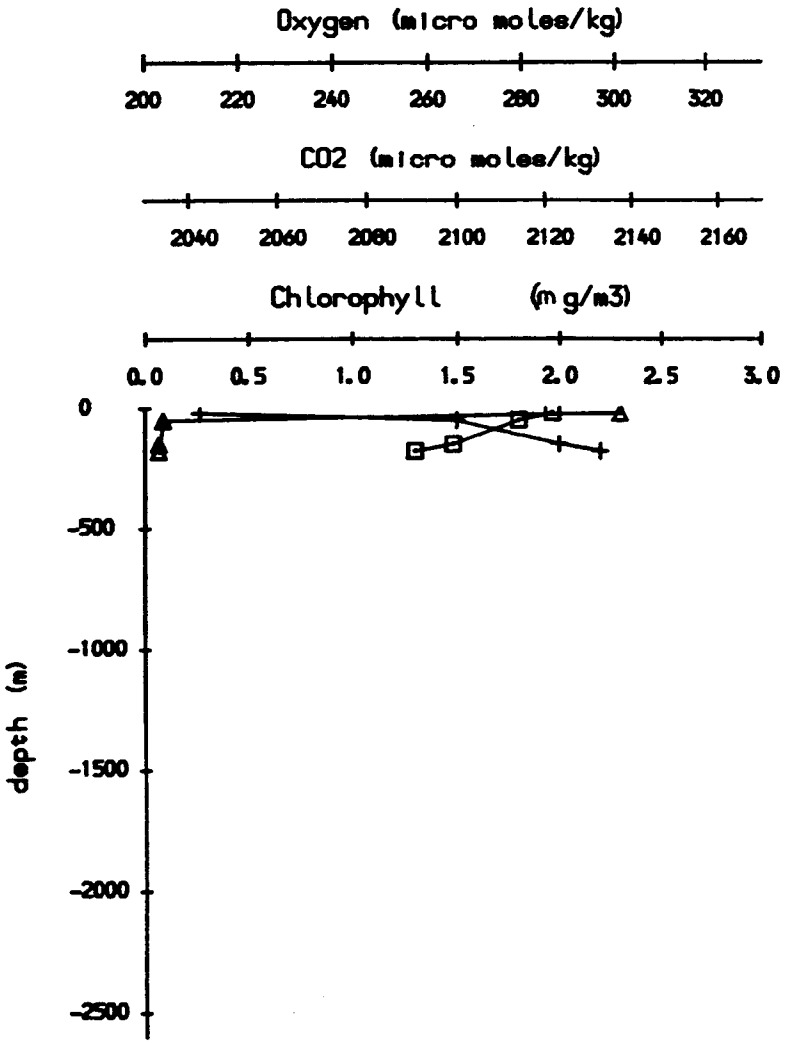


Figure 9.19 **STATION 25**

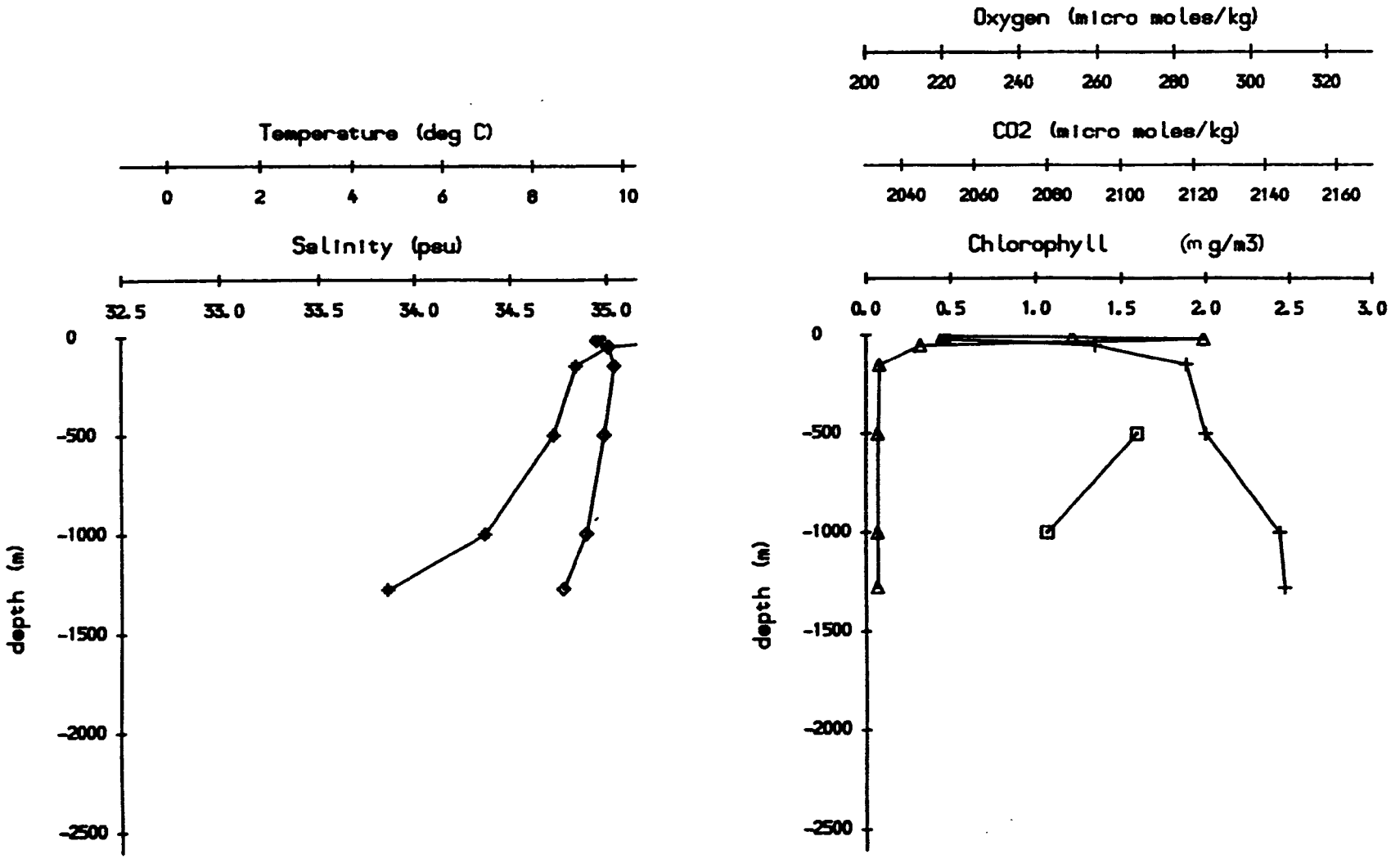
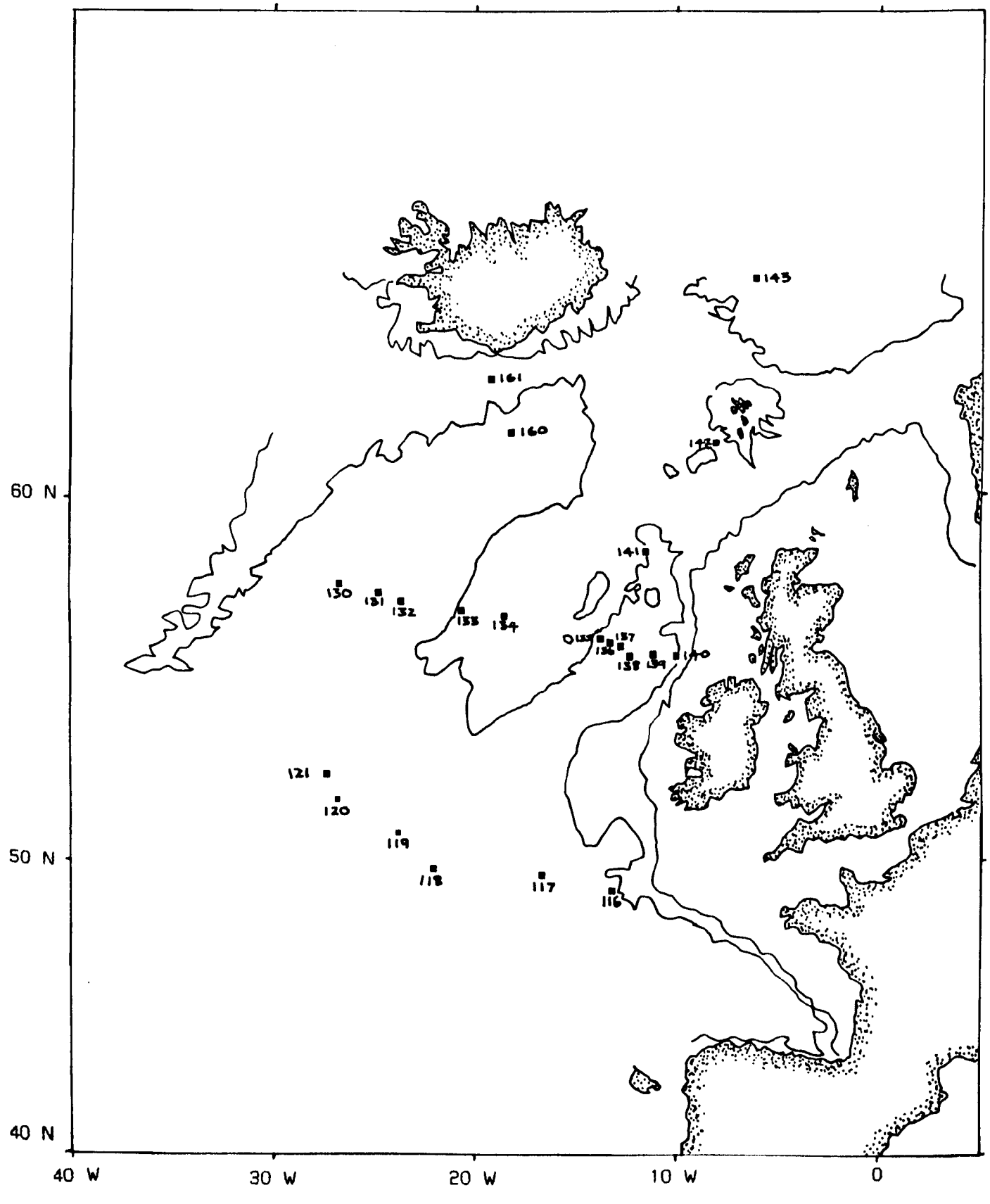


FIGURE 9.20

Position of TTO Expedition (1981) Stations
in N.E.Atlantic.



Position of TTO sampling stations

Figure 9.20

FIGURE 9.21

RRS Challenger 16/87
Position of transects chosen

RRS CHALLENGER CRUISE JUNE 1987

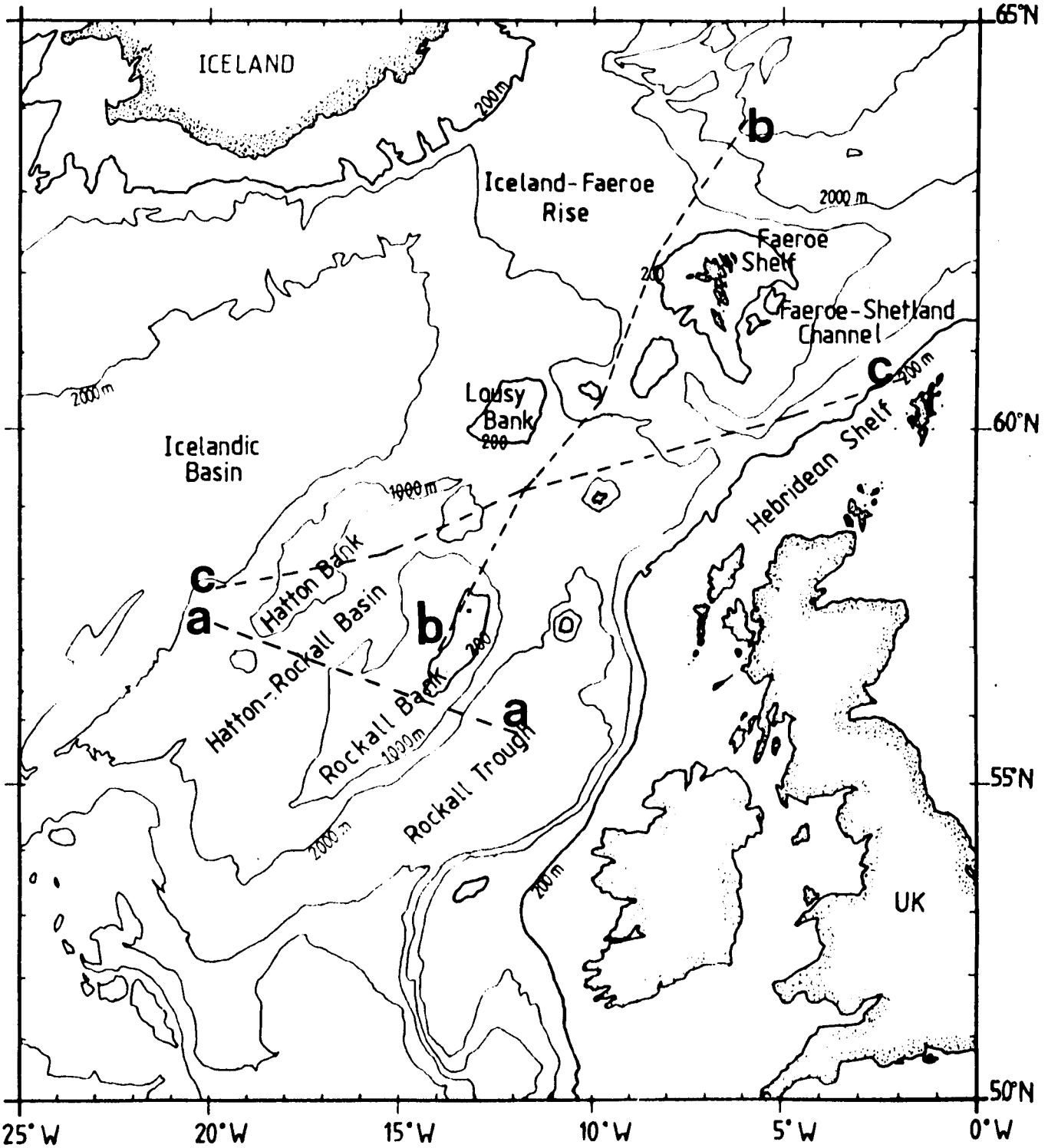


Figure 9.21

FIGURE 9.22

Sub-surface contoured transect
Transect (A) - Stations 10 to 4
TCO_2 (μmol/kg)

Sub-surface contoured transect
Transect (A) - Stations 10 to 4
O_2 (μmol/kg)

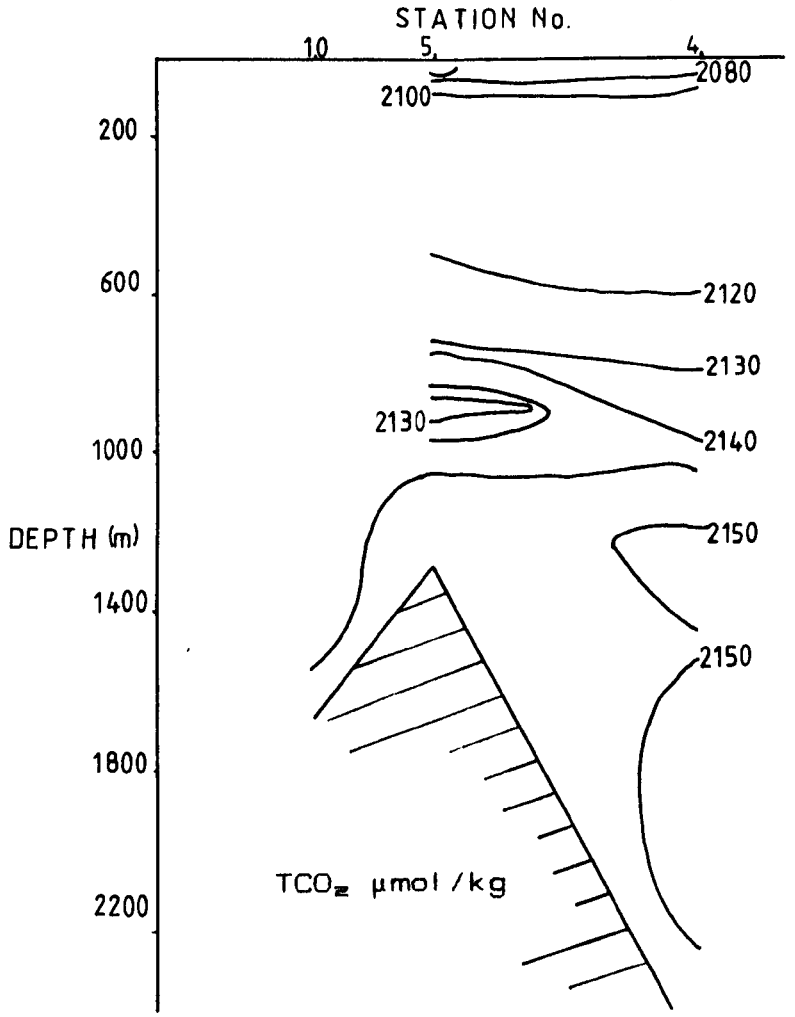

STATION No.
10
5
4
2080
2100
200
600
2120
2130
2130
2140
1000
DEPTH (m)
2150
1400
2150
1800
TCO2 µmol /kg
2200

Figure 9.22

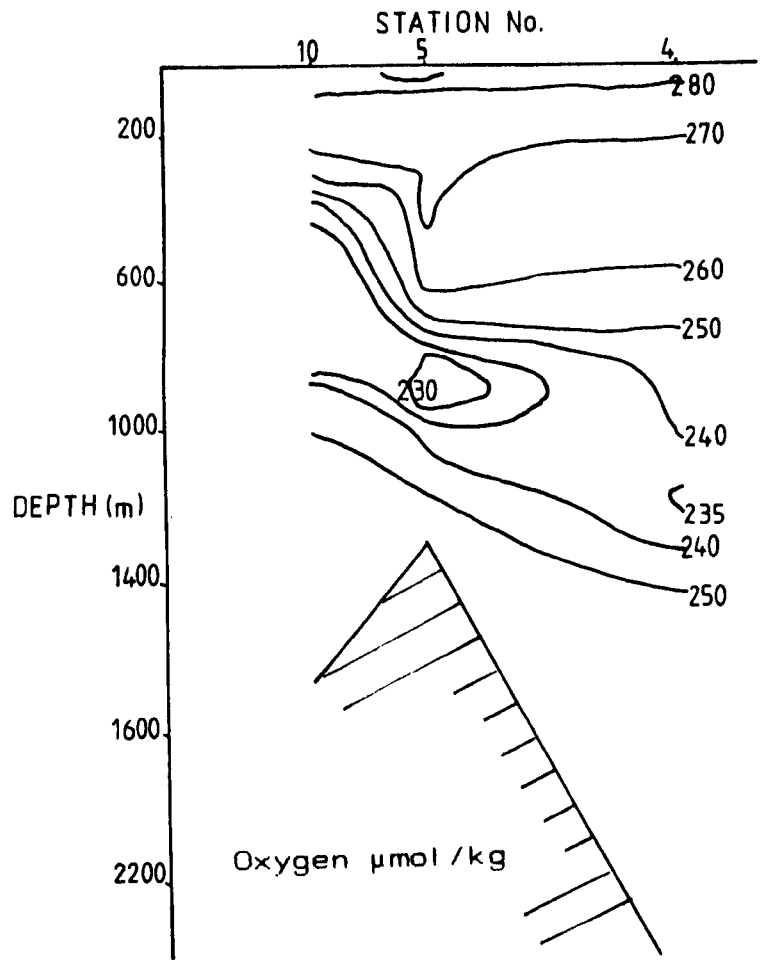

STATION No.
10
5
4
280
200
270
600
260
250
230
1000
240
DEPTH (m)
235
240
1400
250
1600
Oxygen µmol /kg
2200

FIGURE 9.23

Sub-surface contoured transect
Transect (A) - Stations 10 to 4
Salinity (‰)

Sub-surface contoured transect
Transect (A) - Stations 10 to 4
Temperature (^{0}C)

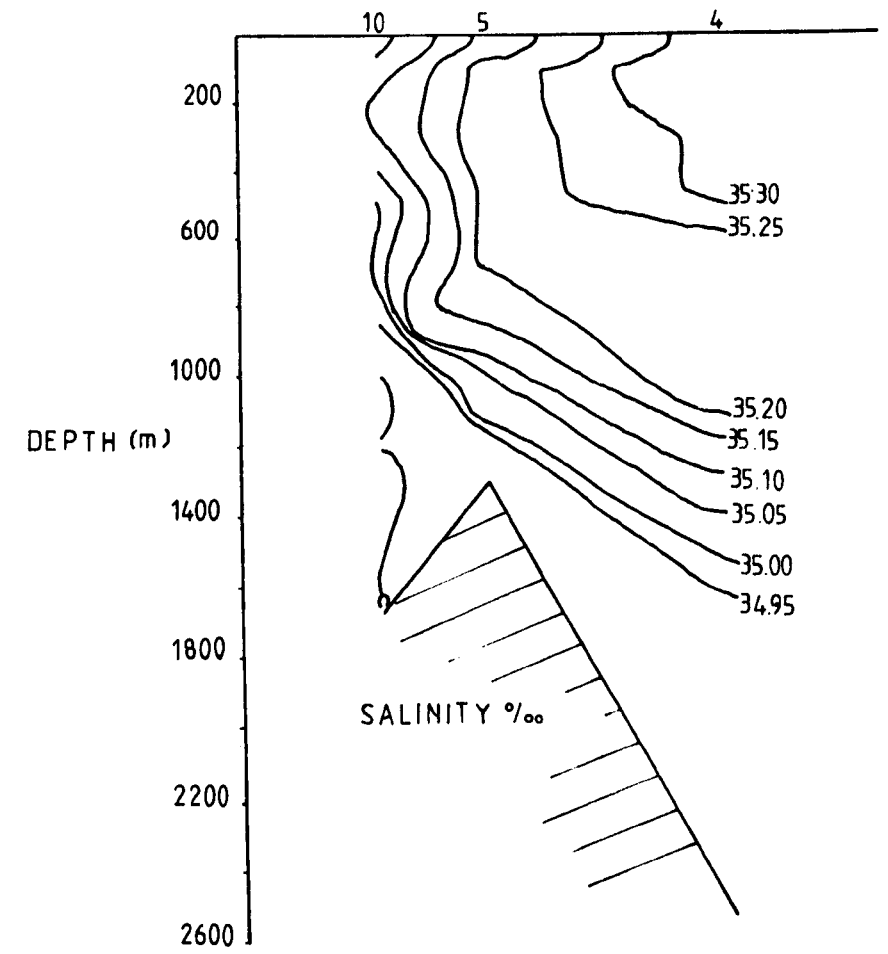

STATION No.
10
5
4
200
600
1000
1400
1800
2200
2600
DEPTH (m)
35.30
35.25
35.20
35.15
35.10
35.05
35.00
34.95
SALINITY ‰

Figure 9.23

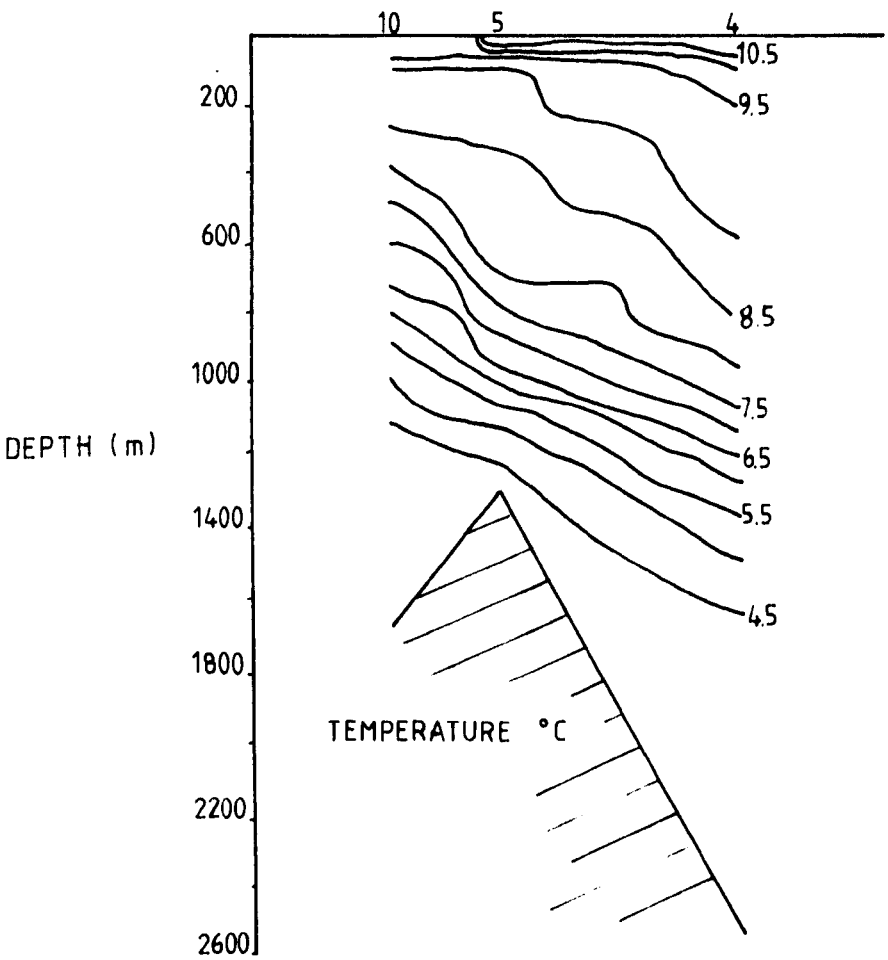

STATION No.
10
5
4
200
600
1000
1400
1800
2200
2600
DEPTH (m)
10.5
9.5
8.5
7.5
6.5
5.5
4.5
TEMPERATURE °C

FIGURE 9.24

Sub-surface contoured transect
Transect (B) - Stations 18 to 24
TCO_2 (μmol/kg)

Sub-surface contoured transect
Transect (B) - Stations 18 to 24
O_2 (μmol/kg)

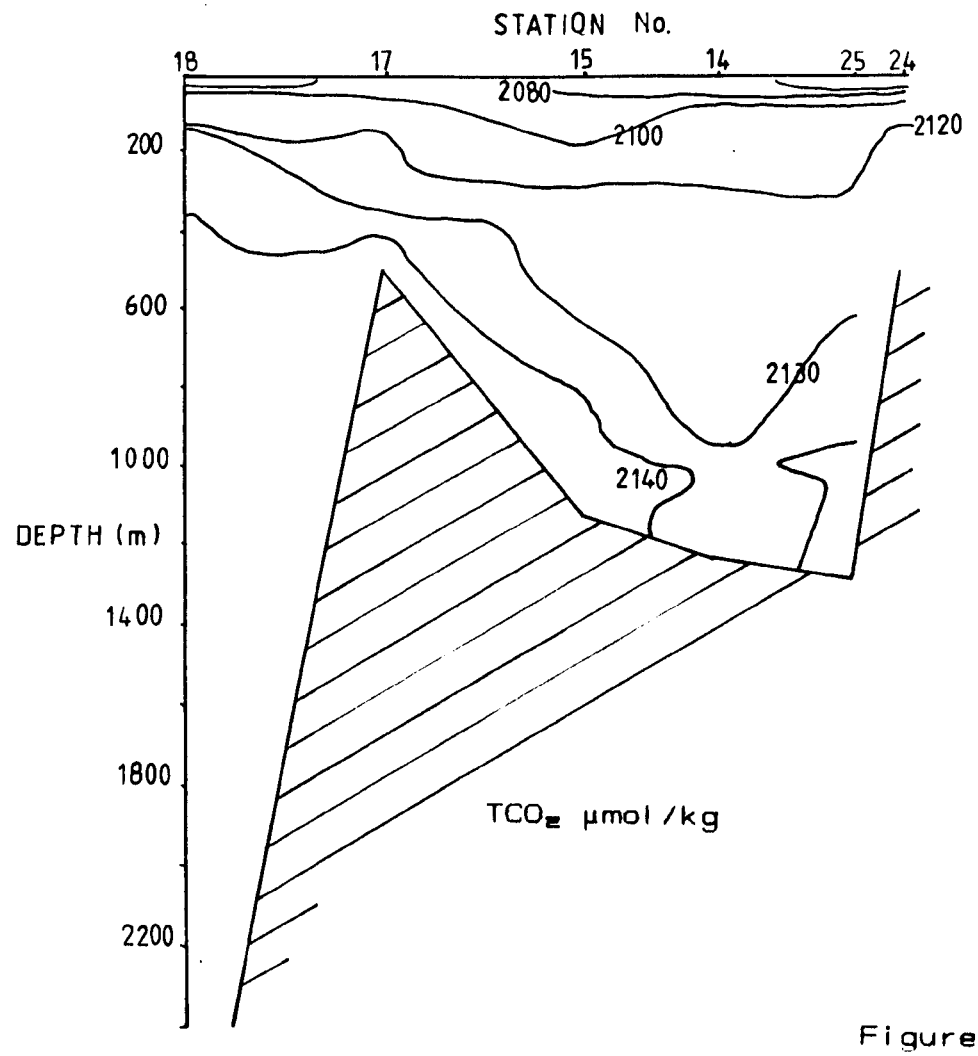

STATION No.
18
17
15
14
25
24
2080
2100
2120
2130
2140
200
600
1000
1400
1800
2200
DEPTH (m)
TCO₂ µmol/kg

Figure 9.24

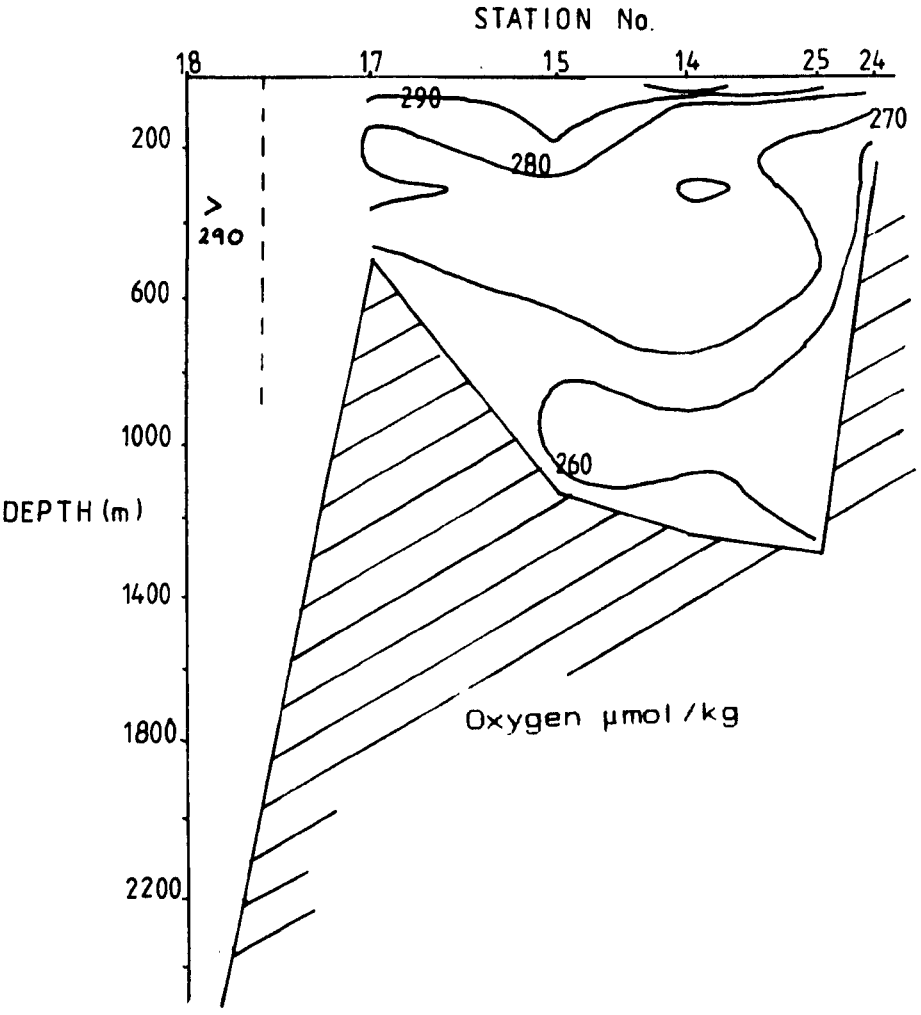

STATION No.
18
17
15
14
25
24
290
280
270
260
> 290
200
600
1000
1400
1800
2200
DEPTH (m)
Oxygen µmol/kg

FIGURE 9.25

Sub-surface contoured transect
Transect (B) - Stations 18 to 24
Salinity (‰)

Sub-surface contoured transect
Transect (B) - Stations 18 to 24
Temperature (^{0}C)

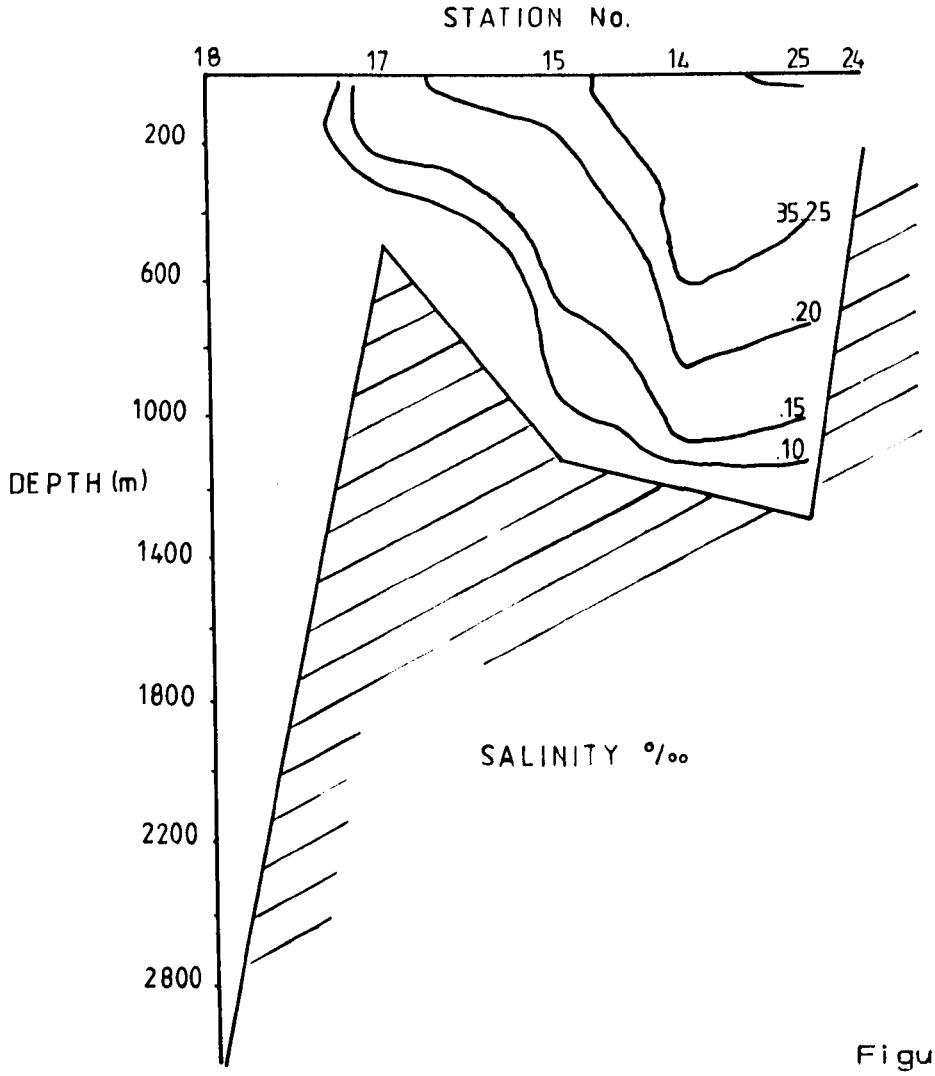

STATION No.
18
17
15
14
25
24
200
600
1000
1400
1800
2200
2800
DEPTH (m)
35.25
.20
.15
.10
SALINITY °/oo

Figure 9.25

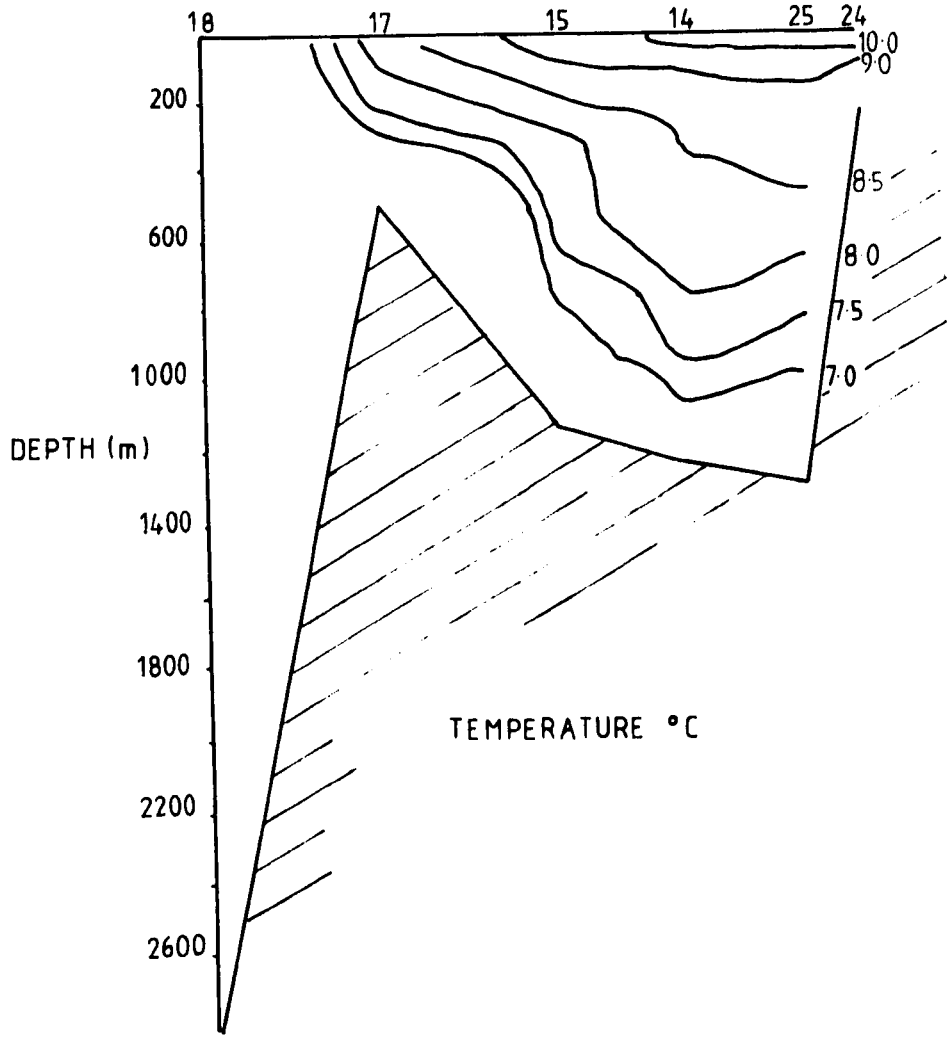

STATION No.
18
17
15
14
25
24
200
600
1000
1400
1800
2200
2600
DEPTH (m)
10.0
9.0
8.5
8.0
7.5
7.0
TEMPERATURE °C

FIGURE 9.26

Sub-surface contoured transect
Transect (C) - Stations 9 to 20
TCO_2 (μmol/kg)

Sub-surface contoured transect
Transect (C) - Stations 18 to 24
O_2 (μmol/kg)

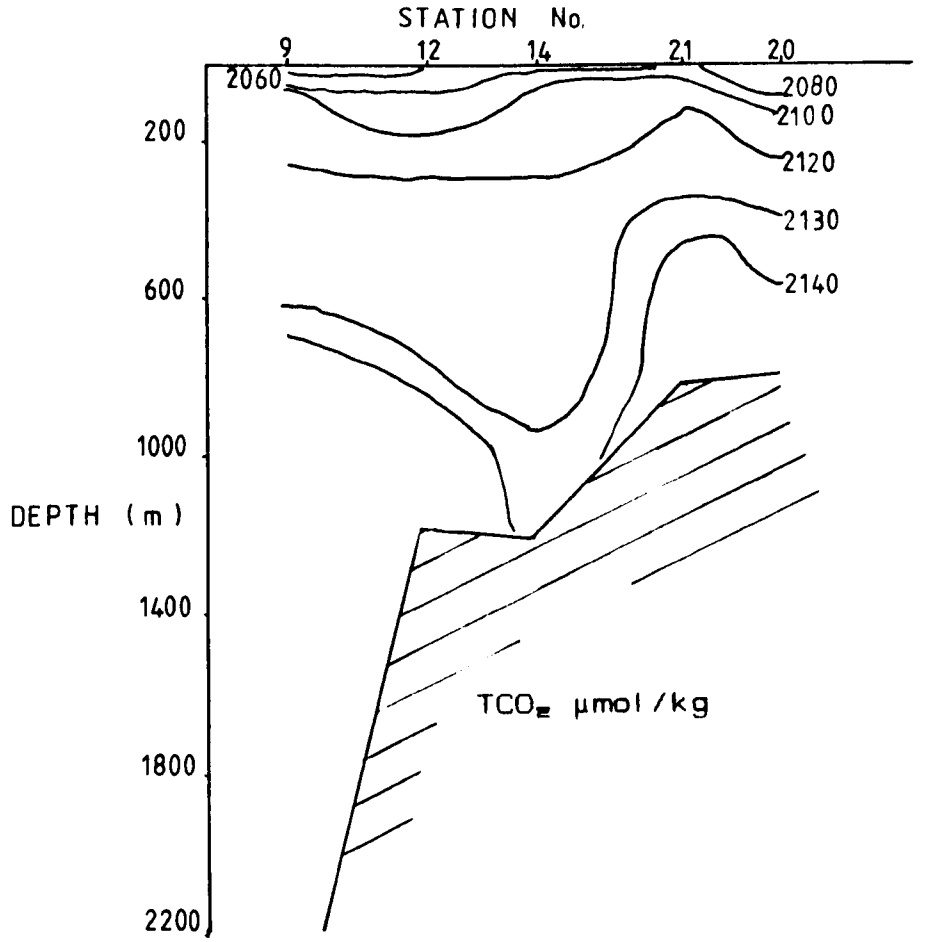

STATION No.
9
12
14
21
20
2060
2080
2100
2120
2130
2140
200
600
1000
1400
1800
2200
DEPTH (m)
TCO₂ µmol/kg

Figure 9.26

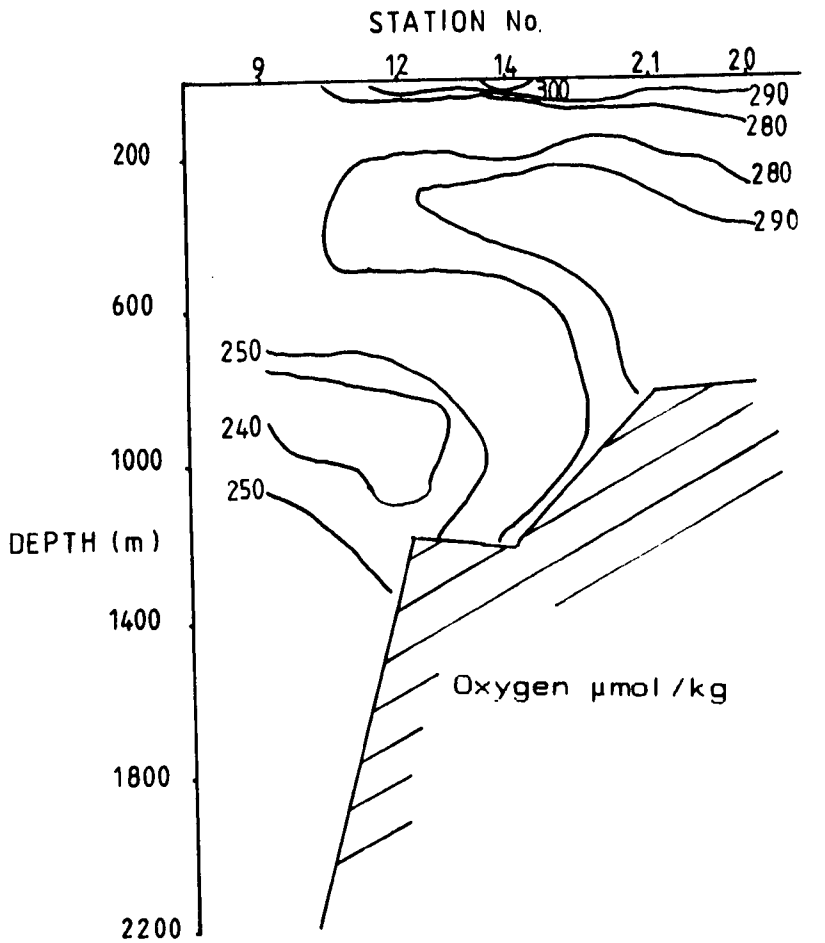

STATION No.
9
12
14
21
20
300
290
280
280
290
250
240
250
200
600
1000
1400
1800
2200
DEPTH (m)
Oxygen µmol/kg

FIGURE 9.27

Sub-surface contoured transect
Transect (C) - Stations 9 to 20
Salinity (‰)

Sub-surface contoured transect
Transect (C) - Stations 18 to 24
Temperature (^{0}C)

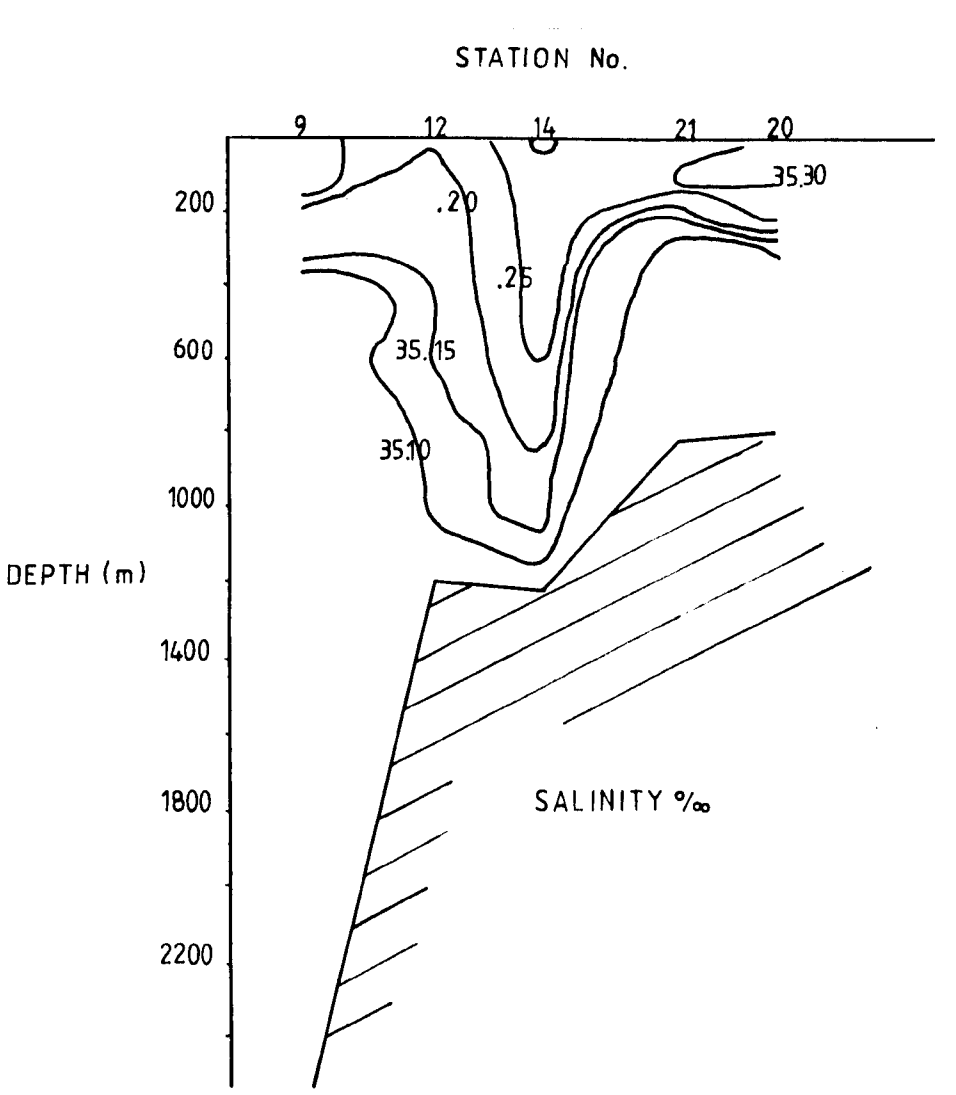

STATION No.
9
12
14
21
20
200
600
1000
1400
1800
2200
DEPTH (m)
35.30
.20
.25
35.15
35.10
SALINITY ‰

Figure 9.27

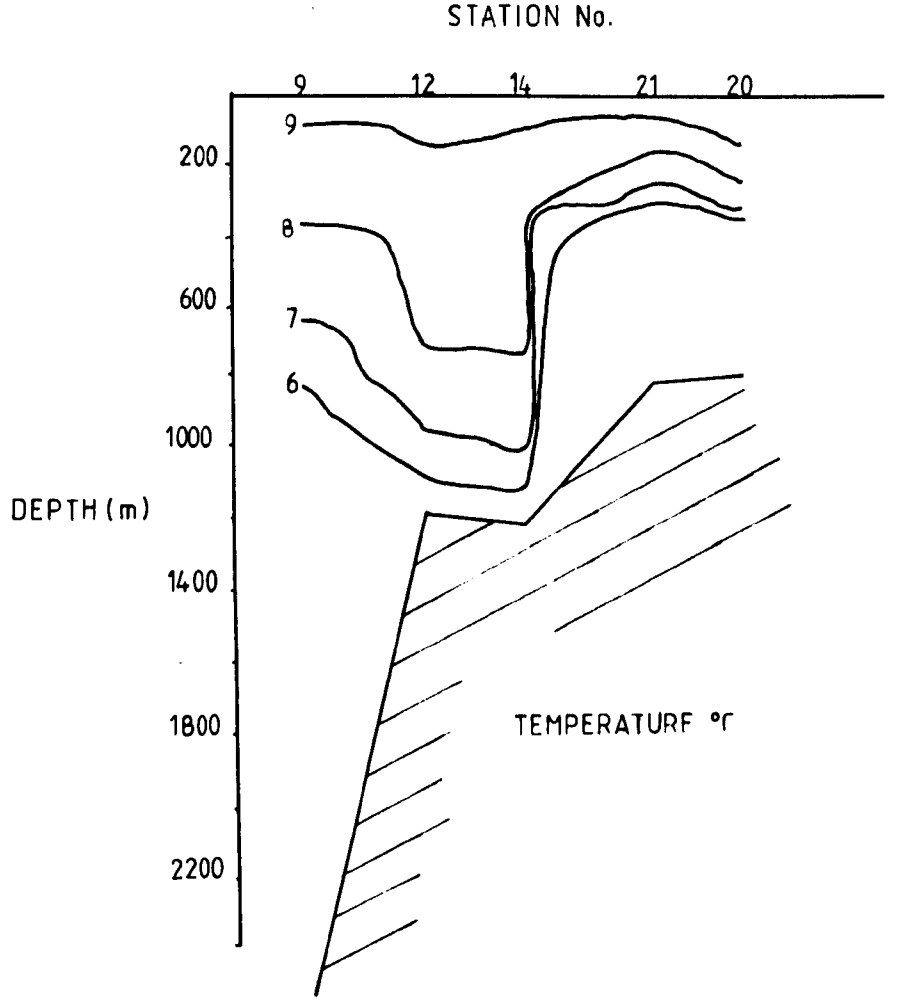

STATION No.
9
12
14
21
20
200
600
1000
1400
1800
2200
DEPTH (m)
9
8
7
6
TEMPERATURE °C

FIGURE 9.28

RRS Challenger 16/87
Cruise track and CTD Stations
First leg (8-22 June)

RRS CHALLENGER CRUISE JUNE 1987

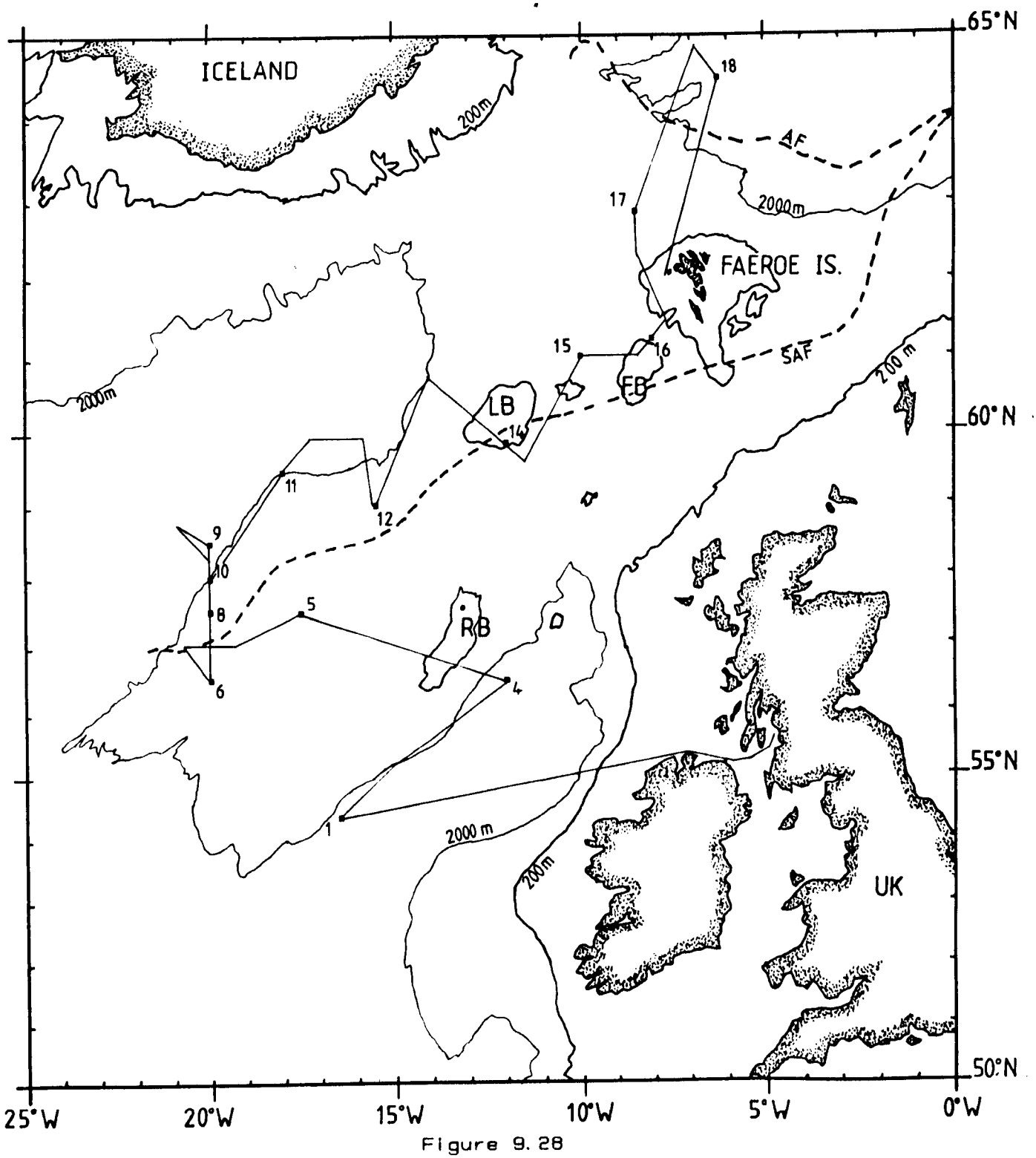


Figure 9.28

• = CTD Station 1st Leg
8-22 JUNE

FIGURE 9.29

RRS Challenger 16/87
Cruise track and CTD Stations
Second leg (23 June - 3 July)

RRS CHALLENGER CRUISE JUNE 1987

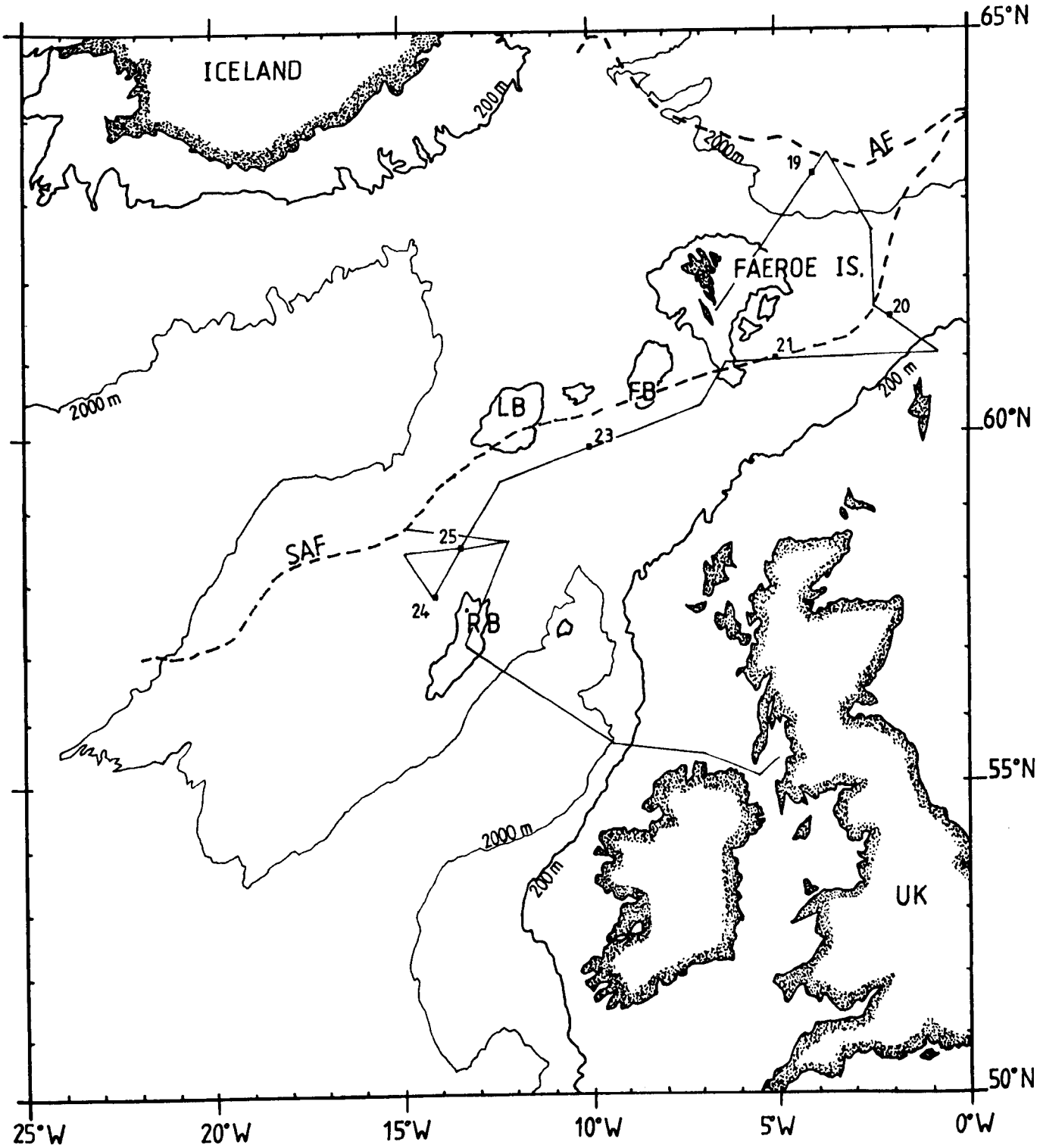


Figure 9.29

• = CTD Station 2nd Leg
23 JUNE - 3 JULY

FIGURE 9.30

RRS Challenger 16/87
Geographical and topographical
features of the region covered
by the cruise

RRS CHALLENGER CRUISE JUNE 1987

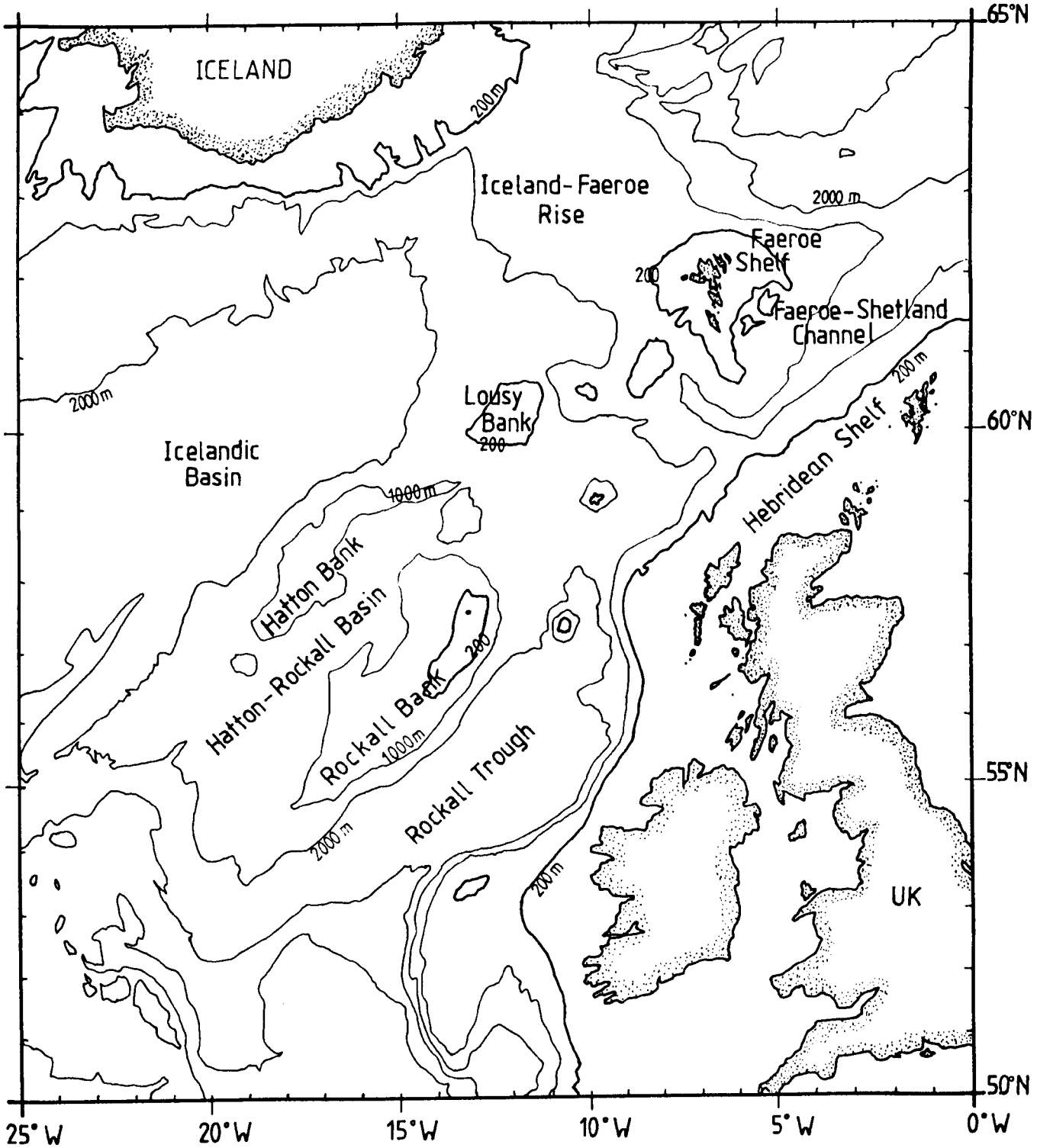


Figure 9.30

FIGURE 9.31

RRS Challenger 16/87
Contour diagram of Temperature (^{0}C)
Surface (3 m)

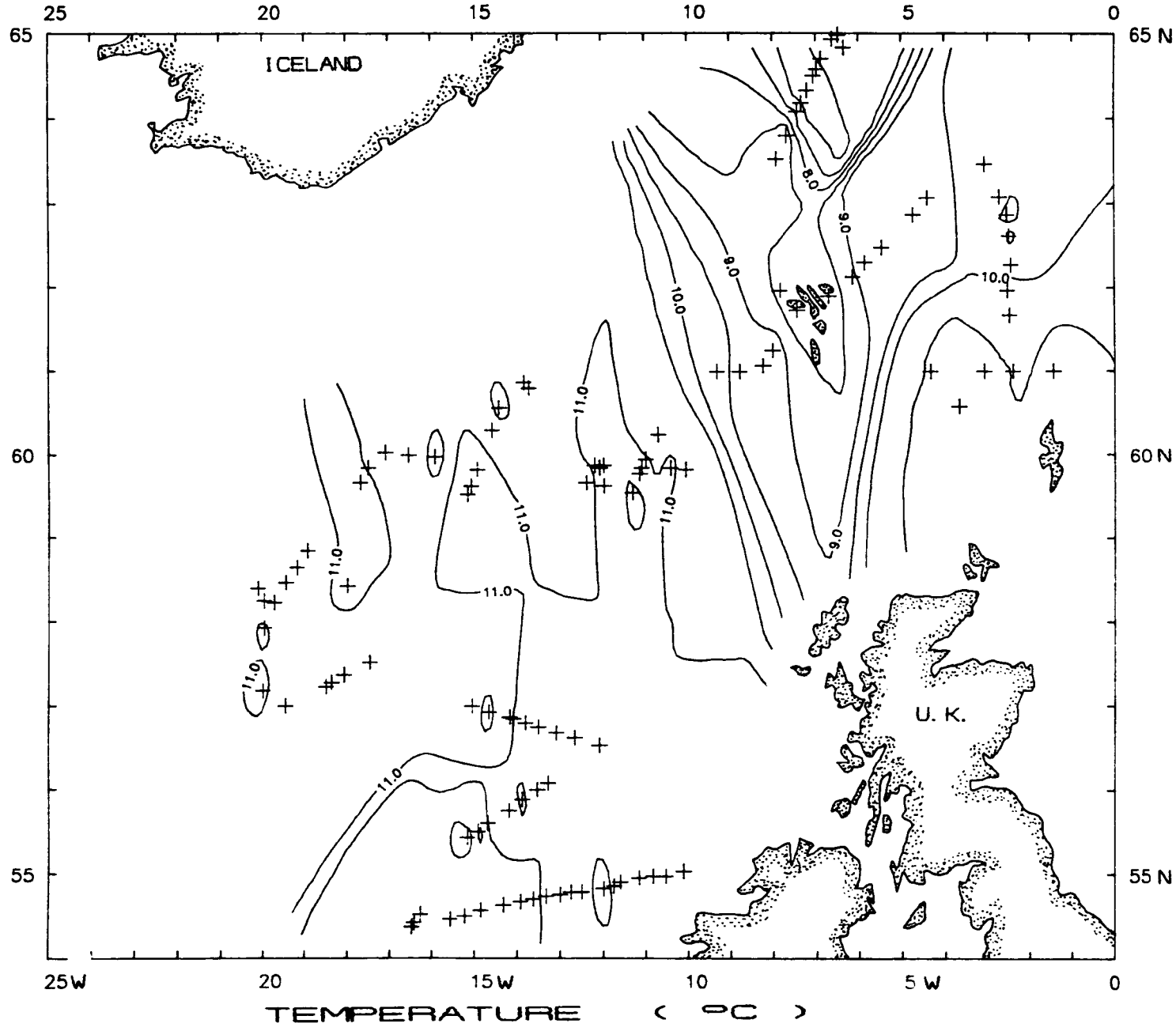

25
20
15
10
5
0
65
65 N
60
60 N
55
55 N
25W
20
15W
10
5 W
0
ICELAND
U. K.
8.0
9.0
9.0
10.0
10.0
11.0
11.0
11.0
11.0
11.0
11.0
TEMPERATURE (°C)

Figure 9.31

FIGURE 9.32

RRS Challenger 16/87
Contour diagram of Salinity (‰)
Surface (3 m)

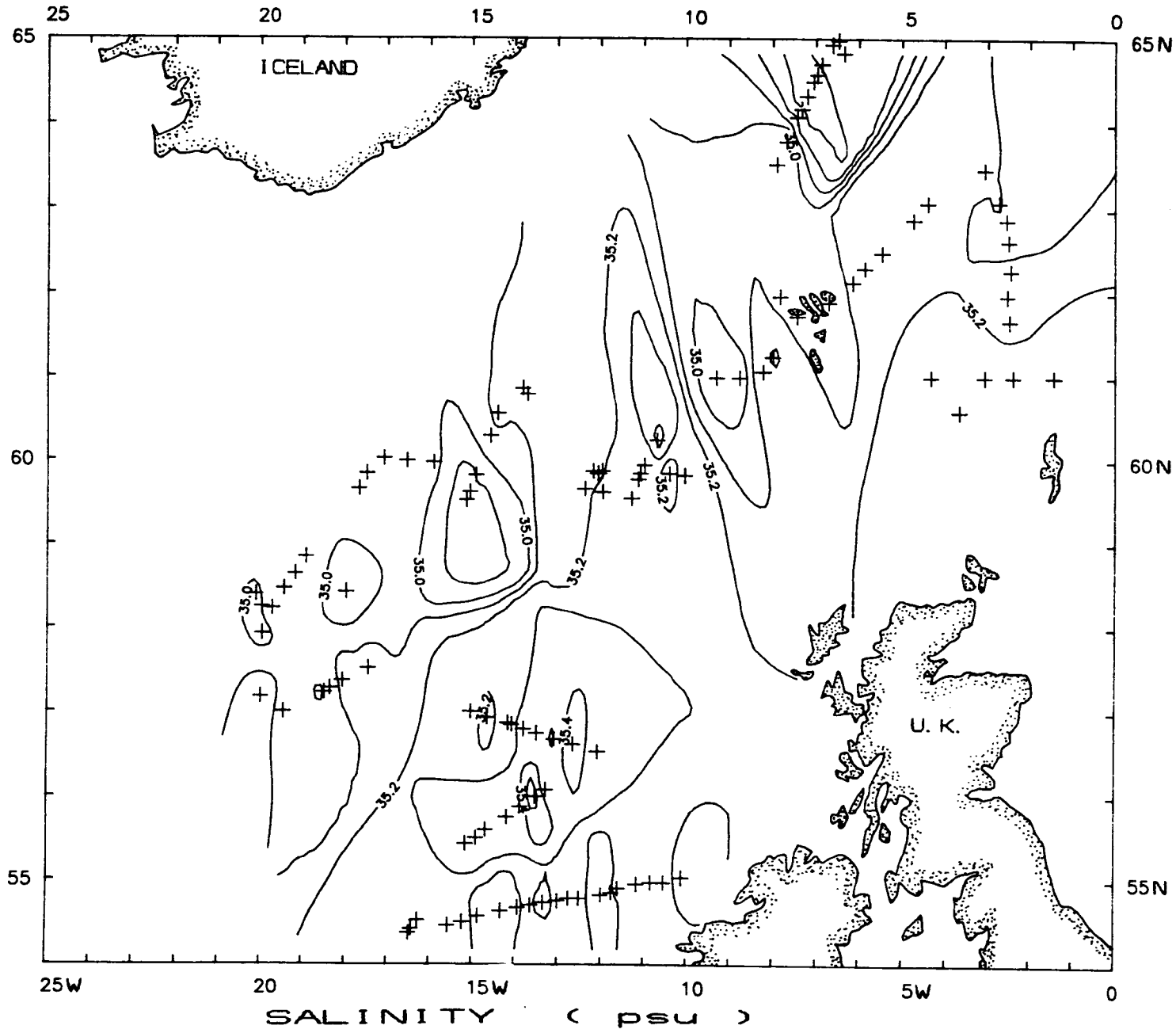

25
20
15
10
5
0
65
65N
60
60N
55
55N
ICELAND
U. K.
35.0
35.2
35.4
25W
20
15W
10
5W
0
SALINITY (psu)

Figure 9.32

FIGURE 9.33

RRS Challenger 16/87
Contour diagram of Beam Attenuation (m^{-1})
Surface (3 m)

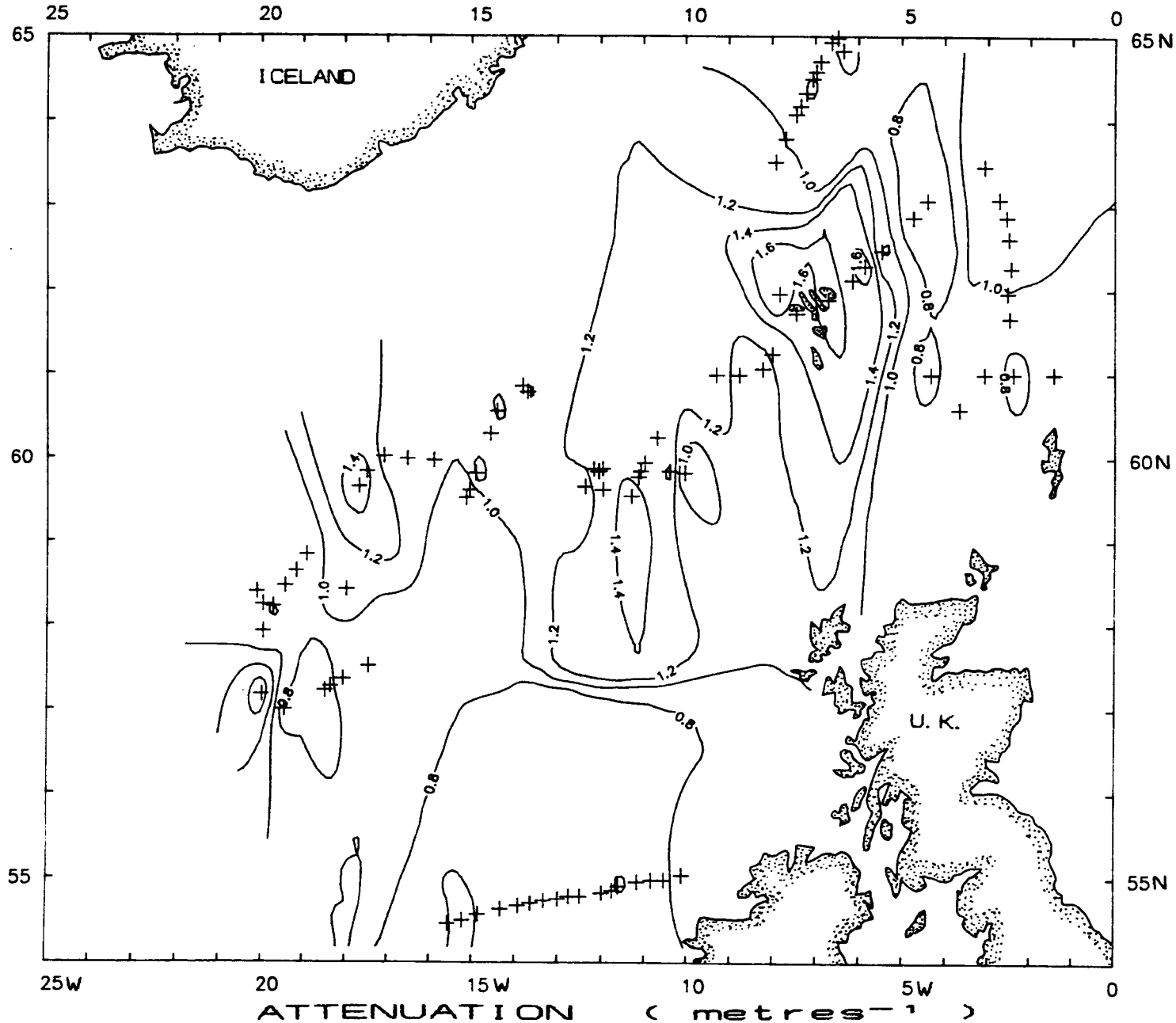

25
20
15
10
5
0
65
65N
60
60N
55
55N
25W
20
15W
10
5W
0
ICELAND
U. K.
ATTENUATION (metres⁻¹)

Figure 9.33

FIGURE 9.34

RRS Challenger 16/87
Contour diagram of Chlorophyll (mg/m^3)
Surface (3 m)

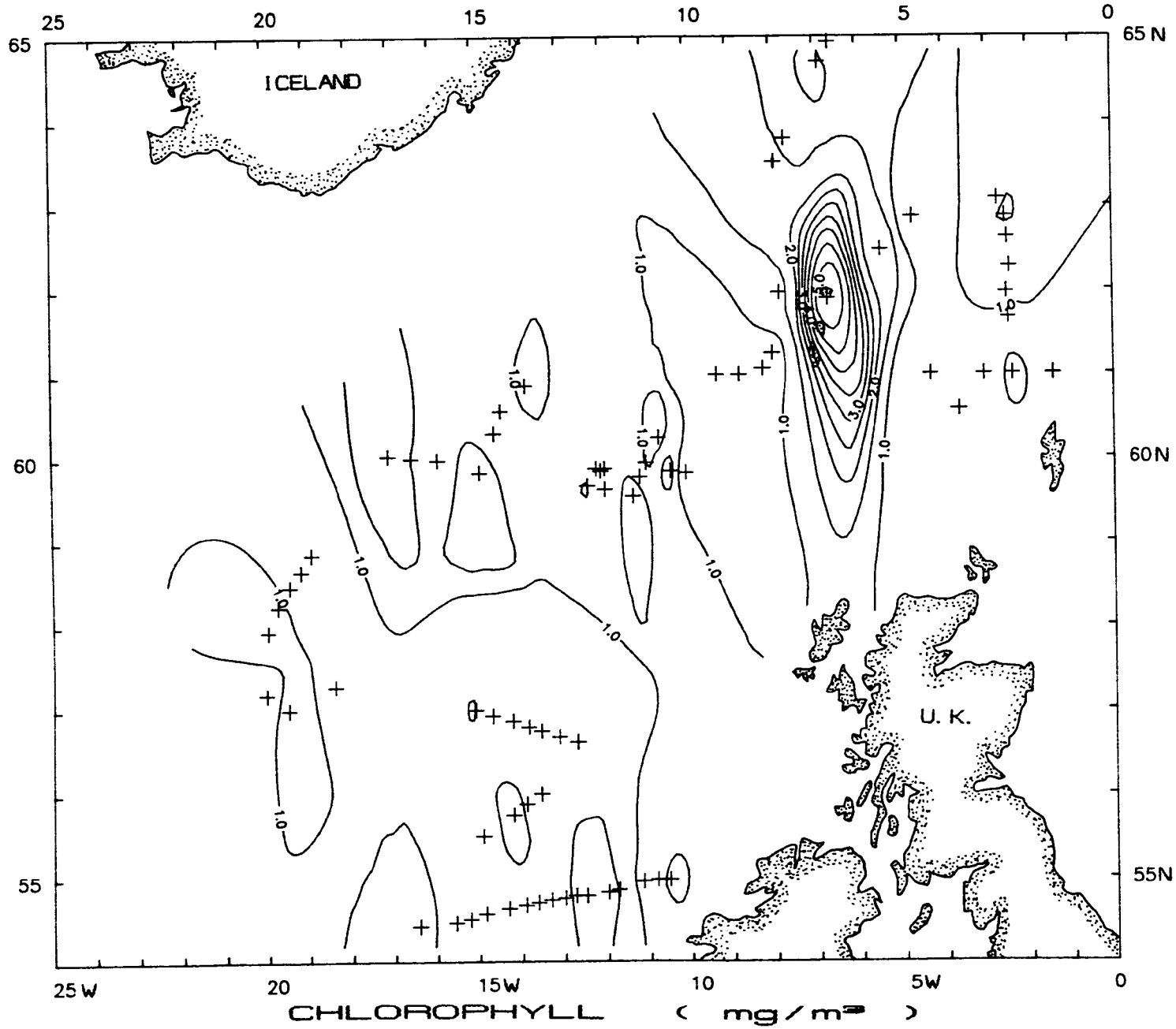
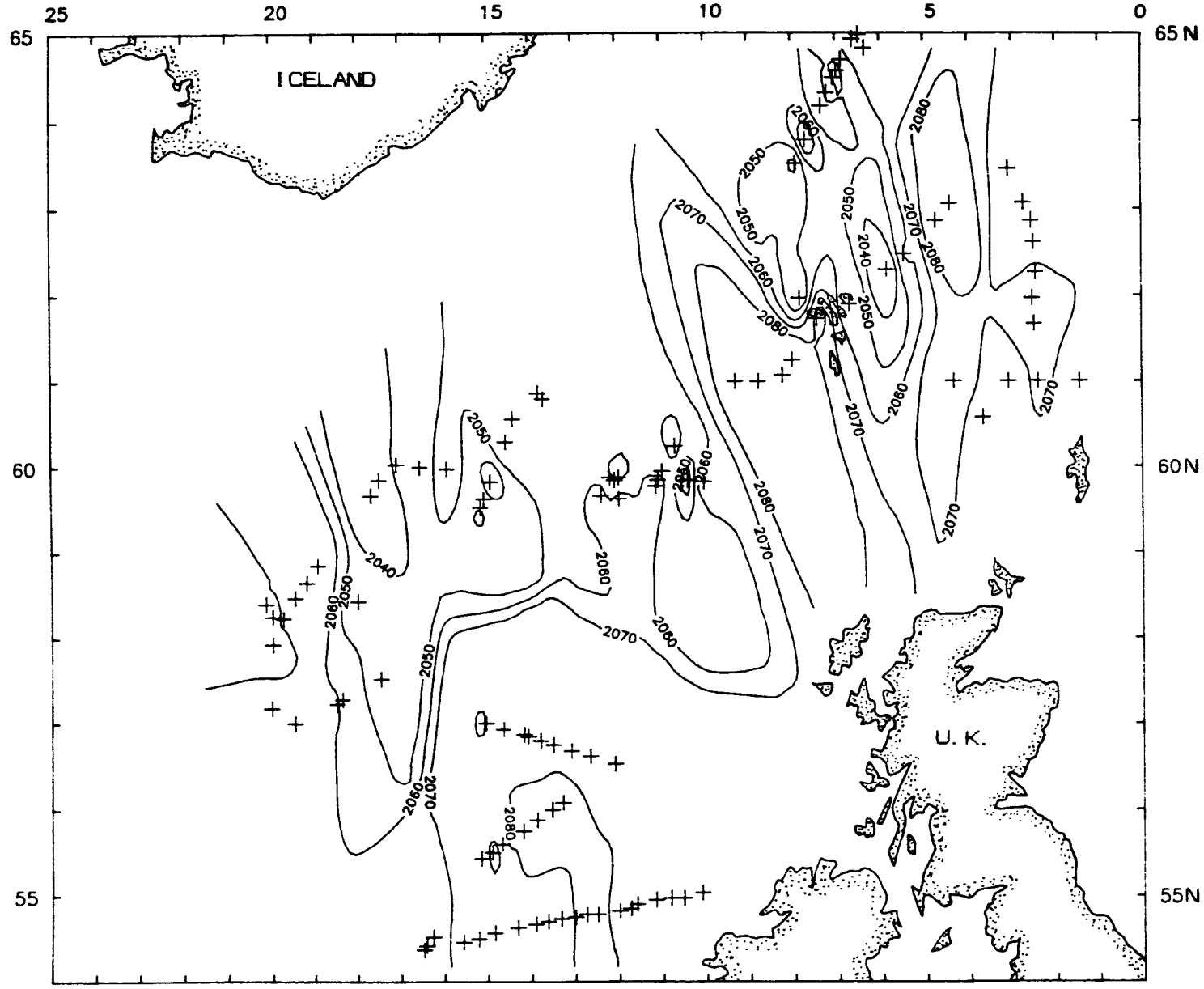

25
20
15
10
5
0
65
65 N
ICELAND
60
60N
55
55N
U. K.
25 W
20
15W
10
5W
0
CHLOROPHYLL (mg/m³)

Figure 9.34

FIGURE 9.35

RRS Challenger 16/87
Contour diagram of TCO_2 (μmol/kg)
Surface (3 m)



TOTAL INORGANIC CARBON
(μmoles/kg)

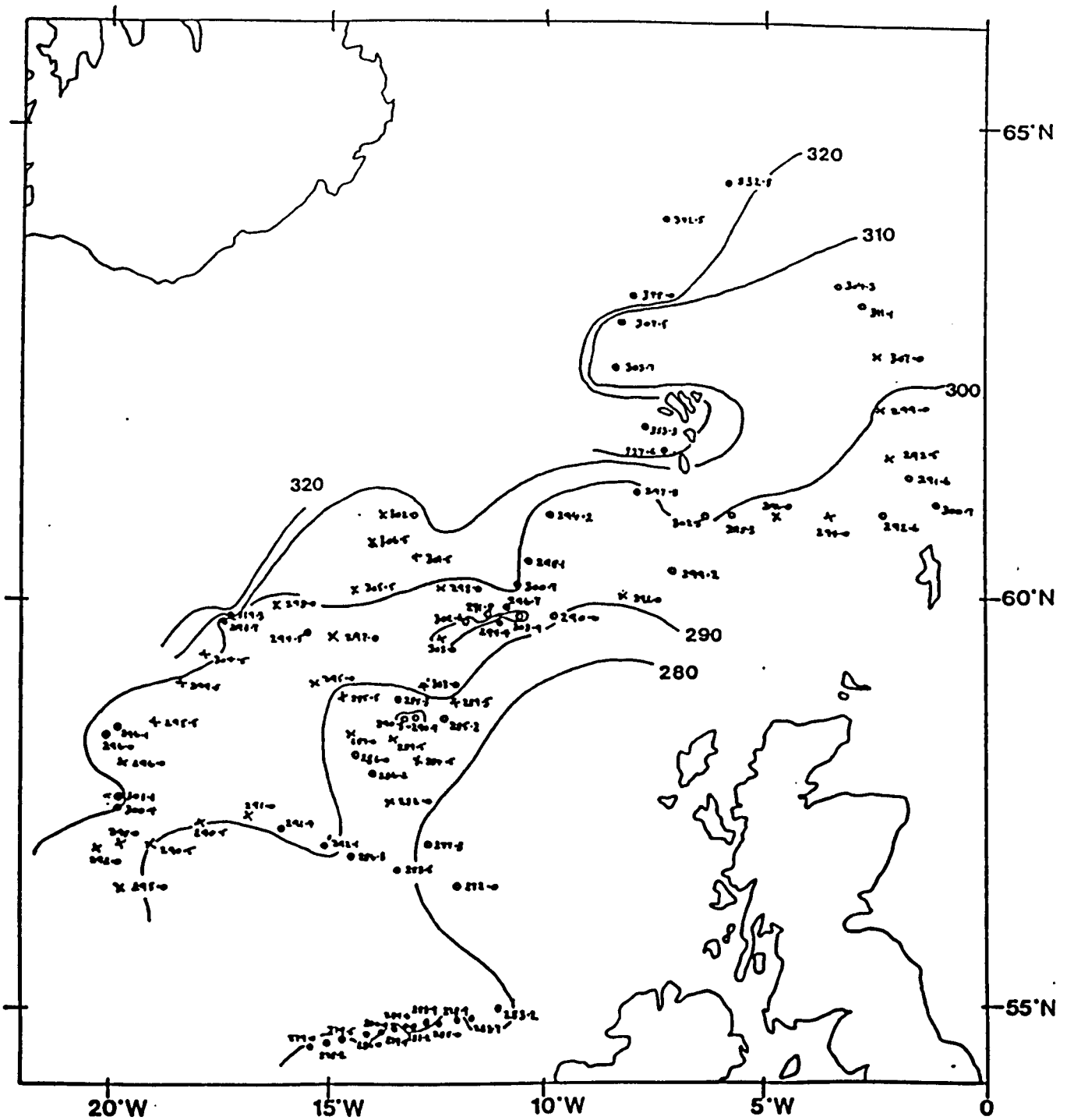
Figure 9.35

FIGURE 9.36

RRS Challenger 16/87
Contour diagram of O_2 (μmol/kg)
Surface (3 m)

Reproduced courtesy of Parkes (1988)

Surface (3m) Oxygen Concentration in the North East Atlantic. (μM/kg



- First leg of the cruise
- Second leg of the cruise
- × Additional values interpolated from oxygen electrode data

Reproduced courtesy of Parkes (1988)

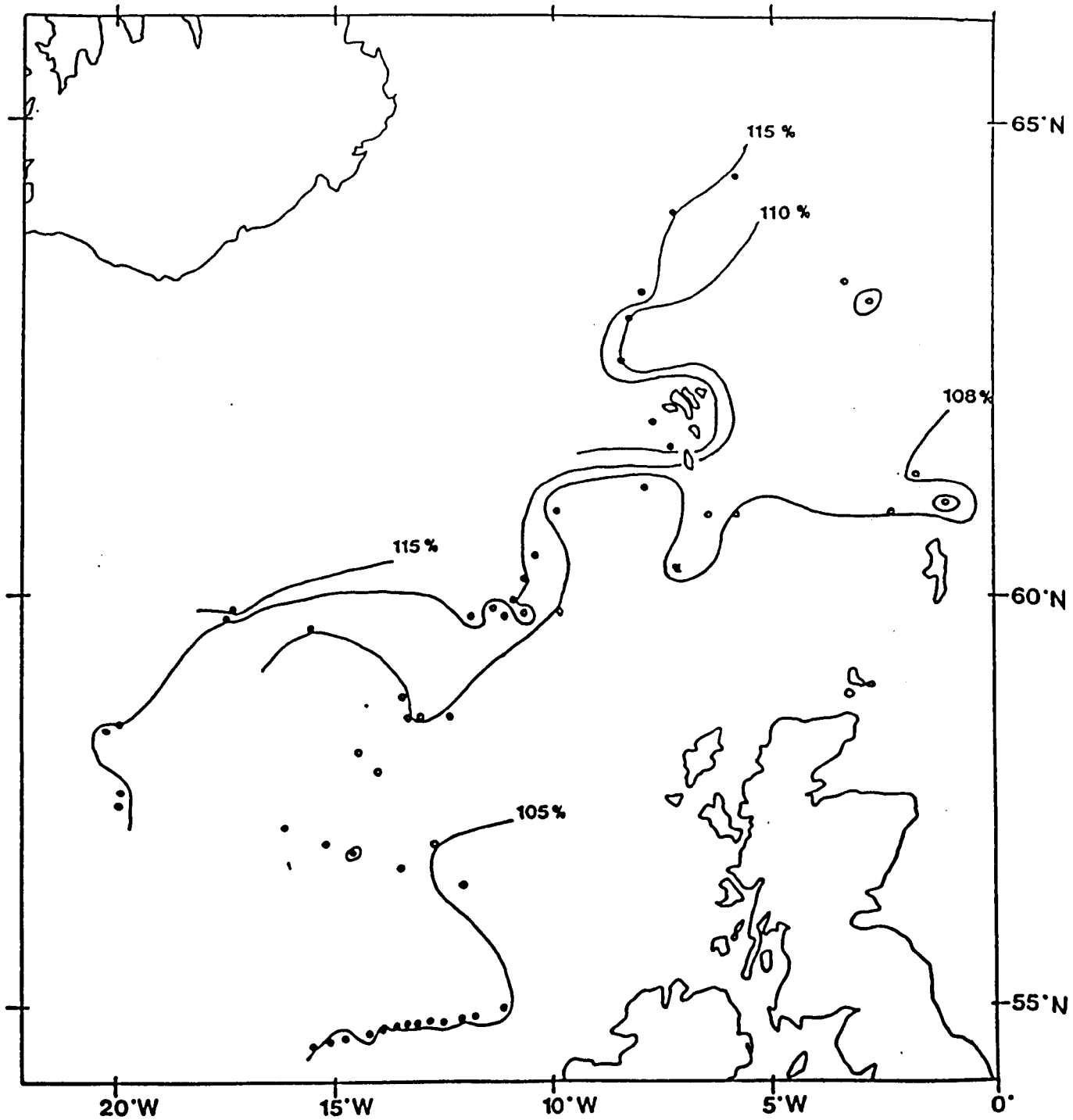
Figure 9.36

FIGURE 9.37

RRS Challenger 16/87
Contour diagram of O_2 (percentage saturation)
Surface (3 m)

Reproduced courtesy of Parkes (1988)

Surface (3m) Oxygen Saturation in the North East Atlantic.



- First leg of the cruise.
- Second leg of the cruise.

Reproduced courtesy of Parkes (1988)

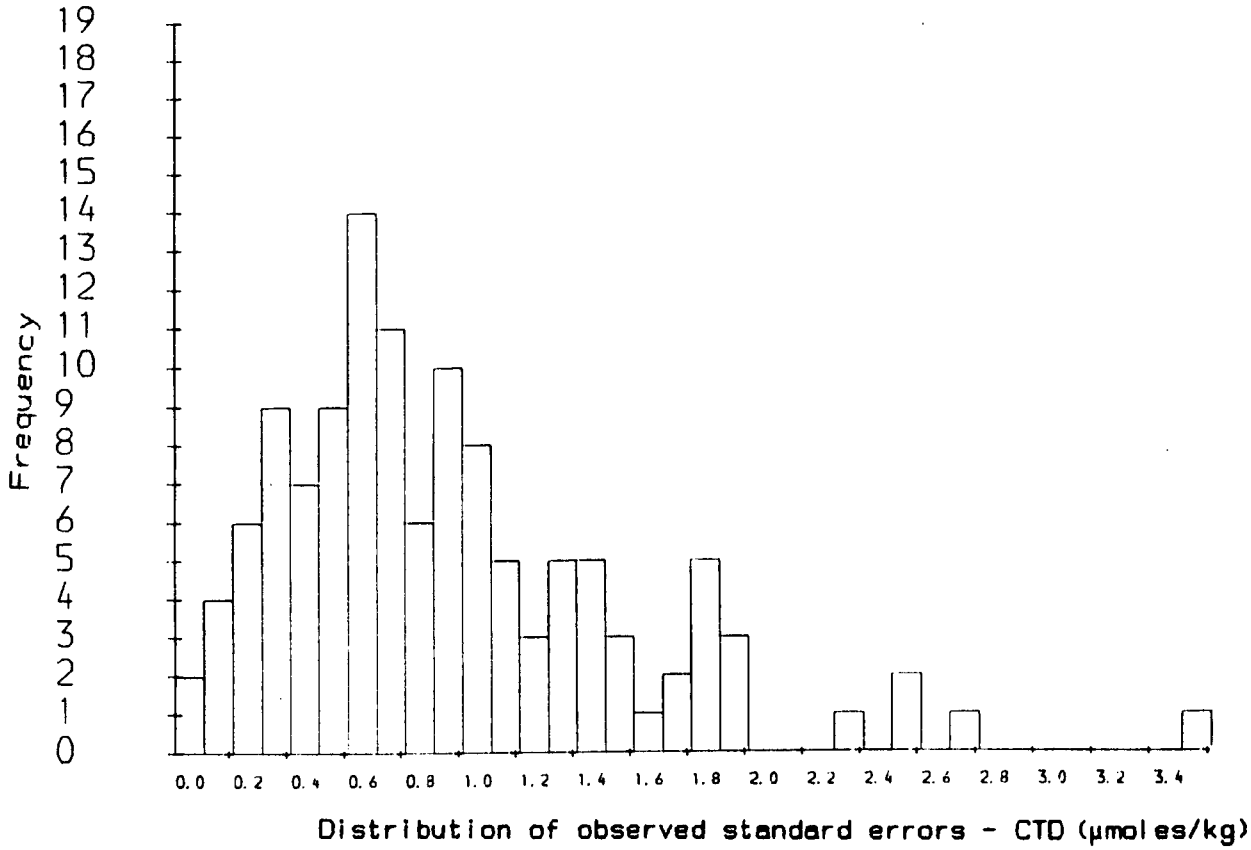
Figure 9.37

FIGURE 9.38

Distribution of standard errors
taken from CTD profiles

Distribution of coefficients of variance
taken from CTD profiles

Figure 9.38


Frequency
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0 3.2 3.4
Distribution of observed standard errors - CTD (µmoles/kg)

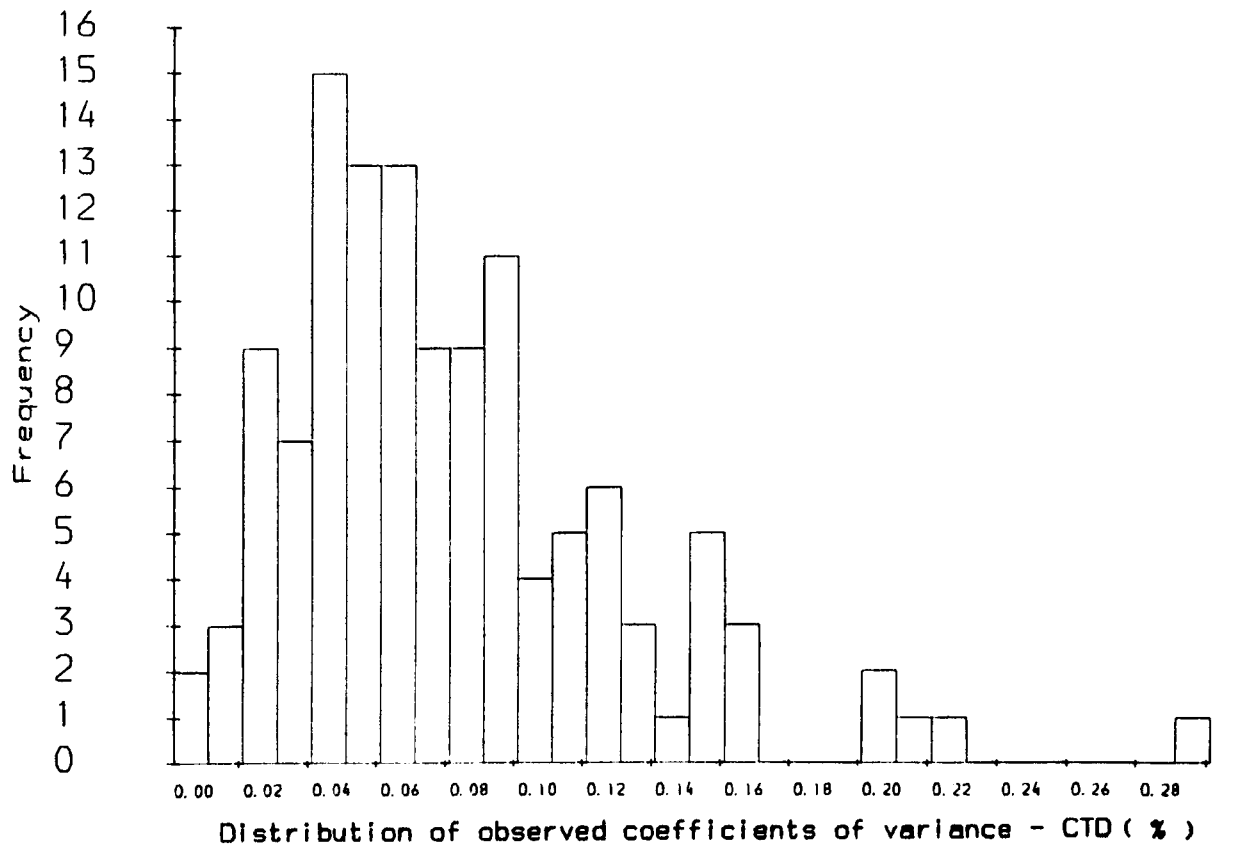
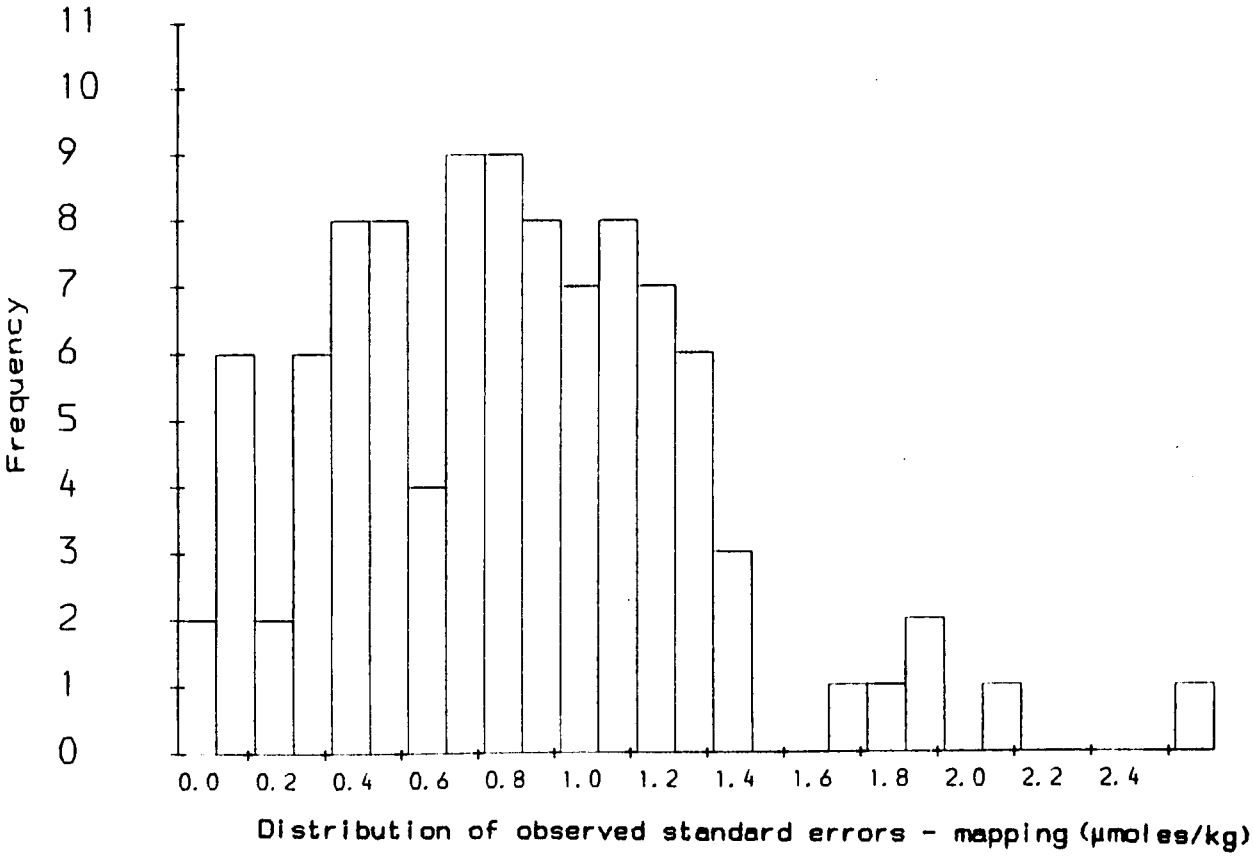

Frequency
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
0.00 0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16 0.18 0.20 0.22 0.24 0.26 0.28
Distribution of observed coefficients of variance - CTD (%)

FIGURE 9.39

Distribution of standard errors
taken from surface mapping

Distribution of coefficients of variance
taken from surface mapping

Figure 9.39


Frequency
11
10
9
8
7
6
5
4
3
2
1
0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
Distribution of observed standard errors - mapping (µmoles/kg)

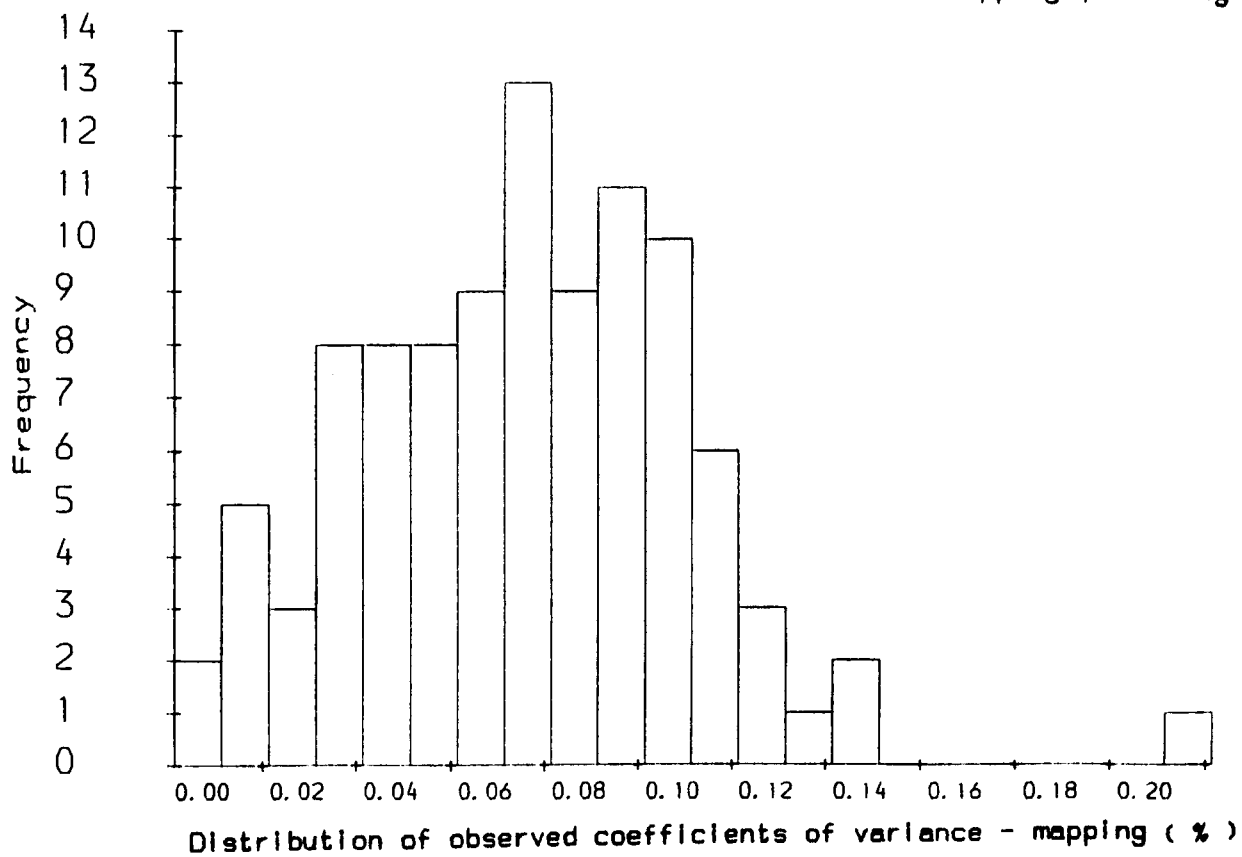

Frequency
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
Distribution of observed coefficients of variance - mapping (%)

TABLE 9.1

Comparison of TTO (1981) and Challenger (1987)
oxygen and TCO_2 (μmoles/kg)

TABLE 9.1

Comparison of oxygen and total carbon dioxide (μmoles/kg) between TTO July 1981 and Challenger 16/1987

Station Details	Position	Depth (m)	O_2 (μmoles/kg)	TCO2 (μmoles/kg)
Station 4	56°31.4'N	2333	268	2150
1987	12°03.5'W			
TTO 136	56°17.7'N	2339	251	2177
1981	13°18.5'W			
TTO 138	55°49.5'N	2385	267	2157
1981	12°00.2'W			
Station 16	61°15.2'N	871	301	2159
1987	07°58.3'W	650	301	2152
		550	296	2142
		400	274	2128
TTO 142	61°20.1'N	815	301	2156
1981	08°00.6'W	716	302	2153
		594	300	2141
		496	285	2132
		253	273	2127
Station 18	64°33.5'N	2862	305	2151
1987	06°17.9'W	1500	303	2147
		800	305	2146
TTO 143	64°49.8'N	3008	305	2154
1981	06°13.5'W	2608	305	2154
		2209	306	2153
		1809	306	2146
		1410	304	2155
		1011	303	2154
		811	302	2147

TABLE 9.2

Kolmogorov-Smirnov Test for normality
of surface measurements.

TABLE 9.2

Test for normality

KOLMOGOROV-SMIRNOV Goodness of Fit Test

Level of significance $\alpha = 0.10$ (90 % confidence)

Variable/ Area	Temperature (°C)	Salinity (‰)	TCO_2 (μmoles/kg)	Chlorophyll (mg/m^3)	Attenuation (m^{-1})
Cruise	101[1]	101	98	73	82
16/87	0.166[2]	0.081	0.095	0.118	0.748
	0.008[3]	0.528	0.335	0.262	(0.056)
Rockall	75	75	73	53	56
	0.054	0.100	0.146	0.134	0.194
	0.983	0.438	0.090	0.296	(0.030)
Faroes	26	26	25	20	26
	0.129	0.081	0.759	0.204	0.206
	0.781	0.995	0.554	0.378	0.218

Test for the normality of the distribution of the variable measured using the Kolmogorov-Smirnov test.

1) Number of cases
2) Test statistic (Z)
3) Two tailed probability

The null hypothesis is that the distribution is normal. If the the value of the test statistic is greater than the calculated Z value according to the no. of cases and the level of signifance then H_0 is rejected and the data is significantly different from the theoretical normal distribution.

The region of rejection consists of all values of Z which are so large that the probability of their occurrence under Ho is equal or less than α = 0.10.

Those variables placed in brackets were transformed by the reciprocal to normalise the data. Surface temperature was not transformed as the bimodal nature of the data was self-evident. Total CO2 could not be satisfactorily transformed.

Test for normality

KOLMOGOROV-SMIRNOV Goodness of Fit Test

Level of significance α = 0.10 (90 %)

Variable/ Area	1/Attenuation (m-1)
Cruise 16/87	82[1]
	0.111[2]
	0.260[3]
Rockall	56
	0.139
	0.227

Test for the normality of the distribution of the variable measured using the Kolmogorov-Smirnov test.

1) Number of cases
2) Test statistic (Z)
3) Two tailed probability

TABLE 9.3

Spearman Ranked Correlation Coefficients
Surface Data (complete cruise)

TABLE 9.3

SPEARMAN RANKED CORRELATION COEFFICIENTS

Level of significance $\alpha = 0.10$ (90 % confidence)

SURFACE DATA (Complete Cruise)

Variable	Temperature (°C)	Salinity (‰)	TCO2 (µmoles/kg)	Chlorophyll (mg/m3)	Attenuation (m-1)
Temp.	-				
	-				
	-				
Sal.	0.44[1]	-			
	0.00[2]	-			
	101[3]	-			
TCO2	0.10	0.51	-		
	0.16	0.00	-		
	98	98	-		
Chloro.	-0.33	-0.46	-0.61	-	
	0.02	0.00	0.00	-	
	73	73	72	-	
Attn.	-0.35	-0.26	-0.51	-0.67	-
	0.01	0.10	0.00	0.00	-
	82	82	79	61	-

1) Correlation coefficient (R_s)
2) Probability of non-linearity
3) Number of cases

TABLE 9.4

Spearman Ranked Correlation Coefficients
Rockall Data

TABLE 9.4

SPEARMAN RANKED CORRELATION COEFFICIENTS

Level of significance α = 0.10 (90 % confidence)

ROCKALL DATA

Variable	Temperature (^{o}C)	Salinity (‰)	TCO2 (μmoles/kg)	Chlorophyll (mg/m3)	Attenuation (m-1)
Temp.	-				
	-				
	-				
Sal.	0.41[1]	-			
	0.00[2]	-			
	75[3]	-			
TCO2	0.35	0.67	-		
	0.00	0.00	-		
	73	73	-		
Chloro.	-0.33	-0.41	-0.72	-	
	0.01	0.00	0.00	-	
	53	53	52	-	
Attn.	-0.28	-0.17	-0.68	-0.70	-
	0.02	0.10	0.00	0.00	-
	56	56	54	41	-

1) Correlation coefficient (R_s)
2) Probability of non-linearity
3) Number of cases

TABLE 9.5

Spearman Ranked Correlation Coefficients
Faroes Data

TABLE 9.5

SPEARMAN RANKED CORRELATION COEFFICIENTS

Level of significance α = 0.10 (90 % confidence)

FAROES DATA

Variable	Temperature (°C)	Salinity (‰)	TCO2 (µmoles/kg)	Chlorophyll (mg/m3)	Attenuation (m-1)
Temp.	-				
	-				
	-				
Sal.	0.61[1]	-			
	0.00[2]	-			
	26[3]	-			
TCO2	0.01	0.16	-		
	0.49	0.22	-		
	25	25	-		
Chloro.	-0.67	-0.58	-0.40	-	
	0.00	0.00	0.04	-	
	20	20	20	-	
Attn.	-0.69	-0.58	-0.29	-0.68	-
	0.00	0.01	0.08	0.00	-
	26	26	25	20	-

1) Correlation coefficient (R_s)

2) Probability of non-linearity

3) Number of cases

TABLE 9.6

Spearman Ranked Correlation Coefficients
Front Data

TABLE 9.6

SPEARMAN RANKED CORRELATION COEFFICIENTS

Level of significance $\alpha = 0.10$ (90 % confidence)

FRONT DATA

Variable	Temperature (°C)	Salinity (‰)	TCO2 (μmoles/kg)	Chlorophyll (mg/m3)	Attenuation (m-1)
Temp.	-				
	-				
	-				
Sal.	0.95[1]	-			
	0.00[2]	-			
	9[3]	-			
TCO2	0.79	0.16	-		
	0.01	0.22	-		
	8	25	-		
Chloro.	1.00	-1.00	-1.00	-	
	0.50	0.50	0.50	-	
	2	2	2	-	
Attn.	0.81	0.81	0.57	-1.00	-
	0.00	0.0	0.07	0.50	-
	9	9	8	2	-

1) Correlation coefficient (R_s)
2) Probability of non-linearity
3) Number of cases

TABLE 9.7

Pearson Correlation Coefficients
Surface data (complete cruise)

TABLE 9.7

PEARSON CORRELATION COEFFICIENTS

Level of significance $\alpha = 0.10$ (90 % confidence)

SURFACE DATA (Complete Cruise)

Variable	Temperature (^oC)	Salinity (‰)	TCO2 (μmoles/kg)	Chlorophyll (mg/m3)	Attenuation (m-1)
Temp.	-				
	-				
	-				
	-				
Sal.	0.35	-			
	12.2%	-			
	11.3%	-			
	0.00	-			
	101	-			
TCO2	0.02	0.49	-		
	0.1%	24.1%	-		
	0.0%	23.4%	-		
	0.83	0.00	-		
	98	98	-		
Chloro.	-0.33	-0.42	-0.69	-	
	10.9%	17.5%	47.9%	-	
	9.6%	16.4%	47.2%	-	
	0.00	0.00	0.00	-	
	73	73	72	-	
Attn.$^{-1}$	0.41	0.21	0.54	-0.65	-
	16.9%	4.4%	29.4%	42.6%	-
	15.9%	3.2%	28.5%	41.6%	-
	0.00	0.17	0.00	0.00	-
	82	82	79	61	-

X Y

1. R_2 - correlation coefficient
2. R^2 - coefficient of determination
3. R^2 - adjusted to fit the population
4. Probability of non-linearity
5. N - number of cases

TABLE 9.8

Pearson Correlation Coefficients
Rockall data

TABLE 9.8

PEARSON CORRELATION COEFFICIENTS

Level of significance $\alpha = 0.10$ (90 % confidence)

ROCKALL DATA

Variable	Temperature (°C)	Salinity (‰)	TCO2 (μmoles/kg)	Chlorophyll (mg/m3)	Attenuation (m-1)
Temp.	-				
	-				
	-				
	-				
	-				
Sal.	0.33	-			
	10.9%	-			
	9.7%	-			
	0.00	-			
	75	-			
TCO2	0.27	0.66	-		
	7.4%	44.0%	-		
	6.1%	43.2%	-		
	0.02	0.00	-		
	73	73	-		
Chloro.	-0.29	-0.41	-0.76	-	
	8.3%	16.9%	57.4%	-	
	6.5%	15.2%	56.6%	-	
	0.04	0.00	0.00	-	
	53	53	52	-	
Attn.$^{-1}$	0.32	0.12	0.70	-0.70	-
	10.3%	1.4%	49.4%	48.4%	-
	8.6%	0.0%	48.5%	47.1%	-
	0.09	0.77	0.00	0.00	-
	56	56	54	41	-

X / Y

1. R_2 - correlation coefficient
2. R^2 - coefficient of determination
3. R^2 - adjusted to fit the population
4. Probability of non-linearity
5. N - number of cases

TABLE 9.9

Pearson Correlation Coefficients
Faroes data

TABLE 9.9

PEARSON CORRELATION COEFFICIENTS

Level of significance α = 0.10 (90 % confidence)

FAROES DATA

Variable	Temperature (°C)	Salinity (‰)	TCO2 (µmoles/kg)	Chlorophyll (mg/m3)	Attenuation (m-1)
Temp.	-				
	-				
	-				
	-				
Sal.	0.54	-			
	29.1%	-			
	26.1%	-			
	0.00	-			
	26	-			
TCO2	0.12	0.03	-		
	1.5%	0.1%	-		
	0.0%	0.0%	-		
	0.56	0.87	-		
	25	25	-		
Chloro.	-0.64	-0.42	-0.61	-	
	41.5%	17.5%	37.6%	-	
	38.3%	13.0%	34.2%	-	
	0.00	0.07	0.00	-	
	20	20	20	-	
Attn.	-0.65	-0.45	-0.52	-0.50	-
	42.0%	20.2%	26.2%	24.7%	-
	39.6%	16.9%	23.0%	20.6%	-
	0.00	0.02	0.01	0.03	-
	26	26	25	20	-

Y

X 1. R_x - correlation coefficient
2. R^2 - coefficient of determination
3. R^2 - adjusted to fit the population
4. Probability of non-linearity
5. N - number of cases

TABLE 9.10

Pearson Correlation Coefficients
Frontal data

TABLE 9.10

PEARSON CORRELATION COEFFICIENTS

Level of significance α = 0.10 (90 % confidence)

FRONT DATA

Variable	Temperature (°C)	Salinity (‰)	TCO2 (µmoles/kg)	Chlorophyll (mg/m3)	Attenuation (m-1)
Temp.	-				
	-				
	-				
	-				
Sal.	0.92	-			
	84.4%	-			
	82.2%	-			
	0.00	-			
	9	-			
TCO2	0.68	0.91	-		
	45.8%	68.9%	-		
	36.8%	64.5%	-		
	0.03	0.01	-		
	8	8	-		
Chloro.	-	-	-	-	
	-	-	-	-	
	-	-	-	-	
	-	-	-	-	
Attn.	0.83	0.79	0.52	-	-
	68.9%	61.7%	26.5%	-	-
	64.5%	56.2%	14.3%	-	-
	0.03	0.06	0.09	-	-
	9	9	8	-	

Y

X
1. R_2 - correlation coefficient
2. R^2 - coefficient of determination
3. R^2 - adjusted to fit the population
4. Probability of non-linearity
5. N - number of cases

TABLE 9.11

Principle Components Analysis
Surface data (complete cruise)

TABLE 9.11

PRINCIPLE COMPONENTS ANALYSIS

Surface Data (Complete Cruise)

Initial Statistics:

Factor	Eigenvalue	Pct. of Var.	Cum. Pct.
1	2.7	53.4	53.4
2	1.0	20.0	73.4
3	0.9	17.2	90.6
4	0.3	6.0	96.6
5	0.2	3.4	100.0

Factor Matrix:

	Factor 1	Factor 2	Factor 3
Temperature	0.51	0.84	0.03
Salinity	0.63	0.04	0.74
TCO_2	0.80	-0.51	0.04
Chlorophyll	-0.88	0.13	0.12
Attenuation	-0.77	-0.10	0.54

TABLE 9.12

Principle Components Analysis
Rockall data

TABLE 9.12

PRINCIPAL COMPONENTS ANALYSIS

Rockall Data

Initial Statistics:

Factor	Eigenvalue	Pct. of Var.	Cum. Pct.
1	2.8	56.6	56.6
2	1.0	20.8	77.5
3	0.8	15.8	93.3
4	0.3	5.3	98.6
5	0.1	1.4	100.0

Factor Matrix:

	Factor 1	Factor 2	Factor 3
Temperature	0.48	0.44	0.75
Salinity	0.64	0.65	-0.36
TCO_2	0.94	-0.01	-0.24
Chlorophyll	-0.88	0.22	0.05
Attenuation	-0.74	0.60	-0.18

TABLE 9.13

Principle Components Analysis
Faroes data

TABLE 9.13

PRINCIPLE COMPONENTS ANALYSIS

Faroes Data

Initial Statistics:

Factor	Eigenvalue	Pct. of Var.	Cum. Pct.
1	2.8	56.9	56.9
2	1.1	22.3	79.2
3	0.5	10.0	89.2
4	0.5	9.4	98.6
5	0.1	1.4	100.0

Factor Matrix:

	Factor 1	Factor 2
Temperature	0.82	0.40
Salinity	0.65	0.57
TCO_2	0.58	-0.78
Chlorophyll	-0.85	0.21
Attenuation	-0.84	0.05

CHAPTER 10

LABORATORY EXPERIMENTS

The following chapter deals with with experimental results obtained in the laboratory during the present study.

10.1 Examination of the blank

The blank signal obtained from the coulometer is apparently inherent within the coulometer cell and a result of the complex electrochemical reactions occurring within the cell. A typical blank correction observed in the laboratory would be 0.9 μmol/kg, based on a seven minute titration time and a blank signal of 0.05 μg C/min. This blank correction rose dramatically whilst at sea, to an average 9 μmol/kg correction. This increase was presumed to be as a result of noise on the ships mains. In an attempt to gain a better understanding of the signal a series of measurements were undertaken. Software was modified to read and then plot the progress of the blank every second. The results are shown in Figures 10.1 and 10.2. Time in minutes is plotted against total carbon signal titrated, the individual data points are plotted first for reference, these are then joined up in order to indicate more clearly the stepping nature of the blank.

Figure 10.1 represents the blank soon after the cell has been started and shows that after approximately 20 minutes the slope of the curve starts to decrease.

This is shown more clearly in Figure 10.2, where it is apparent that it is not the size of the step that decreases rather the time interval between the steps that increases.

Another series of blanks were recorded and an attempt was made to reduce the value of the blank over a certain time interval by titrating samples in between recording the blank. During a series of titrations throughout the day the size of the blank does change, so necessitating frequent determination in order to maintain accuracy.

The reduction in the blank is illustrated by Figures 10.3 to 10.6. Figure 10.3 is the initial signal after five seawater samples have been titrated to settle the cell into a smooth running behaviour. The mean step is 0.45 μg C and the average time interval is 4.27 minutes (slope = 0.11 μg C/min).

Following on from this another five samples were titrated (Figure 10.4) and the step is reduced and the time interval are increased (slope = 0.06 μg C/min). Figure 10.5 shows the signal after another five samples, the step slightly increased along with the time interval (slope = 0.07). Figure 10.6 after a final five titrated samples has not changed to any great extent in either step or time interval (slope = 0.06). This pattern is frequently observed during the running of the machine and titration of a large number of samples. The size of the step does fluctuate around 0.3 whilst the time interval gradually increases and can rise to over 10 minutes after a considerable number of samples have been titrated. The size of the step is built into the firmware of the coulometer and it essentially limits the precision of the analysis and only limited control was possible over the size of the step. However the blank can be reduced by running a large number of samples and so increasing the time interval between the steps.

10.2 Fixing Experiments

The experimental results shown in Tables 10.1 to 10.3, are taken from three typical incubations used to determine the effectiveness of $HgCl_2$ as a preservative for TCO_2 samples. Three replicates were taken from each bottle and a mean value given along an associated standard error.

Table 10.1 shows the results of a long term incubation of 104 days utilising a dense non-axenic culture of Pavlova lutheri . All bottles incubated are placed in the dark and underwater for the length of the incubation. The zero time concentrations are given both for samples containing $HgCl_2$ and for those not given an addition. The addition of the mercury chloride itself does not substantially alter the determined level of TCO_2. Statistical analysis using a two-tailed T test was carried on the difference between the zero time concentrations and both the fixed and non-fixed bottles. The details of the statistical analysis are given in Appendix 5.

Samples not fixed continue to respire with a significant average increase of 230 μmol/kg of TCO_2 at a 99 % confidence level. The fixed bottles fail to show this increased respiration, and are not significantly different than the zero time bottles at a 99 % confidence level. The difference between bottles both within the zero time and fixed bottles can be explained by the filling of the bottles. Variation between bottles will occur unless care is taken to flush the bottles adequately and ensure the culture is evenly dispersed between all bottles.

Table 10.2 is a similar experiment using a non-axenic culture of Tetraselminus chuii and a shorter incubation length. The ability of the preservative to fix is apparent even in unclean bottles. There was some suggestion from field experiments that bottles that are not subject to a vigorous cleaning routine prior to fixation, do not respond to the addition of the preservative. A significant change in concentration of TCO_2 is observed between the zero time and unfixed bottles, whereas no significant difference is observed between the zero time and clean, fixed bottles. The difference between the zero times and uncleaned fixed bottles is only not significant at 99.9 % confidence. Details of the statistical analyses are given in Appendix 5.

Table 10.3 gives the results of an experiment in which clean bottles were incubated for comparison with bottles that had been left to soak for three days in seawater taken from a prawn tank. These bottles were just rinsed and not cleaned. Both the clean and dirty unfixed bottles contain significantly greater TCO_2 than the zero time, however the rate of respiration is reduced in the uncleaned bottles. The fixed bottles both clean and unclean are statistically different at a 95 % confidence level to the initial zero times, however, the difference is a drop in the order of a couple of micromoles whereas the unfixed bottles show an increase of roughly 20 micromoles. An explanation for the drop in concentration associated with the fixed bottles could be an inadequate filling routine. Details of the statistical analyses are given in Appendix 5.

TABLE 10.1

Long term fixing experiment
Incubation length = 104 days
Pavlova lutheri

TABLE 10.1

Long term fixing experiment

Pavlova lutheri Average cell density = 2,800 cells/µl

Incubation length = 104 days

Details	Bottle 1 (µmoles/kg)	Bottle 2 (µmoles/kg)
Zero Time No $HgCl_2$	2021.19 +/- 0.63	2025.82 +/- 0.43
Zero Time $HgCl_2$	2021.17 +/- 0.44	2022.33 +/- 0.74
Clean No $HgCl_2$	2252.15 +/- 1.33	2249.99 +/- 0.95
Clean $HgCl_2$	2020.62 +/- 1.87	2014.75 +/- 1.24

TABLE 10.2

Fixing experiment (8/2/89)
Incubation length = 52 h
Tetraselminus chuii

TABLE 10.2

Fixing Experiment - 8/2/89

Tetraselminus chuii Average cell density = 45 cells/µl

Incubation length = 52 h

Details	Bottle 1 (µmoles/kg)	Bottle 2 (µmoles/kg)	Bottle 3 (µmoles/kg)
Zero Time	2115.63 +/- 1.71	2115.91 +/- 1.59	2113.12 +/- 1.77
Clean No $HgCl_2$	2154.21 +/- 0.38	2151.12 +/- 0.59	
Clean $HgCl_2$	2115.06 +/- 1.10	2119.42 +/- 0.40	
Not clean $HgCl_2$	2118.06 +/- 0.27	2118.52 +/- 0.20	

TABLE 10.3

Fixing experiment (16/2/89)
Incubation length = 49 h
Tetraselminus chuii

TABLE 10.3

Fixing Experiment - 16/2/89

Tetraselminus chuii Average cell density = 20 cells/ul

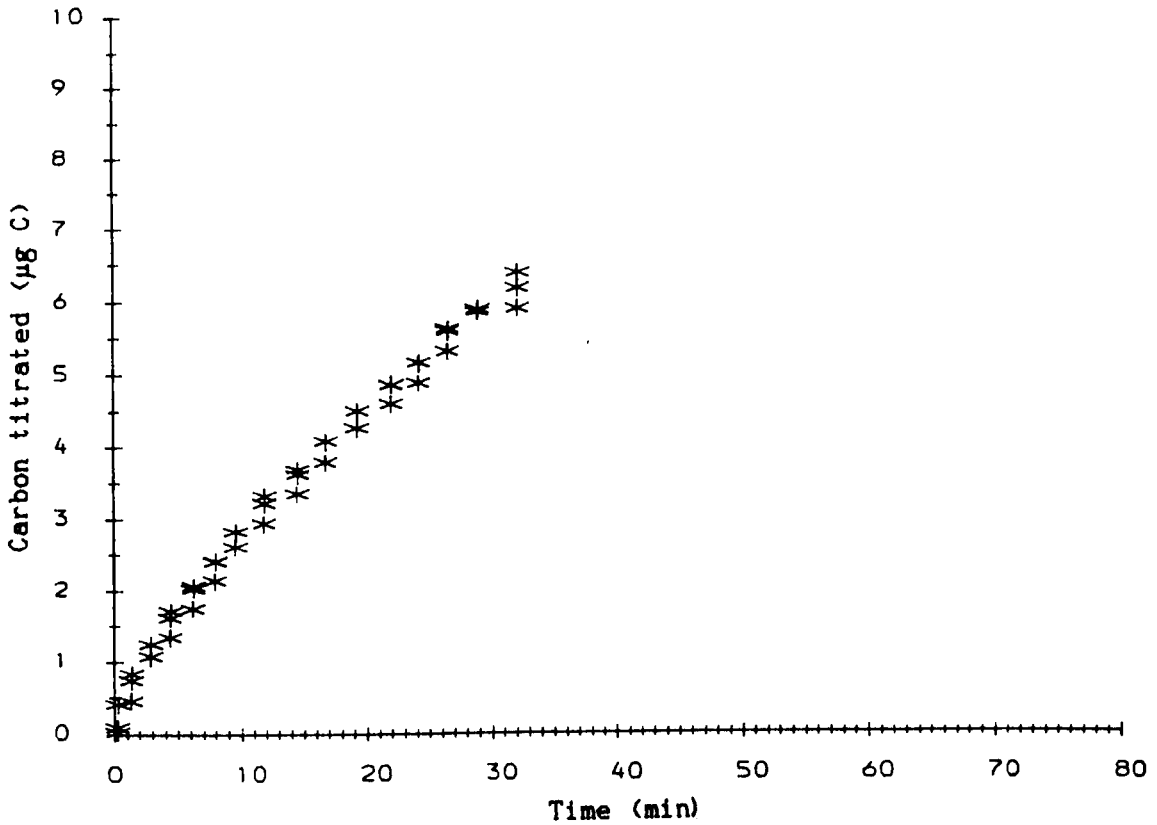
Incubation length = 49 h

Details	Bottle 1 (µmoles/kg)	Bottle 2 (µmoles/kg)	Bottle 3 (µmoles/kg)
Zero Time	2126.40 +/- 0.48	2125.57 +/- 0.48	2124.42 +/- 0.31
Clean No $HgCl_2$	2144.76 +/- 0.44	2142.27 +/- 0.52	
Clean $HgCl_2$	2121.79 +/- 0.42	2123.01 +/- 0.27	
Not Clean No $HgCl_2$	2135.73 +/- 0.11	2135.16 +/- 0.06	
Not Clean $HgCl_2$	2121.86 +/- 0.32	2122.66 +/- 0.16	

FIGURE 10.1

Examination of the blank
Time elasped in minutes plotted against
total carbon titrated.

Figure 10.1


Carbon titrated (µg C)
0
1
2
3
4
5
6
7
8
9
10
0
10
20
30
40
50
60
70
80
Time (min)

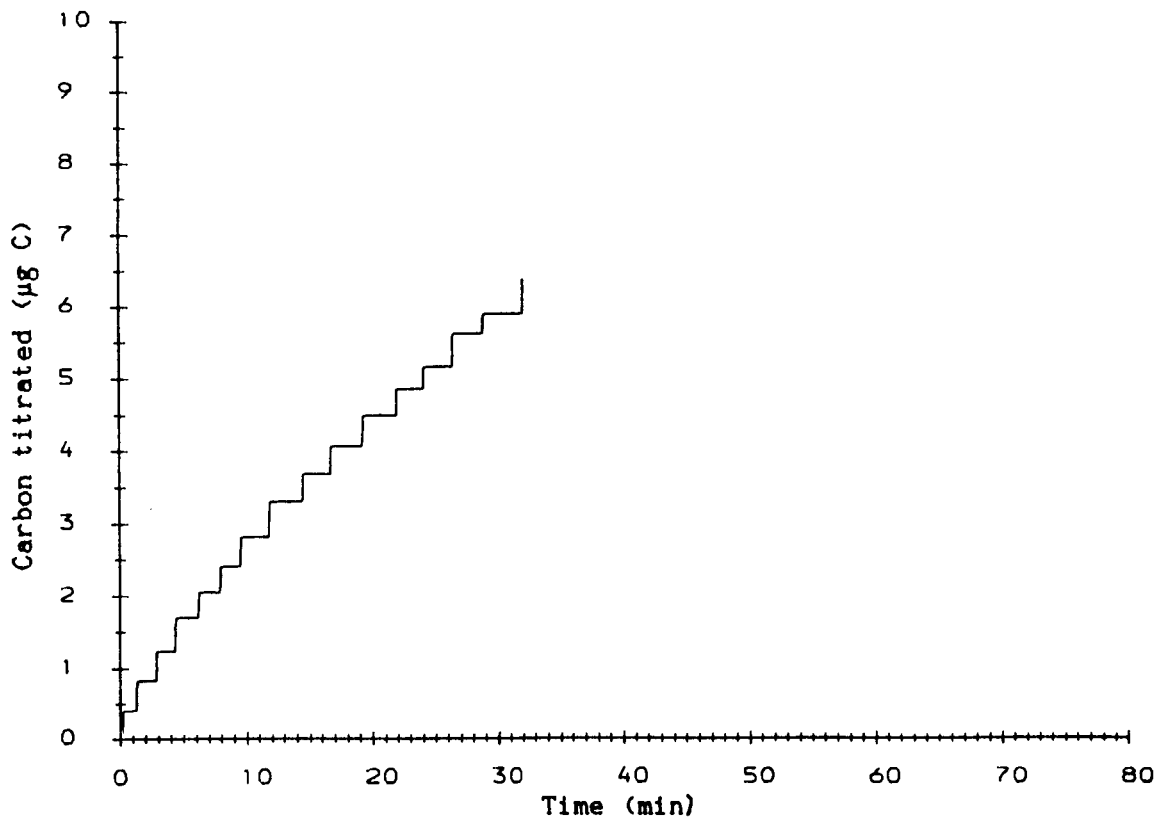
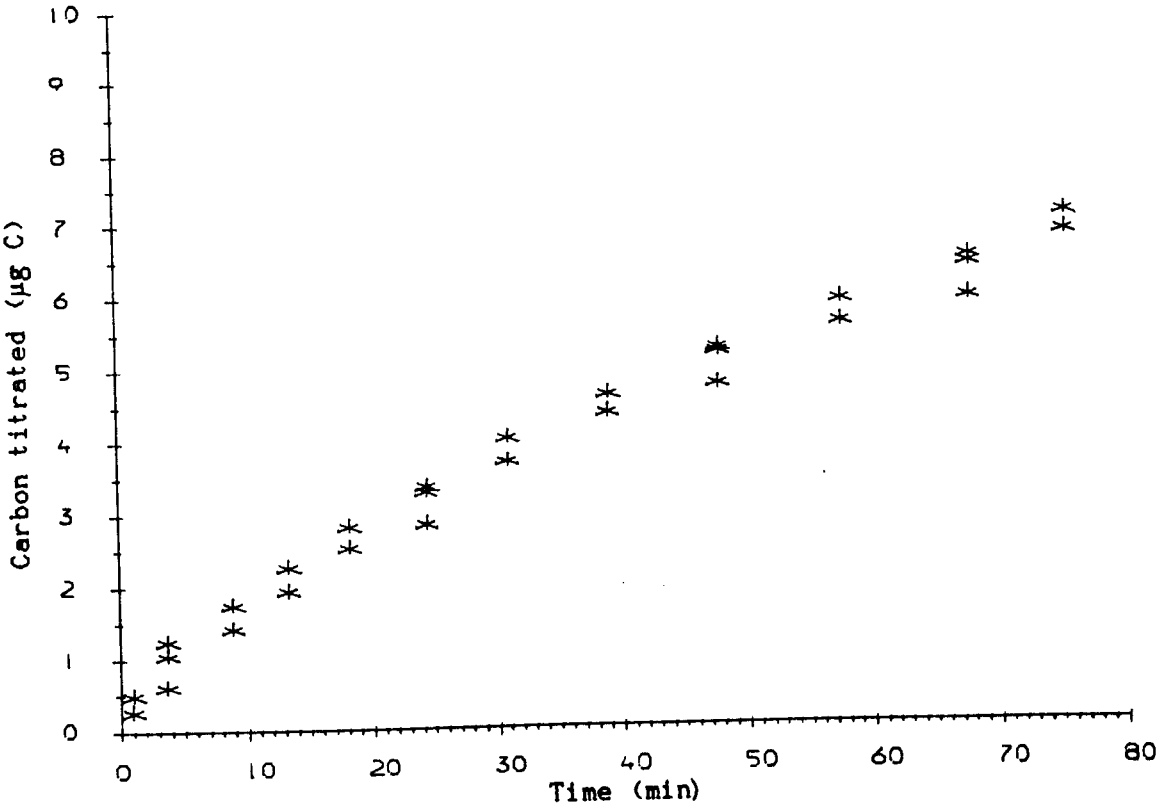

Carbon titrated (µg C)
0
1
2
3
4
5
6
7
8
9
10
0
10
20
30
40
50
60
70
80
Time (min)

FIGURE 10.2

Examination of the blank
Time elasped in minutes plotted against
total carbon titrated.

Figure 10.2


Carbon titrated (µg C)
0
1
2
3
4
5
6
7
8
9
10
0
10
20
30
40
50
60
70
80
Time (min)

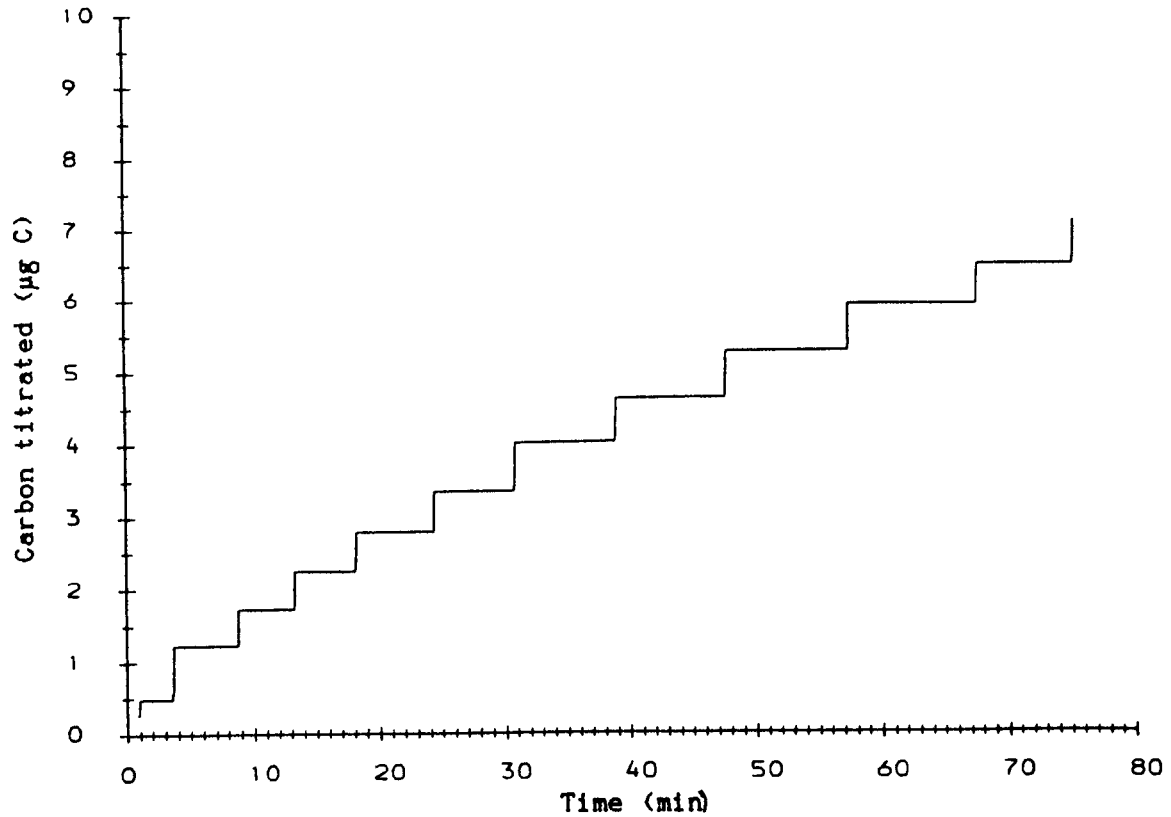

Carbon titrated (µg C)
0
1
2
3
4
5
6
7
8
9
10
0
10
20
30
40
50
60
70
80
Time (min)

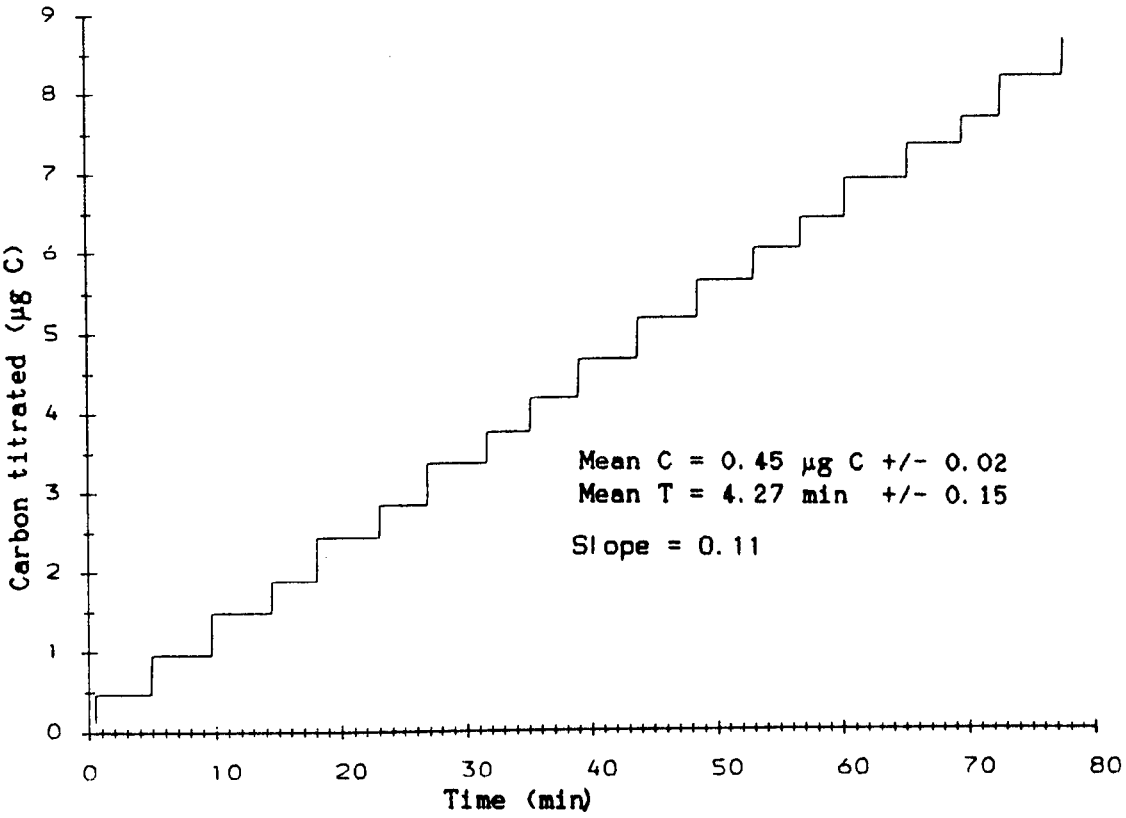
FIGURE 10.3

Examination of the blank
Time elasped in minutes plotted against
total carbon titrated.
Signal after five samples titrated

FIGURE 10.4

Examination of the blank
Time elasped in minutes plotted against
total carbon titrated.
Signal after ten samples titrated

Figure 10.3



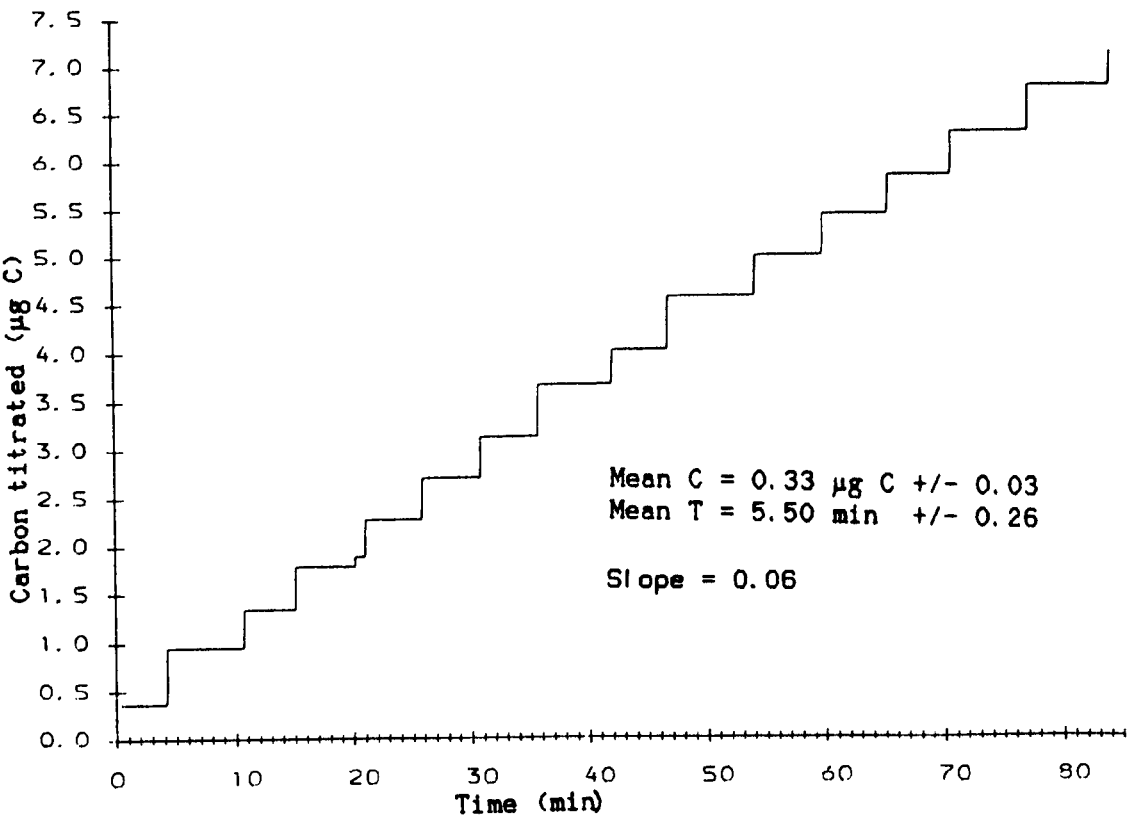


Figure 10.4

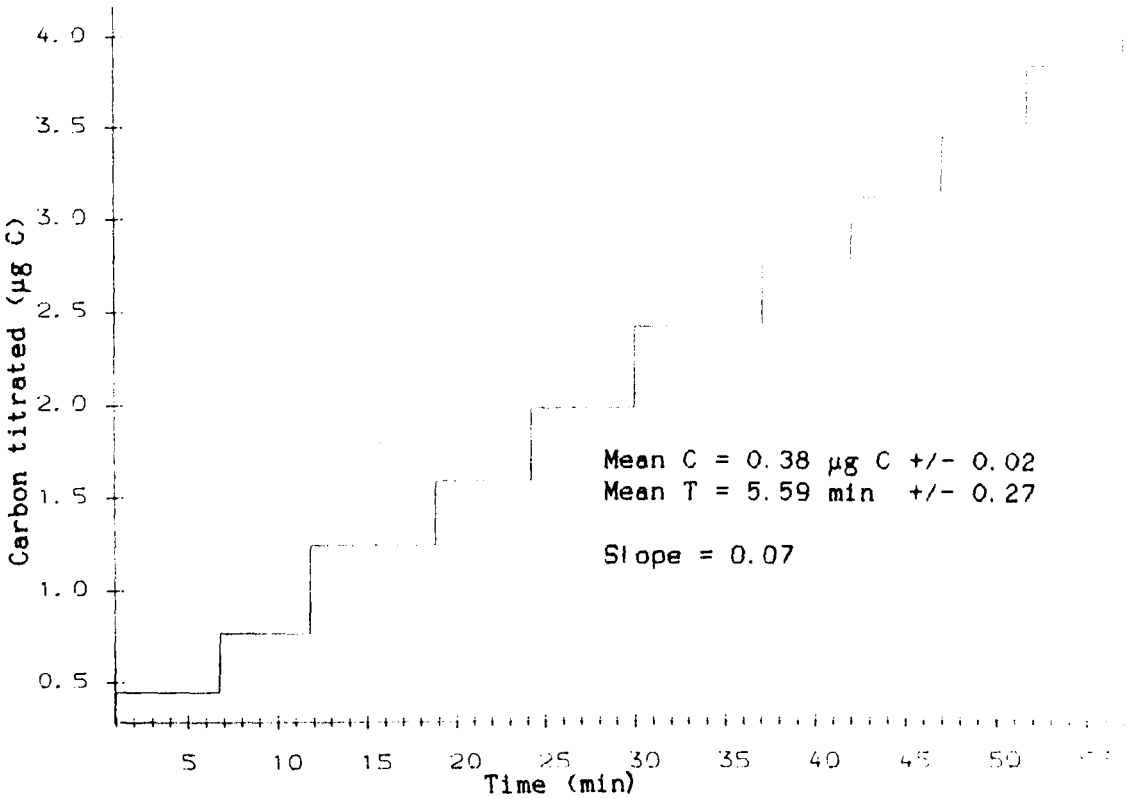
FIGURE 10.5

Examination of the blank
Time elasped in minutes plotted against
total carbon titrated.
Signal after fifteen samples titrated

FIGURE 10.6

Examination of the blank
Time elasped in minutes plotted against
total carbon titrated.
Signal after twenty samples titrated

Figure 10.5



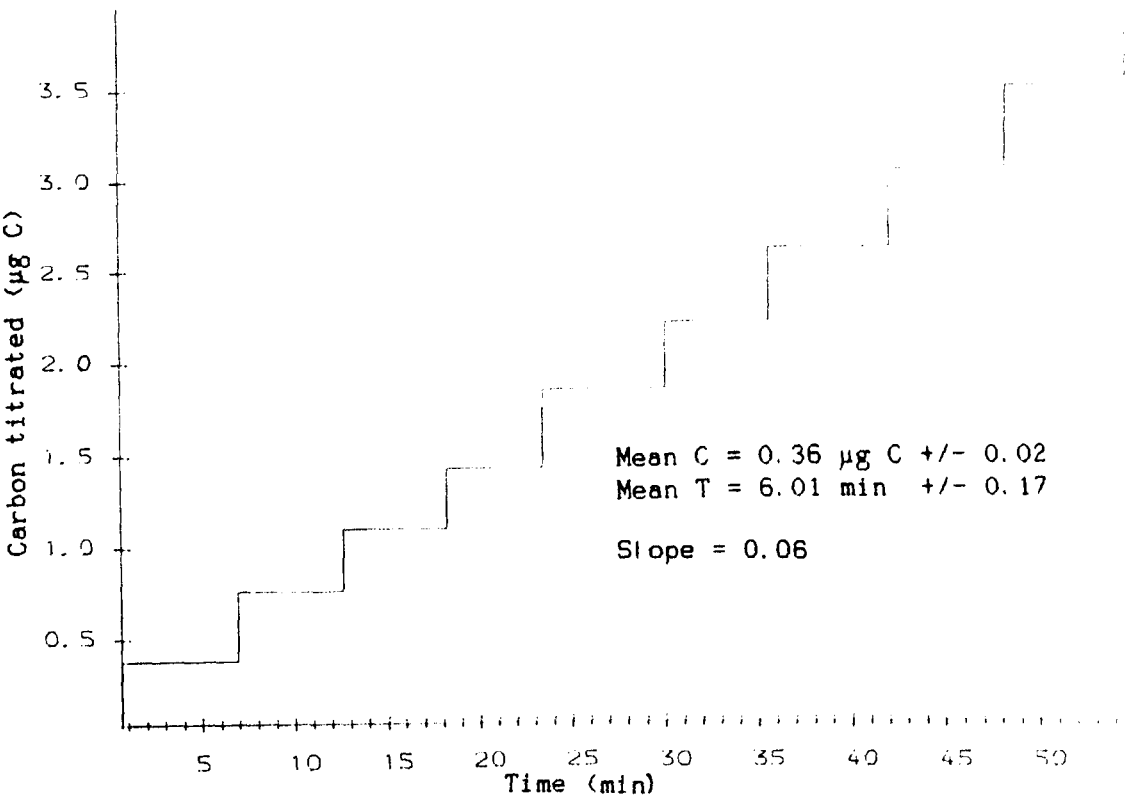


Figure 10.6

CHAPTER 11

DISCUSSION

Three goals were set out in the first chapter of this thesis. It is both convenient and logical to discuss the results presented within this study in relation to these original aims.

1) Evaluation, refinement and testing of the TIC coulometric system for routine productivity measurements and sea-going survey determinations of the carbonate system.

2) Exploration of the stoichiometry of oxygen and carbon dioxide flux pertinent to community metabolism.

3) Examination of the use of mesocosms to provide *in situ* estimates of apparent net community activity in comparison to traditionally used *in vitro* incubations - an assessment of containment and manipulation effects.

11.1 Evaluation of the coulometric system

During the course of this study the coulometric system was considerably refined and tested. The system has proven to be reliable and robust for both routine productivity and sea-going mapping, survey work. The system does require frequent, experienced attention, however, a practised operator can maintain the system continuously if necessary with occasional recourse to new cell solutions.

The system has the potential for accurate and precise determinations of TCO_2. There are a number of major limitations to the system as it currently exists.

1) An obvious limitation to the system in a mapping mode is the size of the sample currently being analysed along with the average time taken to bring the titration to completion. A single replicate averages a ten minute filling and titration cycle. A smaller sample size would reduce the filling time however it would not reduce the titration time which constitutes the major part of the time required.

The maximum titration rate of the coulometer is approximately 750 µg/min. This suggests that the bulk of the usual 30 ml seawater sample should be titrated within the first minute. However the nature of the titration as controlled by software inherent within the coulometer, tempered by the need to not overshoot the end of a titration, means that considerable additional time is required to complete a titration. A smaller sample size would not reduce this requirement.

The current version of the coulometer (Model 5011) being used in the School has a proportional rather than a stepwise control of the titration, this has reduced the titration time by half to approximately four minutes (Dr. C. Robinson, pers. comm.).

2) Preservation of samples has been shown to be successful although unfortunately it generates a large number of bottles that cannot be reliably used for future incubation experiments because they have contained mercury chloride. It will be necessary either to find an alternative non-persistent fixing agent or to be sure of successfully cleaning the glass bottles.

3) Instrument noise or the so-named blank is discussed in in Chapter 10. An average blank correction observed in the laboratory for a seawater sample is 0.9 µmol/kg. This is based on a seven minute titration and a blank signal of 0.05 µg C/min. The blank has been observed to increase dramatically whilst at sea, this is presumed to be a result of noise on the ships mains. During the Challenger cruise a blank correction of 9 µmol/kg was more typical. The rise in the blank can lead to a deterioration in the precision of the end-point, leading to a poor data set. It will be necessary to reduce the size of the blank in order to permit precise titrations at sea, especially if a smaller sample size is employed.

11.2 Productivity determinations

Numerous net, gross production and respiration rates have been obtained from both *in vitro* and *in situ* measurements of TCO_2 in seawater. A comparison of this approach and the Winkler oxygen method is discussed in relation to the third aim of this study.

A routine precision of 2-3 µmoles/kg can be expected from production/respiration measurements involving replicates taken from different bottles. Unambiguous estimates of carbon flux can be obtained with simplified method and handling in comparison to the more usual 14C method. Samples can be fixed and stored for later convenience or concentration determined in real-time. Attention needs to be paid to the sampling technique, for *in vitro* and also *in situ* determinations. Considerable care is necessary in filling bottles either prior to incubation or determination. A similar practise was employed throughout the study to that recommended for Winkler oxygen determinations (Carritt and Carpenter 1966, Williams and Jenkinson 1982).

11.3 Sea-going Capability

Prior to the Challenger 16/87 cruise, no oceanic, coulometric measurements of TCO_2 had been obtained at sea.

The first global survey of the oceanic CO_2 system (GEOSECS) consisted of potentiometric titrations of alkalinity and TCO_2, with a quoted precision of +/- 10.5 µmoles/kg. During the 1981 TTO expedition in the NE Atlantic, an increased precision was obtained (+/- 4 µmoles/kg) using an improved version of the same technique.

Johnson et al (1983)a followed the variation in TCO_2 as determined by infra-red photometry, in free water masses in the mixed layer of the north-western Carribean Sea. A precision of +/- 6 µmoles/kg is quoted for on-board determinations.

Takahashi et al (1985) were the first group to provide seasonal data on both pCO_2 and TCO_2 (coulometric) from the ocean areas west and north of Iceland. All samples were fixed at sea and analysed later on shore. The overall precision of the TCO_2 measurements was estimated to be +/- 4 µmoles/kg.

The coulometric determinations obtained during the Challenger 16/87 cruise during surface mapping provide a spatial resolution of 8 km (average ship speed of 8 knots) with a mean standard error of +/- 0.87 µmoles/kg (CV = 0.07 %), taken typically as three replicates per sample. Inter-bottle variability is obviously not accounted for in this single bottle method of sampling and it can be expected that from previous incubation experiments the precision would then fall to 2-3 µmoles/kg. Nevertheless, the precision obtained is clearly an improvement over previous methods for the measurement of the carbonate system in seawater.

An alternative approach in order to increase spatial resolution, would be to analyse a single replicate per sample. During a recent EROS (European River Ocean System) cruise in the Meditteranean, Dr C Robinson employed the coulometric system in such a mode. This provided a mapping resolution of 1.3 - 2.0 km (Robinson, pers. comm.), depending on the ships speed. Use of the new model of the coulometer enabled a resolution of approximately one km during a 780 km transect of the N.E. Atlantic (Dr. C. Robinson, pers. comm.).

Although initially attractive, this approach assumes that the precision obtained from alternative replicated sampling can be applied to the single determination. This is not entirely satisfactory as the coulometer does fluctuate with regards to reproducibility (Figure 9.39). In addition, closer examination of data obtained during the Challenger cruise indicates occasional spurious values. (Data Appendix - Challenger Cruise). Unless spatial coverage is of over-riding importance, the best precision will be obtained through replication of samples.

The main aim of the Challenger cruise was to define the carbonate system through the determination of two system variables, TCO_2 and pH. In the event only one was successfully obtained, however the observed distribution of TCO_2 values can still be discussed in relation to previous TTO measurements and other recorded variables.

11.3.1 Comparison between Challenger 16/87 and TTO 1981

The similarity between comparable stations is initially encouraging. However, there is no *a priori* reason to assume the CTD profiles should be identical. The sampling was done at different times of the year and not all depths or positions coincide.

Recent work by Bradshaw and Brewer (1988, 1988) has shown a serious discrepancy can exist between estimates of TCO_2 determined from potentiometric titrations and those determined directly by manometric or gasometric techniques (coulometric titration of a gas stripped from an acidified sample may be considered to be in this category).

During the TTO expedition titrimetric estimates were always found to be higher with a difference of up to 20 μmoles/kg observed in surface waters. The mean difference observed depended on the depth:

Depth < 1000m Difference = 7.2 +/- 5.9 μmoles/kg
Depth > 1000m Difference = 4.0 +/- 2.9 μmoles/kg

It is not possible to use the limited data set obtained during Challenger 16/87 in order to test for the differences observed during the TTO expedition, however it is encouraging that both the oxygen and TCO_2 data obtained are similar to the TTO data. Due to the uncertainty currently attached to the determination of TCO_2 through a solution chemical or titration method, the data set obtained during the Challenger cruise provides the only rigorous series of TCO_2 measurements for this area of the N E Atlantic. Further measurements during the 1989 BOFS and JGOFS scientific initiatives are set to add to this data set and aim to over-determine the carbonate system, in relation to biological and physical controls.

11.3.2 Correlation of TCO_2 to other measured variables

Surface measurements

The concentration of total dissolved inorganic carbon dioxide in a given seawater sample is a function of biological, chemical and physical characteristics and history of the sample concerned.

Temperature and salinity control the solubility of gases in seawater and can serve as an indicator to the extent of mixing between two water masses. Alkalinity changes through carbonate solution and/or precipitation will effect TCO_2. Biological activity will change TCO_2 levels and can be coupled with corresponding changes in oxygen.

It is to be expected that any relationship between TCO_2 and other parameters will be complex and most likely non-linear. A rigorous analysis of any potential relationships would be best achieved by use of a modelling approach. However a rough approximation may be obtained by use of a series of regression equations (Ben-Yaakov 1972).

Regression analysis (Tables 9.3, 9.4, 9.5) demonstrated a strong negative correlation between TCO_2 and the so-named 'biological' variables (attenuation = - 0.68, chlorophyll = - 0.72). A strong positive correlation is obtained with salinity, which is to expected due to the presumed salinity/alkalinity relationship. A poor correlation is observed with temperature (0.35).

When the data obtained around the region of the Arctic front is examined, the reverse is observed (Table 9.6). A stronger correlation is observed between TCO_2, temperature and salinity. It should be noted however that these observations are based on only 8 or 9 sample points.

There is widespread disagreement as to the relative importance of biological or physical controls on the CO_2 chemistry of the surface ocean. Brewer (1987) in a plea for complete information suggested a co-ordinated programme combining biological, chemical and physical measurements of the highest accuracy and precision.

Simpson and Zirino (1980) measured pH, salinity and chlorophyll fluorescence in surface waters off Peru and concluded that biological controls were dominant. Johnson et al (1979) followed changes in pH, alkalinity and oxygen in the surface waters off British Columbia for a 15 day period. They concluded that the exchange of both gases with the atmosphere depended primarily on the net amount of primary production. Codispoti et al (1982) followed changes in pCO_2 in the Bering Sea. They concluded the dominant control was utilisation of CO_2 by phytoplankton during the spring bloom.

Alternatively, a number of papers have been presented advocating the case for physical control. Weiss et al (1982b) made repeated determinations of TCO_2 and pCO_2 in the Pacific and found very strong correlation with both temperature and salinity. Takahashi (1980) using GEOSECS data found that TCO_2, normalised to a constant salinity, was closely correlated with temperature.

On the basis of the sparse data set obtained during the Challenger cruise coupled with the lack of pCO_2 data it is not possible to advance any further over the possible controls in this region, however a rough, first approximation suggests a stronger correlation with biolgical than physical variation.

Vertical Profiling

A number of profiles were obtained during the cruise from a series of discrete sampling points throughout the water column. These have limited value due to the infrequent sampling points throughout the water column. Nevertheless, the similarity between TCO_2 and O_2 is encouraging.

A general symmetry is observed sub-surface, differences that do occur, for example minimum and maximum being displaced up or down relative to each other are potentially informative. However, the sparsity of the data points coupled with no information on the previous history of the water mass concerned, makes it impossible to accurately explain the differences. A further detailed series of measurements both spatially and temporally is necessary.

Craig and Weiss (1970) commented on TCO_2 measurements taken from the 1969 GEOSECS station off California. They observed an increase in TCO_2 close to the seafloor and presumed this was the result of redissolution of CO_2 from the sediments. Examination of the TTO data set also suggests that at certain stations a rise in TCO_2 was observed close to the seafloor. A number of the stations during the Challenger cruise contained a sample taken close to the sea floor. The majority of these stations show a steady increase in TCO_2 with depth and no obvious sharp rises at the sea floor (Stations ie 14, 20, 23, 25). However in other stations a rise is observed (Stations 15, 16, 17, 19) although this rise is difficult to differentiate from a general increase with depth.

11.4 Planktonic photosynthetic and respiratory quotients

The importance and expected theoretical range of planktonic photosynthetic quotients was discussed in detail in Chapter Four. A maximum theoretical range, based on biochemical considerations, was shown to vary from 0.88 to 1.92. However, it is expected that the extreme ends of this potential span could only be maintained for a very short-time period. A more typical range would be expected to be from 1 to 1.6 depending on the form of combined nitrogen source (Strickland 1960).

Most estimates of the value of the quotient have been obtained by using carbon flux estimates provided by radiocarbon techniques. These estimates are not strictly compatible with any corresponding oxygen flux measurements.

The oxygen method provides estimates of gross and net production whereas the 14C-$NaHCO_3$ technique measures a rate between net and gross photosynthesis, depending on the physiological circumstances.

Other approaches have involved estimating flux of TCO_2 through indirect methods ie pH and alkalinity as an attempt to remove any systematic errors due to an incompatibility between the oxygen and 14C-$NaHCO_3$ methods. Johnson et al 1981 summarised previous studies using TCO_2 and oxygen based estimates of net community activity. This summary has been revised, updated and is presented in Table 11.1. It is important to note that only one other study (Johnson et al 1981) involved a comparison of oxygen and direct TCO_2 determinations.

A direct estimation of TCO_2 increases the precision of the determination of the quotient and reduces the possibility of systematic errors (Bradshaw and Brewer 1988, 1988).

Nevertheless, from these previous studies, where indirect estimates of TCO_2 were obtained, it is apparent (Table 11.1) that photosynthetic and respiratory quotients are consistently outside the accepted theoretical range.

Due to the common practise of using the 14C-$NaHCO_3$ technique to provide carbon flux estimates, few determinations of respiratory quotients exist in the literature. In general the RQ is taken to be the reciprocal of the PQ ie that the biochemical stoichiometry of respiration is the reverse of photosynthesis. There is a complication in making this simple assumption in that nitrate assimilation (inferring nitrate reduction) occurs in the euphotic zone, the reciprocal of nitrification seems to occur in deeper water so surface water RQ values will consequently fall into a narrower range than the PQs.

It is possible to compare the quotients, both photosynthetic and respiratory (in vitro) along with molar ratios (in situ) obtained from two mesocosm experiments in relation to previous literature and established convention. The present study is the first to provide a number of compatible and directly measured respiratory quotients.

11.5 Swedish Mesocosm Experiment

11.5.1 In vitro measurements

The PQs and associated S.E. observed from in vitro experiments ranged from 0.99 +/- 0.06 to 1.17 +/- 0.06 (Table 7.8). This is very close to the conventionally adopted value of 1.0 or 1.2 (Parsons et al 1984). The range of respiratory quotients is 0.52 +/- 0.04 to 2.87 +/- 0.60.

The photosynthetic quotients observed are compatible with the mesocosm being based on an ammonia nitrogen source. The bag was dosed twice throughout the experiment with ammonium salts. It is expected that phytoplankton will metabolise ammonium in preference to any other nitrogen source.

The *in vitro* PQ range observed suggests that no obvious biochemical discrepancy exists in contrast with the observations of Oviatt *et al* 1986, Johnson *et al* 1983b.

The range for the respiratory quotients is much greater than that observed for the PQs. A large error in precision on the largest RQ observed does reduce the range somewhat, even so the observed spread is consistent with previous observations (Table 11.1) from indirect estimates of TCO_2 determination.

The range of respiratory quotients obtained suggests that respiration, as implied by the RQ cannot be simply considered as the stoichiometric opposite of photosynthesis. Johnson *et al* (1983) suggested that low RQ values observed were due to bacterial activity occuring in anaerobic microzones within the water column. This hypothesis has yet to be proven and in this experimental period only one low RQ was observed (0.52 +/- 0.04), all other quotients were close or greater than one.

11.5.2 In situ measurements

A number of molar ratios can be calculated from the in situ measurements. These ratios can be divided into two sections, those obtained over the first sampling period (2/7/86 1845h to 3/7/86 0900h), where sampling was carried out every three hours. Secondly, a series of twelve hourly sampling periods from 7/7/86 to 11/7/86.

2/7/86-3/7/86 (Table 7.7)
Observed molar ratios: 0.79 to 1.50

excluded from the above are those quotients where one or both of the gas fluxes recorded is less than the precision attached to the estimate.

7/7/87-11/7/87 (Table 7.10)
Observed molar ratios: 0.41 to 1.43

excluded from the above are those quotients where one or both of the gas fluxes recorded is less than the precision attached to the estimate.

A detailed discussion of the advantages and limitations of in situ measurements as opposed to in vitro incubations is given later in relation to the third aim of the study.

Possible errors concerning physical mixing and gas exchange within the mesocosm suggests that these ratios are not as reliable as the in vitro incubations and so no certainty can be placed on their absolute value. Nevertheless, it is interesting to note that neither sampling period provided the extensive and unusual range of ratios observed by Oviatt et al 1986 (0.0 to 5.0).

A correction for physical mixing has been made to the observed in situ fluxes enabling a series of corrected ratios to be calculated. These are given in Tables 7.7 and 7.8. However as discussed early in Chapter Seven this correction lacks accuracy and because of this uncertainty is omitted from further discussion.

In conclusion, although the observed molar ratios are not adequately corrected for air-sea exchange or diffusion, it is expected that both gases would be affected equally by physical mixing. The differential effects of gas exchange with the atmosphere may also be expected to be a minor source of error away from the surface in relation to the scale of fluxes being observed. Hence the observed ratios can be taken as a rough approximation and it is important to note that the range is not as large as has been quoted elsewhere in the literature (Oviatt et al 1986).

Ignoring potential bottle effects on the in vitro incubations it is apparent that biochemical convention regarding the nature of the products produced during photosynthesis is substantiated by these results for the photosynthetic quotients. However, the range of RQs observed is greater than commonly given in the literature, this suggests that the biochemical stiochiometry of respiration is not the reciprocal of photosynthesis.

11.6 Scottish Mesocosm Experiment

11.6.1 In vitro measurements

Only three photosynthetic quotients and associated S.E. were determined from in vitro incubations.

(-56.7), 1.44 +/- 0.177, 1.33 +/- 0.151

The first quotient (Incubation 2, Table 8.7) is anomalous and can may be explained by a poor precision coupled with only two replicates for the mean light oxygen value, along with a high supersaturation of oxygen within the sample. For this incubation a drop in oxygen is observed in the light, suggesting that the experimental details were at fault rather than this result being a true reflection of metabolic activity during this incubation.

The two other quotients are in accordance with conventional expectations on the assumption that nitrate added to the bag at regular intervals was the nitrogen source for the phytoplankton. The range of RQ values obtained varied from 0.86 +/- 0.161 to 1.58 +/- 0.147. Once again it is apparent that the RQ is not merely the reciprocal of the PQ and a much greater range with higher RQ values than conventionally adopted was observed.

Excluded from the above are those quotients where one or both of the gas fluxes recorded is less than the precision attached to the estimate.

11.6.2 In situ measurements

The first attempt to follow an *in situ* diurnal signal was not successful due to intense gradients of O_2 and CO_2 within the bag. A change of approximately 50 μmoles/kg of oxygen occurred over a depth range of 5 m. With such a sharp gradient sampling problems are at an extreme. The main supposition with sampling *in situ* is the ability to sample the same water mass at the same depth consistently. Changes in external density may give rise to differences in the geometry of the bag and so shifting the vertical gradients within the bag. If strong gradients are present, this makes accurate repeated sampling difficult.

Subsequent to the first mixing of the bag, a series of molar ratios were calculated (Table 8.8). These range from -0.55 through to 4.72. Ignoring the anomalous negative ratio and the two extreme ratios, 0.20 and 4.72, all other ratios fall between 0.49 +/- 0.164 to 1.50 +/- 0.273. The drop in TCO_2 at 1 m depth during the second night-time period (molar ratio = - 0.55) may be explained by the proximity to the sea surface and be due to the effects of either air/sea exchange, night-time convection or wind-mixing.

The two extreme ratios 4.72 and 0.20 are both calculated from the 6 m sample depth. The magnitude of the changes observed at 6 m is greater than all other depths (Figures 8.17 and 8.18). The large drop in TCO_2 from 0615 to 1830 h 19/08/87, is suprising as there will be reduced light at 6m compared to other depths and fluorescence profiles indicated that the chlorophyll maximum to occur at 4-5 m. Additionally, no corresponding rise was observed for the following night-time period. One possible explanation is that the bag is not fully mixed to that depth. The gradient of TCO_2 can be seen to increase relatively below 4m and so there is some justification in ignoring these values.

The precision for all sampling points relevant to these two ratios is the same as for the remainder of the depths. If the above three ratios are ignored then the remaining uncorrected spread of molar ratios is similar to that obtained during the first mesocosm experiment in Sweden. No correction for physical mixing and air-sea exchange has been made, so once again little certainty can be placed on the absolute values. However as described for the first mesocosm experiment, these may still be regarded as a rough approximation.

Following the second mixing of the bag, another series of molar ratios can be calculated (Table 8.9). During this period a far larger range is observed with extreme and negative ratios. The range is from -2.98 +/- 0.343 to 10.15 +/- 2.013 with several ratios greater than 7.00. A closer examination of the fluxes of the two gases (Figures 8.19 and 8.20) demonstrates an obvious discrepancy between oxygen and TCO_2 fluxes within the bag. Oxygen fluxes for the both the two day-time and three night-time periods are shown in Figure 8.19. A diurnal signal is apparent for the first four metres. At 5 metres an increase is observed during the first day-time period but a decrease in the second. At 6 m no daytime increase is observed, rather a gradual drop in oxygen concentration with time.

In comparison to the oxygen signal, corresponding measurements of <u>in situ</u> TCO_2 do not exhibit a complementary or consistent pattern. This is reflected in the anomalous molar ratios calculated from this series of measurements (Table 8.9).

Examination of temperature profiles taken within the bag (Section 8.4) indicated nocturnal convection occurring down to 2 m depth, also daytime surface heating penetrating to 3 m depth. As the first three metres appears to be considerably influenced by physical processes it may be justified to ignore any molar ratios calculated from these depths. This does involve all anomalous negative coefficients observed. However it is difficult to explain why a diurnal pattern is still evident from oxygen measurements but not in TCO_2 flux.

In the previous time series a consistent and symmetrical pattern had been observed between the two gases, as had also all time series measurements from the Swedish mesocosm. The reason for the large discrepancy between the two gases in this time series, may be explained by the difference in gradients that exist within the water column.

The gradient is much greater for TCO_2 than oxygen at the beginning of sampling for both gases (Figures 8.19 and 8.20). A gradient of 27 μmoles/kg is apparent for oxygen in comparison to 100 μmole/kg for TCO_2, over a 6 metre depth interval.

It may be suggested that the increased gradient with respect to TCO_2 has led to sampling errors, as discussed earlier, regarding the water depth that is sampled. However, by the end of the sampling period (Figure 8.19, 23/08 1615 h) the gradient can be seen to increase substantially for both gases, oxygen to 100 μmoles and TCO_2 to 140 μmoles/kg.

Only three depths sampled (4,5 and 6) do suggest a partially consistent pattern in symmetry with the oxygen measurements (Figures 8.20 and 8.21). The ratios for the first night-time period are large (Table 8.9)

4 m = 7.54 +/- 0.344
5 m = 7.25 +/- 1.026
6 m = 10.15 +/- 2.013

These large ratios may be the result of the large gradient for TCO_2 in the water column. The following day and night-time periods provide ratios from 0.46 +/- 0.126 to 1.03 +/- 0.124 (Table 8.9).

The second day-time period has two negative ratios at 5 and 6m depth. This is the result of a drop in oxygen at those depths, during the day, coupled with a drop in TCO_2. I would suggest that due to the reduction in light at those depths coupled with in increasing gradient in oxygen has meant that any small rise in oxygen has been obscured.

In conclusion, on the basis of these and previous time series experiments (Sweden), within certain limitations it is possible to measure a series of molar ratios in situ. The ratios observed in situ are consistent with conventional expectations.

Correction of these ratios is difficult and it is assumed that the influence of physical processes and air-sea exchange with the atmosphere will be minimal. Work carried out within the Scottish mesocosm suggested that intense gradients of both gases within the bag coupled with physical processes and air-sea exchange with the atmoshpere has made interpretation of these measurements difficult.

11.7 In situ measurements within mesocosms

A thorough discussion of the history and back-ground to inter-method comparisons is given in Chapter 4, along with a discussion of the different approaches, advantages and disadvantages of measurements made in situ in comparison to the more typical in vitro incubations. A significant part of the controversy regarding productivity calculations concerns problems that are not unique to the 14C-$NaHCO_3$ technique, but are common to all in vitro based production rates. These problems include containment, manipulation and incubation effects and proper sampling strategy (Fahnenstiel and Carrick 1988).

The measurement and observation of an in situ diurnal rhythmn for either TCO_2 and/or O_2 is a difficult process. A variety of factors can interfere with curve interpretation: turbulence of water masses, air-sea exchange and most significantly horizontal advection. There are in general two main approaches to measurements made in situ. First are freewater changes, using of drogues to mark the watermass. Second, is the use of an enclosed volume of water, a mesocosm. A mesocosm can only mimic freewater changes and so must still be regarded as having certain containment effects.

However, in situ data collection, analysis and budgeting within a large contained ecosystem is much simpler than freewater diel measurements. The advantages of using mesocosms are that they are presumed to largely eliminate horizontal advection and reduce vertical processes considerably.

Where data does exist for *in situ* diurnal changes, calculated rates in comparison to *in vitro* measurements are sometimes observed to be higher (Tijssen 1979, Johnson *et al* 1981, Fahnenstiel and Carrick 1988) and sometimes not (Williams *et al* 1983, Davies and Williams 1984). The only recent comparison involving a mesocosm was carried out by Davies and Williams (1984). They demonstrated no significant difference in oxygen flux due to containment in glass bottles.

11.8 Physical characteristics of mesocosms

The use of enclosed volumes of water in order to study planktonic processes has become increasingly popular (Bender *et al* 1987, Oviatt *et al* 1986, Davies and Williams 1984).

Mesocosms allow the simulation of 'real' conditions within a controlled environment. The aim of the experiments in Sweden and Scotland was to measure fluxes of biological gases. As discussed elsewhere in the work any change in concentration at a certain depth over time is a combination of both physical and biological processes. To provide an estimate of biological fluxes the observed total fluxes observed need to be corrected for any physical contribution.

An estimation of physical mixing processes is simplified by use of an enclosure. The bag eliminates mixing on scales beyond the dimensions of the bag itself. The assumption is that the removal of larger scale horizontal processes facilitates the use of a simple one dimensional vertical model to provide mixing rates.

The model to do this is described by James (1977) and uses the one dimensional equation for temperature

$$\frac{dT}{dt} = \frac{d}{dz} (K_z . dT/dz)$$

K_z is the coefficient of vertical eddy diffusion of heat. The z axis represents depth. This classical method of estimating the K_z and using it to calculate fluxes is analagous to molecular transport. It assumes that the turbulent fluxes can be expressed by the gradient of the transported quantity multiplied by an appropriate eddy diffusion coefficient. Bachmann and Goldman (1965), Hesslein and Quay (1973), Jassby and Powell (1975) have used the method within the thermocline, however it must be noted that its physical basis is precarious (Dr. A. Elliott, pers. comm.).

Eddy transport coefficients are complicated functions of space and local stability conditions, which have to be determined empirically. This method breaks down when gradients vanish or coupled fluxes of two conservative quantities transport one of them against its own gradient.

Hesslein and Quay (1973) used a variety of methods in order to estimate K_z, temperature, dye and radon measurements. They found significant differences between the methods and recommended use of radon. However for the purposes of these experiments a general simplification is sufficient hence only the temperature was used in the first mesocosm experiment and then temperature and dye methods in the second.

In order to use the model certain requirements need to be satisfied :-

1) Neglible vertical advection.
2) Horizontal thermal homogeneity.
3) No external heat sources.

These assumptions require further examination in order to assess their validity in this instance.

1) Vertical Advection

Possible causes are as follows:

a) Wind-induced advective and entrainment processes. Due to the diameter of the bag and the surrounding raised platforms, it is evident that the sheltered surface and reduced fetch minimises wind effects.

b) Movement of the bag walls due to the fluctuating motion of the surface floats.

c) Convection. Convection is likely to be important during nocturnal cooling and perhaps at the surface during the day. However salt stratification will inhibit convection.

d) Density forcing. Temperature changes outside the bag are followed more slowly by corresponding changes within so that density differences can be set up causing a 'squeezing' effect tc the bag walls. Steele et al (1977) found that the walls of the bag act as a low pass filter so that only temperature fluctuations with an an approximate period of > 48 hrs are transmitted through the wall.

e) Buoyancy layers. Andersson and Rahm (unpublished 1988) showed that the temperature differences within and outside the bag force an interior vertical circulation by buoyancy layers at the walls while the interior is still horizontally homogeneous. They demonstrated a vertical advective and diffusion balance occasionally degenerating into an advective dominated one. Thorpe et al (1969) in a laboratory study of a heated sidewall observed a series of convective cells set up along the wall.

2) Horizontal thermal homogeneity.
Boyce (1974) accounted for similar temperature profiles in and out of an enclosure by horizontal heat diffusion due to thermal conduction through the bag walls, the model required vertical diffusion to be molecular.

3) External heat sources.
Bachmann and Goldmann (1965) calculated solar heating to be 81-62% of total heating rate at 5-25m respectively in a freshwater lake. They suggest that direct solar heating rather than turbulent mixing is responsible for the thermal profile. Hesslein and Quay (1973) found that the solar heating contribution was 15% at 3m and 1% at 6m. Additional calculations of 'biological' heating calculated from the heat of formation of CO_2 from simple organics (ie respiration) resulted in an increasing percentage addition of 5% at 3m and 16% at 6m. The combined effects of solar radiation and biological heat contribute approximately 15-20% of the total temperature increases at the 3-6m depths (Hesslein and Quay 1973).

11.8.1 Diffusivity calculations : Swedish mesocosm

A number of temperature profiles were taken during the Swedish mesocosm experiment. The results are given in Chapter 7. A limited number of diffusivity coefficients were obtained that varied in both size and sign. The cause of anomalous high and negative coefficients may be the result of two possible explanations. The first is that the model used was too simplistic and several assumptions were incorrect. The second explanation is that the limited data set is not representative and further measurements were necessary in order to allow possible experimental errors to be disregarded.

In an attempt to remedy this situation during the Scottish mesocosm experiment a thermistor chain was used to provide continuous temperature measurements. This was supplemented bya dye study. The intention being to examine the mixing processes occurring within a mesocosm in much greater detail.

11.8.2 Diffusivity calculations : Scottish mesocosm

Temperature profiles

Previous work concerning enclosures noted the similarity of temperature profiles within and outside the enclosure (Boyce 1974, Andersson and Rahm, unpublished 1988) allowing for some smoothing and lag aspects. In this experiment different profiles were observed, with stronger stratification exterior to the bag. The depth of the thermocline was (7m) exterior compared to 3m interior.

Within the bag, a weak continual thermocline persisted from 2-3 m (Figure 8.3). Convective cooling is apparent at night (Figure 8.3). The limit to which nocturnal convection can penetrate depends on the external air temperature and the intensity of salt stratification. Fig 8.3 indicates a convective mixing to 2 m depth.

Hourly eddy diffusion coefficients (K_z) can be calculated under the assumptions of the model (Table 8.3). The surface channel from the thermistor chain was ignored due to the irregular nature of the profile. In common with coefficients calculated using the dye concentrations the irregular nature of the signs suggests the one dimensional diffusion model is not appropriate.

Coefficients calculated at the thermocline are in an area where vertical advection would be at a minimum and below the convective depth of mixing however the premise of vertical diffusion alone is still inadequate in this region.

Dye Method

Eddy diffusion coefficients (K_z) were calculated using the dye concentrations recorded (Table 8.4). Horizontal homogeneity and minor vertical advection were originally assumed. The coefficients calculated do not support these assumptions due to the irregular nature of the signs accompanying them. Mass recovery of the dye after each profile is recorded in Table 8.5. The variation observed suggests that horizontal advection is present within the bag.

Steele et al (1977) observed a secondary maximum in a dye study on a similar bag and concluded that a description of vertical mixing in terms of diffusion alone was simplistic and inaccurate. The dye profiles from this experiment indicate a progressive stepping movement down the bag though not completely smooth or regular, no obvious sharp maximum or minimum were observed. The gradual stepping is mirrored by the corresponding temperature profiles (Fig 8.13). The stepping is a gradual reversion of the temperature distribution to that prior to mixing and cannot be explained by Fickian diffusion.

Steele et al (1977) used a derivation of the diffusion equation to provide an estimate of K_z for each profile dependent on the variance of the distribution. Using that approach the following coefficients were calculated.

Profile 1 - $K_z = 0.86\ cm^2/sec$
Profile 2 - $K_z = 1.24\ cm^2/sec$
Profile 3 - $K_z = 0.31\ cm^2/sec$
Profile 4 - $K_z = 0.14\ cm^2/sec$
Profile 5 - $K_z = 0.11\ cm^2/sec$

This approach is limited in the assumption of no boundaries and an initial thin layer addition midwater. However it does provide positive signed coefficients albeit higher than expected. An alternative model could be used to simulate a thin layer addition at the surface however the theoretical basis is solely diffusion as before. The dye and thermistor data both indicate the inadequacy of this approach and so the model was not employed.

In conclusion, the use of a simple one-dimensional diffusion model to describe physical mixing within the Scottish mesocosm is inaccurate rather than simplistic as described by Steele et al (1977). This would also appear to be true for the Swedish mesocosm although a limited series of temperature measurements excludes a definite conclusion.

Previous work within enclosures of the type used in Loch Ewe (Steele et al 1977, Gamble et al 1977) has indicated that physical mixing may have little or insignificant effect on the overall fluxes observed. However in these particular experiments the physical mixing within those mesocosms appeared to be reasonably described using this one dimensional model approach. This is not the case for the Scottish mesocosm experiment.

The suitability of the use of mesocosms for this type of flux study is questionable. A complicated mixing regime is apparent, any future attempt to correct observed changes within the bag for mixing would need to take this into account. A thorough examination of temperature structure within the bag would need to be continuously recorded, both spatially and temporally. This is often difficult to achieve whilst endeavouring to provide chemical and biological measurements alongside.

An alternative approach would be to accept that if a large enough signal can be generated by dosing the bag to provide bloom conditions, then other potentially interfering processes may be ignored as being minimal. A limited number of physical measurements may be necessary to confirm that the scaling effect is indeed small in relation to the biological signal being observed. This approach unfortunately will provide conditions not realistic in comparison to those occurring naturally within the water column.

11.9 Summary

The precise and extensive capabilities of a microprocessor controlled coulometric system for measuring TCO_2 has been described. The system has proven to be a robust and reliable method for both routine productivity and seagoing mapping, survey work. Future measurements regarding the carbonate system in seawater may be accurately and precisely obtained using this method in either a discrete (this study) or continous mode (Dr. C. Robinson, pers. comm.). Increased precision will be dependent on reducing the size of the blank signal and the increased noise observed during measurements at sea.

The use of mesocosms for future *in situ* measurements should be associated with extensive wind speed and physical measurements, if corrections to observed *in situ* fluxes are required. The circulation within these bags has been shown to be complex and not suitable for a simple one dimensional vertical diffusion model.

There are photosynthetic and respiratory quotients (Andersen and Sand-Jensen 1980, Gallegos *et al* 1983, Johnson *et al* 1983, Oviatt *et al* 1985, Megard *et al* 1985, Fahnenstiel and Carrick 1988) which are difficult, if not impossible to explain in terms of current understanding regarding biochemical stoichiometry of photosynthesis. If these quotients do reflect true biochemical photosynthetic and respiratory processes then a major reconstruction of algal biochemistry is necessary.

There is the possibility of interfering factors aliasing the anomalous quotients quoted in the literature. Potentially the most serious is methodological error, the problem of incompatible estimates of carbon and oxygen flux has been addressed in this study through the use of the coulometric TCO_2 determinations.

Experimental work presented in this thesis provided no anomalous discrepancies for *in vitro* photosynthetic quotients and uncorrected molar ratios observed *in situ*. This suggests that conventional understanding of the algal biochemistry during photosynthesis is adequate. However, a greater range was observed for the respiratory quotient.

The RQs obtained suggest that the biochemical stoichiometry of respiration cannot be considered to be the reciprocal of photosynthesis. Additional work is necessary to examine this fundamental and important observation.

Addendum

References

BOLIN, B. 1977. Changes of land biota and their importance for the carbon cycle. Science, 196, 613-615.

BONIFACE, H.J. & JENKINS, R.H. 1971. The determination of carbon in steel by coulometric determination in partially aqueous medium. Analyst, 96, 37-46.

BROECKER, H.C., PETERMANN, J. & SIEMS, W. 1978. The influence of wind on carbon dioxide exchange in a wind wave tunnel, including the effects of monolayers. J. Mar. Res., 36, 595-610.

CARTER, H.H. 1974. The measurement of rhodamine tracers in natural systems by fluorescence. Rapp. P.-v. Reun. Const. Int. Explor. Mer, 167, 193-200.

DANCKWERTZ, P.V. 1970. Gas-Liquid Reactions. pub. McGraw-Hill, N.Y.

DAVIES, J.M., BAIRD, I.E., MASSIE, L.C. & WARD, A.P. 1980. Chemical and productivity measurements in an enclosed water column. ICES C.M., 1980.

EPPLEY, R.W. 1980. in Primary Productivity in the Sea. ed. FALKOWSKI, P.G. pub. Plenum Press. 231-242.

FASHAM, M.J.R., PLATT, T., IRWIN, B. & JONES, K. 1985. Factors affecting the spatial pattern of the deep chlorophyll maximum in the region of the Azores front. Prog. Ocean., 14, 129-165.

GREENBERG, G. 1932. Industr. Engng. Chem., 4, 309-311.

GRIPENBERG, S. 1937. Fifth Hydrol. Conf. Helsingfors. Comm., 10B.

HUFFMAN, E.W.D. 1977. Performance of a new automatic carbon dioxide coulometer. Microchem. Journal, 22, 567-573.

JAHNE, B., MUNNICH, K.O. & SIEGENTHALER, U. 1979. Measurements of gas exchange and momentum transfer in a circular wind tunnel. Tellus, 31, 321-329.

JOHNSON, K.S. 1979. Biological production and the exchange of oxygen and carbon dioxide across the sea surface in Stuart Channel British Columbia. Limnol. Ocean., 24, 474-482.

LEDWELL, J.J. 1984. The variation of the gas transfer coefficient with molecular diffusivity. In Gas Transfer at Water Surfaces. eds. BRUTSAERT, W. & JIRKA, G.H., pub. Reidel Dortrecht.

LEWIS, W.K. & WHITMAN, W.G. 1924. Principles of gas absorption. Ind. Engng. Chem., 16, 1212-1220.

LINGANE, J.J. 1958. Electroanalytical Chemistry. pub. Interscience Publishers Inc., N.Y.

LISS, P.S. 1973. Processes of gas exchange across an air-water interface. Deep Sea Res., 20, 221-238.

McCARTHY, J.J., WYNNE, D. & BERMAN, T. 1982. The uptake of dissolved nitrogenous nutrients by Lake Kinneret (Israel) microplankton. Limnol. Ocean., 27, 673-680.

MERLIVAT, L. & MEMERY, L. 1983. Gas exchange across an air-water interface: experimental results and modelling of bubble contribution to transfer. J. Geophys. Res., 88, 707-724.

RILEY, G.A. 1951. Oxygen and phosphate and nitrate in the Atlantic ocean. Bull. Bing. Ocean. Coll., 13, 93-102.

SAWYER, D.T. & ROBERTS, J. Jr. 1974. Experimental Electrochemistry for Chemists. pub. Wiley. N.Y.

SZEBELLEDY, L. & SOMOGYI, Z. 1938. Die coulometrische analyses als prazisions methode. I. Z. Anal. Chem., 112, 313-323.

WHITMAN, W.G. 1923. The two film theory of gas absorption. Chem. Met. Engng., 29, 146-148.

WONG, C.S. 1970. Quantitative analysis of total carbon dioxide in seawater: a new extraction method. Deep Sea Res., 17, 9-17.

REFERENCES

ANDERSON, J.M. & SAND-JENSEN, K. 1980. Discrepancies between the O_2 and 14C methods for measuring phytoplankton gross photosynthesis at low light levels. Oikos, 35, 359-364.

ANDERSON, D.H. & ROBINSON, R.J. 1946. Ind. Eng. Chem. (Anal.), 18, 767.

ANDERSON, L. 1981. Some novel photometric techniques. Application to the study of the sea water carbonate system. Ph.D. Thesis University of Goteborg Sweden.

ANTIA, N.J., MCALLISTER, C.D., PARSONS, T.R., STEPHENS, K. & STRICKLAND, J.D.H. 1963. Further measurements of primary production using a large-volume plastic sphere. Limnol. Ocean., 8, 166-183.

BACHMANN, R.W. & GOLDMAN, C.R. 1965. Hypolimnetic heating in Castle Lake, California. Limnol. Ocean., 10, 233-239.

BARNOLA, J.M., RAYNAUD, D., NEFTEL, A. & OESCHSGER, H. 1983. Comparison of CO_2 measurements by two laboratories on air from bubbles in polar ice. Nature, 303, 410-413.

BATES, R.G. 1975. pH scales for seawater In: The nature of sea water. Phys. Chem. Sci. Res., Rep. 1 Dahlem Conf., 315-338.

BATES, R.G. & CULBERSON, C.H. 1977. Hydrogen ions and the thermodynamic state of marine systems. In: The fate of fossil fuel CO_2 in the oceans., ed. ANDERSON, N.R. & MALAHOFF, A., 45-61, pub. Plenum Press.

BATES, R.G. & MACASKILL, J.B. 1975. Acid-Base measurements in sea water. Adv. Chem. Ser., 147, 110-123.

BENDER, M., GRANDE, K., JOHNSON, K., MARRA, J., WILLIAMS, P.J.LEB., SIEBURTH, J., PILSON, M., LANGDON, C., HITCHCOCK, G., ORCHARDO, J., HUNT, C., DONAGHAY, P. & HEINEMANN, K. 1987. A comparison of four methods for determining planktonic community production. Limnol. Ocean., 32, 1085-1099.

BENSON, B.B. & PARKER, P.D.M. 1961. Nitrogen/Argon and nitrogen isotope ratios in aerobic sea water. Deep Sea Res., 7, 237-253.

BEN-YAAKOV, S. 1972. On the CO_2-O_2 system in the Northeastern Pacific. Mar. Chem., 1, 3-26.

BERMAN, T. & EPPLEY, R.W. 1974. The measurement of phytoplankton parameters in nature. Sci. Prog., 61, 219-239.

BERRY, J., BOYNTON, J., KAPLAN, A. & BADGER, M. 1976. Growth and photosynthesis of Chlamydomonas reinhardtii as a function of CO_2 concentration. Carnegie Inst. Wash. Year Book, 75, 423-432.

BEYERS, R.J. 1963. The metabolism of twelve aquatic laboratory microecosystems. Ecol. Monogr., 33, 282-306.

BIDWELL, R.G.S. 1977. Photosynthesis, light and dark respiration in freshwater algae. Can. J. Bot., 55, 809-818.

BOLIN, B. 1977. Changes of land biota and their importance for the carbon cycle. Science, 196, 613-615.

BOWERS, P.M., KELLY, C.A., FEE, E.J., SHEARER, J.A., DECLERQ, D.R. & SCHINDLER, D.W. 1987. Simultaneous measurement of primary production by whole lake and bottle radiocarbon additions. Limnol. Ocean., 32, 299-312.

BOYCE, F.M. 1974. Mixing within experimental enclosures; a cautionary note on the limnocorral. J. Fish. Res. Bd., 31, 1400-1405.

BRADSHAW, A.L., BREWER, P.G., SCHEFER, D.K. & WILLIAMS, R.T. 1981. Measurements of TCO_2 and alkalinity by potentiometric titration in the GEOSECS programme. Earth Plant. Sci. Lett., 55, 99-115.

BRADSHAW, A.L. & BREWER, P.G. 1988. High precision measurements of alkalinity and TCO_2 in SW by potentiometric titration - 1. Presence of unknown protolyte(s) ? Mar. Chem., 23, 69-86.

BRADSHAW, A.L. & BREWER, P.G. 1988. High precision measurements of alkalinity and TCO_2 in SW by potentiometric titration - 2. Measurements on standard solutions. Mar. Chem., 24, 155-162.

BREWER, P.G., BRADSHAW, A.L. & WILLIAMS, R.T. 1984. Measurements of total carbon dioxide and alkalinity in the North Atlantic ocean in 1981. In: The Changing Carbon Cycle A Global Analysis, ed. TRABALKA, J.R. & REICHLE, D.E., pub. Springer Verlag, 348-370.

BROECKER, W.S. & TAKAHSHI, T. 1966. Calcium carbonate precipitation on the Bahamas Banks. J. Geophys. Res., 71, 1575.

BROECKER, W.S., LI, Y. & PENG, T-H. 1971. Carbon dioxide - Mans unseen artifact. In: Impingement of Man on the Oceans, ed. HOOD, D.W., pub. Wiley and Sons NY., 287-324.

BROECKER, W.S, TAKAHASHI, T., SIMPSON, H.J. & PENG, T-H. 1979. Fate of fossil fuel CO_2 and global carbon budget. Science, 206, 409-418.

BROECKER, W.S., PENG, T-H. & ENGH, R. 1980. Modelling the carbon system. Radiocarbon, 22, 565-598.

BROECKER, W.S. & PENG, T-H. 1982. Tracers in the Sea. pub., Eldigio Press.

BROWN, A.H. & WEISS, D. 1959. Relation between respiration and photosynthesis in the green algae, Ankistrodesmus braunii. Pl. Physiol. Lan., 34, 177-364.

BROWN, A.H. & WHITTINGHAM, C.P. 1955. Identification of the CO_2 burst in Chlorella using the recording mass spectrophotometer. Pl. Physiol. Lan., 30, 231-237.

BRUNEAU, L., JERLOV, N.G. & KOCZY, F.F. 1953. Rep. Deep Sea Exp. 1947-1948, 3, 99.

BRYAN, J.R., RILEY, J.P. & WILLIAMS, P.J.LeB. 1976. A Winkler procedure for making precise measurements of oxygen concentration for productivity and related studies. J. Exp. Mar. Biol. Ecol., 21, 191-197.

BURRIS, J.E. 1977. Photosynthesis, photorespiration and dark respiration in eight species of algae. Mar. Biol., 39, 371-379.

BURRIS, J.E. 1980. Respiration and photorespiration in marine algae. In: Primary Productivity in the Sea, ed. FALKOWSKI, P., pub. Plenum Press NY., 411-431.

BURRIS, J.E. 1981. Effects of O_2 and inorganic carbon concentrations on the photosynthetic quotients of marine algae. Mar. Biol., 65, 215-219.

CAPERON, J. & MEYER, J. 1972. Nitrogen-limited growth of marine phytoplankton I. Changes in population characteristics with steady-state growth rate. Deep Sea Res., 19, 601-618.

CARPENTER, J.H. 1965. The accuracy of the Winkler method for dissolved oxygen analysis. Limnol. Ocean., 10, 135-140.

CARPENTER, J.H. 1966. New measurements of oxygen stability in pure and natural water. Limnol. Ocean., 11, 264-277.

CARPENTER, E.J. & LIVELY, J.S. 1980. Review of estimates of algal growth using 14C tracer techniques. In: Primary Productivity in the Sea, ed. FALKOWSKI, P.G., pub. Plenum Press NY., 161-178.

CARRITT, D.E. & KANWISHER, J.W. 1959. An electrode system for measuring dissolved oxygen. Anal. Chem., 31, 5-9.

CARRITT, D.E. & CARPENTER, J.H. 1966. Comparison and evaluation of currently employed modifications of the Winkler method for determining dissolved oxygen in sea water: A NASCO Report. J. Mar. Res., 24, 287-318.

CHAVEZ, F.P. & BARBER, R.T. 1987. An estimate of new production in the equatorial Pacific. Deep Sea Res., 34, 1229-1245.

CODISPOTI, L.A., FRIEDERICH, G.E., IVERSON, R.L. & HOOD, D.W. 1982. Temporal changes in the inorganic carbon system of the south-eastern Bering Sea during Spring 1980. Nature, 296, 242-245.

COPIN-MONTEGUT, C. 1985. A method for the continuous determination of the partial pressure of CO_2 in the upper ocean. Mar. Chem., 17, 13-21.

CRAIG, H. & WEISS, R.F. 1970. The 1969 Geosecs Intercalibration Station: Introduction, hydrographic features and TCO_2 - O_2 relationships. J. Geophys. Res., 75, 7641-7647.

CRAIGIE, J.S. 1974. Storage products. In: Algal Physiology and Biochemistry, ed. STEWART, W.D.P., pub. Blackwell Scientific Oxford, 206-236.

CRANE, A.J. 1985. Possible effects of rising CO_2 on climate. Plant Cell and Environment, 8, 371-379.

CULBERSON, C., PYTKOWICZ, R.M. & HAWLEY, J.E. 1970. Sea water alkalinity determination by the pH method. J. Mar. Res., 28, 15-21.

CULBERSON, C.H. 1980. Calculation of the in situ pH of sea water. Limnol. Ocean., 25, 150-152.

CULBERSON, C.H. 1981. Direct Potentiometry. In: Marine Electrochemistry, ed. WHITFIELD, M. & JAGNER, D., pub. Wiley, 187-261.

CURL, H. & DAVEY, E.W. 1967. Improved calibration and sample injection systems for non-destructive analysis of permanent gases, TCO_2 and DOC in water. Limnol. Ocean., 12, 545-548.

DAVIES, J.M. & WILLIAMS, P.J.LeB. 1984. Verification of 14C and O_2 derived primary organic production measurements using an enclosed ecosystem. J. Plank. Res., 6, 457-473.

DECKER, J.P. 1955. A rapid post-illumination deceleration of respiration in green leaves. Plant Physiol., 30, 82-84.

DENMAN, K.L. & GARGETT, A.E. 1983. Vertical mixing and advection of phytoplankton in the upper ocean. Limnol. Ocean., 28, 801-815.

DICKSON, A.G. & RILEY, J.P. 1978. The effect of analytical error on the evaluation of the components of the aquatic carbon dioxide system. Mar. Chem., 6, 77-85.

DICKSON, A.G. 1984. pH scales and proton-transfer reactions in a saline media such as seawater. Geochim. Cosmochim. Acta, 48, 2299-2308.

DICKSON, A.G. & MILLERO, F.J. 1987. A comparison of equilibrium constants for the dissociation of carbonic acid in seawater media. Deep Sea Res., 34, 1733-1745.

DILLON, T.M. & CALDWELL, D.R. 1980. The Batchelor spectrum and dissipation in the upper ocean. J. Geophys. Res., 85, 1910-1916.

DRING, M.J. & JEWSON, D.H. 1982. What does 14C uptake by phytoplankton really measure ? A theoretical modelling approach. Proc. R Soc. Lond. B, 214, 351-368.

DRYSSEN, D. 1965. Acta Chem. Scand., 19, 1265-1275.

DRYSSEN, D. & SILLEN, L.G. 1967. Alkalinity and total carbonate in seawater. A plea for p-T independent data. Tellus, 19, 113-121.

EDMOND, J.M. & GIESKES, J.M. 1970. On the calculation of the degree of saturation of seawater with respect to calcium carbonate under in situ conditions. Geochim. Cosmochim. Acta,, 34, 1261-1291.

EDMONDSON, W.T. & EDMONDSON, Y.H. 1947. Measurements of production in fertilised salt water. J. Mar. Res., 6, 228-231.

ELLETT, D.J., KRUSEMAN, P., PRANGSMA, G.J., POLLARD, R.T., VAN AKEN, H., EDWARDS, A., DOOLEY, H. & GOULD, W.J. 1983. Water masses and mesoscale circulation of the North Rockall Trough waters during JASIN 1978. Phil. Trans. R. Soc. Lond. A, 308, 231-252.

EPPLEY, R.W. & SLOAN, P.R. 1965. Carbon balance experiments wih marine phytoplankton. J. Fish Res. Bd. Can., 22, 1083-1097.

EPPLEY, R.W. & SHARP, J.H. 1975. The dark loss of carbon in 24 h incubations. Limnol. Ocean., 20, 981-987.

FAHNENSTIEL, G.L. & CARRICK, H.J. 1988. Primary production in lakes Huron and Michigan : in vitro and in situ comparisons. J. Plank. Res., 10, 1273-1283.

FINDENEGG, G.R. 1974. Planta, 116, 123-131.

FOGG, G.E. 1975. Primary productivity. In: Chemical Oceanography, vol. 2 2nd edn., ed. RILEY, J.P. & SKIRROW, G., pub. Academic Press London.

FOGG, G.E. 1977. Excretion of organic matter by phytoplankton. Limnol. Ocean., 22, 576-577.

GAARNDER, T. & GRAN, H.H. 1927. Investigation of the production of plankton in the Oslo fjord. Rapp. et Proc-verb. Const. Internat. Explor. Mer, 42, 1-48.

GALLEGOS, C.L., ROBBINS CHURCH, M., KELLY, M.G. & HORNBERGER, G.M. 1983. Asynchrony between rates of oxygen production and inorganic carbon uptake in a mixed culture of phytoplankton. Arch. Hydrobiol., 96, 164-175.

GESSNER, F. & PANNIER, F. 1958. Influence of oxygen tension on respiration of phytoplankton. Limnol, Ocean., 3, 478-450.

GIESKES, W.W.C., KRAAY, G.W. & BAARS, M. 1979. Current 14C methods for measuring primary productivity - Gross underestimates in oceanic waters. Neth. J. Sea Res., 13, 58-78.

GIESKES, W.W.C. & KRAAY, G.W. 1982. Effect of enclosure in large plastic bags on diurnal change in oxygen concentration in tropical water. Mar. Biol., 70, 99-104.

GIESKES, W.W.C. & KRAAY, G.W. 1984. Phytoplankton, its pigments and primary production at a central North Sea station in May, July and September 1981. Neth. J. Sea Res., 18, 51-70.

GLIDEWELL, S.M. & RAVEN, J.A. 1975. Measurement of simultaneous oxygen evolution and uptake in Hydrodictyon africanum. J. Exp. Bot., 26, 479-488.

GOLDSWORTHY, A. 1970. Photorespiration. Bot. Rev., 36, 321-340.

GRAN, G. 1952. Determination of the equivalence point in potentiometric titrations. Part II. Analyst, 77, 661-670.

GRANDE, K. (in press). Primary production in the North Pacific gyre : A comparison of three techniques. Limnol. Ocean.

GRANELI, A. & ANFALT, T. 1977. A simple automatic phototitrator for the determination of total carbonate and total alkalinity of seawater. Anal. Chim. Acta, 91, 175-180.

GRASSHOFF, K. 1962. Untersuchungen uber die Sauerstoff bestimmung im Meerwasser. Kieler Meeres., 18, 42-50.

GRASSHOFF, K. 1963. Untersuchungen uber die sauerstoffbestimmung im meerwasser. Kieler Meeres., 19, 8-15.

GRASSHOFF, K. 1981. Standard methods. In: Marine Electrochemistry, ed. WHITFIELD, M. & JAGNER, D., pub. Wiley.

GRASSHOFF, K. 1983. Methods of seawater analysis. ed. GRASSHOFF, K. & EHRHARDT, M. & KREMLING, K., 2nd edn., pub. Verlag Chemie FRG.

GREEN, E.J. & CARRITT, D.E. 1966. An improved iodine determination flask for whole bottle titration. Analyst, 91, 207-208.

GRIBBIN, J. 1988. The greenhouse effect. New Scientist, 22, 1-4.

HANNSON, I. 1973. A new set of pH scales and standard buffers for seawater. Deep Sea Res., 20, 479-491.

HANNSON, I. & JAGNER, D. 1973. Evaluation of the accuracy of Gran plots by means of computer calculations. Application to the potentiometric titration of the total alkalinity and carbonate content of seawater. Anal. Chim. Acta, 65, 363-372.

HARRIS, G.P. & PICCININ, B.B. 1977. Photosynthesis by net phytoplankton populations. Archiv. fur Hydrobiol., 80, 405-457.

HARRIS, G.P. 1978. Photosynthesis, productivity and growth: the physiological ecology of phytoplankton. Arch. Hydrobiol. Beih. Ergrb. Limnol., 10, 1-171.

HARRIS, G.P. 1984. Phytoplankton productivity and growth measuements: past, present and future. J. Plank. Res., 6, 219-237.

HARRIS, G.P. 1986. Phytoplankton Ecology Structure Function and Fluctuation. pub. Chapman and Hall.

HARTWIG, E.O. & MICHAEL, J.A. 1978. A sensitive photoelectric Winkler titrator for respiration measurements. Environ. Sci. Tech., 12, 712-715.

HATTORI, A. 1962. Light induced reduction of nitrate, nitrite and hydroxylamine in a blue-green alga Anabaena cylindrica. Plant Cell Physiol., 3, 355-369.

HERCZEG, A.L., BROECKER, W.S., ANDERSEN, R.F. & SCHIFF, S.L. 1985. A new method for monitoring temporal trends in the acidity of freshwater. Nature, 315, 133-135.

HESSLEIN, R. & QUAY, P. 1973. Vertical eddy diffusion studies in the thermocline of a small stratified lake. J. Fish Res. Bd. Can, 30, 1491-1500.

HOBSON, L.A., MORRIS, W.J. & PIRQUET, K.T. 1976. Theoretical and experimental analysis of the 14C technique and its use in studies of primary production. J. Fish Res. Bd. Can, 33, 1715-1721.

HOLLIGAN, P.M., WILLIAMS, P.J.LEB., PURDIE, D. & HARRIS, R.P. 1984. Photosynthesis, respiration and nitrogen supply of plankton populations in stratified, frontal and tidally mixed shelf waters. Mar. Ecol. Prog. Ser., 17, 201-203.

HORRIGAN, S.G., CARLUCCI, A.F. & WILLIAMS, P.M. 1981. Light inhibition of nitrification in sea surface films. J. Mar. Res., 39, 557-565.

HOUGHTON, R.A., HOBBIE, J.E., MELILLO, J.M., MOORE, B., PETERSON, B.J., SHAVER, G.R. & WOODWELL, G.M. 1983. Changes in the carbon content of terrestrial biota and the soil between 1860 and 1980. Ecol. Monogr., 53, 235-262.

HUMPHREY, G.F. 1975. The photosynthesis : respiration ratio of some unicellular marine algae. J. Exp. Mar. Biol. Ecol., 18, 111-119.

JACKSON, W.A. & VOLK, R.J. 1970. Photorespiration. Ann. Rev. Plant Physiol., 21, 385-432.

JASSBY, A. & POWELL, T. 1975. Vertical patterns of eddy diffusivity during stratification in Castle Lake, California. Limnol. Ocean., 20, 530-543.

JENKINS, W.J. 1982. O_2 utilisation rates in N.Atlantic subtropical gyre and primary productivity in oligotrophic systems. Nature, 300, 246-248.

JENKINS, W.J. & GOLDMAN, J.C. 1984. Seasonal oxygen cycling and primary productivity in the Sargasso Sea. J. Mar. Res., 43, 465-491.

JOHNSON, K.M., BURNEY, C.M. & SIEBURTH, J.McN. 1981. Enigmatic marine ecosystems metabolism measured by direct diel TCO_2 and O_2 flux in conjunction with DOC release and uptake. Mar. Biol., 65, 49-60.

JOHNSON, K.M., BURNEY, C.M. & SIEBURTH, J.McN. 1983.a Precise and accurate determination by infra-red photometry of CO_2 dynamics in marine ecosystems. Mar. Ecol. Prog. Ser., 10, 251-256.

JOHNSON, K.M., DAVIS, P.G. & SIEBURTH, J.McN. 1983.b Diel variation of TCO_2 in the upper layer of oceanic waters reflects microbial composition, variation and possibly methane cycling. Mar. Biol., 77, 1-10.

JOHNSON, K.M. & KING, A.E.. & SIEBURTH, J.McN. 1985. Coulometric TCO_2 analyses for marine studies (An Introduction). Mar. Chem., 16, 61-82.

JOHNSON, K.M., SIEBURTH, J., WILLIAMS, P.J.LEB. & BRANDSTROM, L. 1987. Coulometric TCO_2 analysis for marine studies : automation and calibration. Mar. Chem., 21, 117-133.

JOIRIS, C. 1977. On the role of heterotrophic bacteria in marine ecosystems. Helgo. wiss. Meeres., 30, 611-621.

KANWISHER, J. 1960. pCO_2 in seawater and its effect on the movement of CO_2 in nature. Tellus, 12, 209-215.

KEELING, C.D., RAKESTRAW, N.W. & WATERMAN, L.S. 1965. CO_2 in the surface waters of the Pacific Ocean. I Measurements of the distribution. J. Geophys. Res., 70, 6087-6097.

KEELING, C.D. & WATERMAN, L.S. 1968. Carbon dioxide in surface ocean waters. III Measurements on Lusiad expedition 1962-1963. J. Geophys. Res., 73, 4529-4541.

KESSLER, E. 1959. Reduction of nitrate by green algae. In: Symp. Soc. Exp. Biol, 13, 87-105.

KHOO, K.H., RAMETTE, R.W., CULBERSON, C.H. & BATES, R.G. 1977. Determination of hydrogen ion concentrations in seawater from 5-40 ^{o}C : Standard potentials at salinities from 20-45 . Anal. Chem., 49, 29-34.

KIRK, J.T.O. 1983. Light and photosynthesis in aquatic ecosystems. pub. Cambridge University Press.

KROGH, A. 1910. Some experiments on the invasion of oxygen and carbonic oxide into the water. Skand. Arch. Physiol., 23, 224-227.

LAANE, R.W., GIESKES, W., KRAAY, G. & EVERSDIJK, A. 1985. Oxygen consumption from natural waters by photo-oxidising processes. Neth. J. Sea Res., 19, 125-128.

LANCELOT, C. & MATHOT, S. 1985. Biochemical fractionation of primary production by phytoplankton in Belgian coastal waters during short and long-term incubations with 14C. I Mixed diatom populations. Mar. Biol., 86, 219-226.

LAWS, E.A. & CAPERON, J. 1976. Carbon and nitrogen metabolism by Monochrysis lutherii : Measurement of growth rate dependent respiration rates. Mar. Biol., 36, 85-97.

LAWS, E.A., REALJE, D.G., HAAS, L.W., BIENFANG, P.K., EPPELEY, R.W., HARRISON, W.G., KARL, D.M. & MARRA, J. 1984. High phytoplankton growth and production rates in oligotrophic Hawaiian coastal waters. Limnol. Ocean., 29, 1161-1169.

LAWS, E.A., DITULLIO, G.R. & REDALJE, D.G. 1987. High phytoplankton growth and production rates in the North Pacific subtropical gyre. Limnol. Ocean., 32, 905-919.

LEFTLEY, J.W., BONIN, D.J. & MAESTRINI, S.Y. 1983. Problems in estimating marine phytoplankton growth, production and metabolic activity in nature : An overview of methodology. Oceanogr. Mar. Biol. Ann. Rev., 21, 23-66.

LEWIS, G.N. & RANDALL, M. 1961. Thermodynamics. pub. McGraw-Hill NY.

LI, Y-H., TAKAHASHI, T. & BROECKER, W.S. 1969. Degree of saturation of $CaCO_3$ in the oceans. J. Geophys. Res., 74, 5507-5517.

LLOYD, N.D.H., CANVIN, D.T. & CULVER, D.A. 1977. Photosynthesis and photorespiration in algae. Pl. Physiol., 59, 936-940.

LOVELOCK, J.E. 1979. Gaia a new look at life on Earth., pub. Oxford Uni. Press.

MATHIS, P. & PAILLOTIN, G. 1981. Primary processes of photosynthesis. In: The Biochemistry of Plants vol.8, eds. HATCH, M.D. & BOARDMAN, N.K., pub. Academic Press NY., 97-161.

McALLISTER, C.D., SHAH, N & STRICKLAND, J.D.H. 1964. Marine phytoplankton photosynthesis as a function of light intensity : A comparison of methods. J. Fish Res. Bd. Can., 21, 159-181.

McCORMICK, M.J., CLITES, A.H. & CAMPBELL, J.E. 1985. Water-tracking ability of satellite tracked drifters in light winds. Mar. Tech. Soc., 19, 12-17.

McEWEN, G.F. 1929. Bull. Scripps Inst. Oceanogr. Univ. Calif. (Tech. Ser), 2, 306-317.

MEGARD, R.O., TONKYN, D.W. & SENFT, W.H. 1984. Kinetics of oxygenic photosynthesis in planktonic algae. J. Plankton Res., 6, 325-337.

MEGARD, R.O., BERMAN, T., CURTIS, P.J. & VAUGHAN, P.W. 1985. Dependence of phytoplankton assimilation quotients on light and nitrogen source : implications for oceanic primary productivity. J. Plankton Res., 7, 691-702.

MEHRBACH, C., CULBERSON, C.H., HAWLEY, J.E. & PYTKOWICZ, R.M. 1973. Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. Limnol. Ocean., 18, 897-907.

MILLERO, F.J. 1986. The pH of estuarine waters. Limnol. Ocean., 31, 839-847.

MOORE, A. 1981. A simple model for analysis of the role of terrestrial ecosystems in the global budget . In: SCOPE 16, Carbon Cycle Modelling, ed. BOLIN, B., pub. Wiley NY., 365-385.

MORRIS, I., YENTSCH, C.M. & YENTSCH, C.S. 1971. Relationship between light CO_2 fixation and dark CO_2 fixation by marine algae. Limnol. Ocean., 16, 854-858.

MORRIS, I. 1980. Physiological Ecology of Phytoplankton, pub. Blackwell.

MYERS, J. & CRAMER, M. 1948. Metabolic conditions in Chlorella. J. Gen. Physiol., 32, 103-109.

NATIONAL ACADEMY OF SCIENCES. 1983. Changing climate. Report of the CO_2 assessment committee. pub. Nat. Acad. Press., 186-215.

OAKEY, N.S & ELLIOTT, J.A. 1982. Dissipation within the surface mixed layer. J. Phys. Oceanogr., 12, 171-185.

OESCHGER, H., SIEGENTHALER, U., SCHOTTERER, U. & GUGELMANN, A. 1975. A box diffusion model to study the carbon dioxide exchange in nature. Tellus, 27, 168-192.

OVIATT, C.A., RUDNICK, D.T., KELLER, A., SAMPOU, P. & ALMQUIST, G. 1986. A comparison of system (O_2 and CO_2) and 14C measurements of metabolism in estuarine mesocosms. Mar. Ecol. Prog. Ser., 28, 57-67.

PARK, K., HOOD, D.W. & ODUM, H.T. 1958. Diurnal pH variation in Texas bays and its application to primary production estimation. pub. Inst. mar. Sci. Univ. Texas, 5, 4-64.

PARKES, G. 1988. Dissolved oxygen and production in the N.E. Atlantic during June 1987. MSc. Thesis, Southampton University.

PARSONS, T.R., MAITA, Y. & LALLI, C.M. 1984. A manual of chemical and biological methods for seawater analysis. pub. Pergamon Press.

PAUL, J.S., SULLIVAN, C.W. & VOLCANI, B.E. 1975. Photorespiration in diatoms. Arch. Biochem. Biophys., 169, 152-159.

PAUL, J.S. & VOLCANI, B.E. 1976. Glycolate metabolism in a diatom. Arch. Microbiol., 110, 247-252.

PETERSON, B.J. 1978. Radiocarbon uptake : its relation to net particulate carbon production. Limnol. Ocean., 23, 179-184.

PETERSON, B.J. 1980. Aquatic primary productivity and the 14C method, a history of the productivity problem. Ann. Rev. Ecol. Syst., 11, 359-385.

PLATT, T. 1984. Primary productivity in the central N.Pacific, comparison of O_2 and CO_2 (carbon) fluxes. Deep Sea Res., 31, 1311-1319.

PLATT, T., LEWIS, M. & GENDER, R. 1984. Thermodynamics of energy and materials in marine ecosystems. In: Flows of energy and materials in marine ecosystems. pub. Plenum Press, 49-84.

PLATT, T. & HARRISON, W.G. 1985. Biogenic fluxes of carbon and oxygen in the ocean. Nature, 318, 55-58.

PLATT, T. & HARRISON, W.G. 1986. Reconciliation of carbon and oxygen fluxes in the upper ocean. Deep Sea Res., 33, 273-276.

POSTMA, H. & ROMMETS, J.W. 1979. Dissolved and particulate organic carbon in the North Equatorial current of the Atlantic Ocean. Neth. J. Sea Res., 13, 85-98.

PYTKOWICZ, R.M. & HAWLEY, J.E. 1974. Bicarbonate and carbonate ion-pairs and a model of seawater at 25 ^{o}C. Limnol. Ocean., 19, 223-234.

RAINE, R.C.T. 1985. The effect of nitrogen supply on the PQ of natural phytoplankton assemblages. Bot. Mar., 26, 417-423.

RAVEN, J.A. 1968. The mechanism of photosynthetic use of bicarbonate by Hydrodictyon africanum. J. Exp. Bot, 19, 193-206.

RAVEN, J.A. 1970. Exogenous inorganic carbon sources in photosynthesis. Biol. Rev., 45, 167-221.

RAVEN, J.A. 1972. Endogenous inorganic carbon sources in plant photosynthesis. I Occurence of dark respiratory pathways in illuminated green cells. New Phytol., 71, 227-248.

RAVEN, J.A. 1972. Endogenous inorganic carbon sources in plant photosynthesis. II Comparison of total CO_2 production with measured CO_2 evolution in the light. New Phytol., 71, 995-1014.

RAVEN, J.A. 1974. Carbon dioxide fixation. In: Algal Physiology and Biochemistry, ed. STEWART, W.D.P., pub. Univ. California Press, 434-455.

RAVEN, J.A. & GLIDEWELL, S.M. 1975. Photosynthesis, respiration and growth in the shade alga, Hydrodictyon africanum. Photosynthetica, 9, 361-371.

RAVEN, J.A. & BEARDALL, J. 1981. Respiration and photorespiration. Can. Bull. Fish Aq. Sci., 210, 55-82.

RICHARDSON, K. 1983. Adaption of unicellular algae to irradiance: an analysis of strategy. New Phyto., 93, 157-191.

RILEY, G.A. 1944. The carbon metabolism and photosynthetic efficiency of the Earth as a whole. Amer. Sci., 32, 129-131.

RYTHER, J.H. & VACCARO, R.F. 1954. A comparison of the oxygen and 14C methods of measuring marine photosynthesis. J. du Cons., 20, 25-34.

RYTHER, J.H. 1954. The ratio of photosynthesis to respiration in marine planktonic algae and its effect upon the measurement of productivity. Deep Sea Res., 2, 134-139.

RYTHER, J.H. 1956. The measurement of primary production. Limnol. Ocean., 1, 72-84.

SAKAMOTO, M., TILZER, M., GACHTER, R., HAKUMAT, R., CARLOS, Y., TSCHUMI, P., BERNER, P., ZBAREN, D., ZBAREN, J., DOKULIL, M., BOSSARD, P., UEHLINGER, U. & NUSCH, E. 1984. Joint field experiments for comparisons of measuring methods of photosynthetic production. J. Plank. Res., 6, 365-383.

SARGENT, M.C. & HINDMAN, J.C. 1943. The ratio of CO_2 consumption to O_2 evolution in seawater in the light. J. Mar. Res., 5, 131-141.

SCAVIA, D. & FAHNENSTIEL, G.L. 1987. Dynamics of Lake Michigan phytoplankton : mechanisms controlling epilimnetic communities. J. Great Lakes Res., 13, 103-120.

SCHOLANDER, P.F., VAN DAM, L., LLOYD CLAFF, C., KANWISHER, J.W. 1955. Microgasometric determination of dissolved O_2 and nitrogen. Biol. Bull. Woods Hole, 109, 328-334.

SHARP, J.H. 1977. Excretion of organic matter by phytoplankton : do healthy cells do it ? Limnol. Ocean., 22, 381-399.

SHULENBERGER, E. & REID, J.L. 1981. The Pacific shallow oxygen maximum, deep chlorophyll maximum and primary productivity, reconsidered. Deep Sea Res., 28, 901-919.

SIEBURTH, J.McN. 1977. International Helgoland Symposium : Convenors report on the informal session on biomass and productivity of micro-organisms in planktonic ecosystems. Helgo. wiss. Meeres., 30, 697-704.

SIEGENTHALER, H. 1983. Uptake of excess CO_2 by an outcrop-diffusion model of the ocean. J. Geophys. Res., 88, 3599-3608.

SILLEN, L.G. 1967. Master variables and activity scales. In: Equilibrium concepts in natural water systems., ed. GOULD, R.F., pub. American Chemical Society, 45-56.

SIMPSON, J.J & ZIRINO, A. 1980. Biological control of pH in the Peruvian coastal upwelling area. Deep Sea Res., 27, 733-744.

SMITH, S.V. & MARSH, J.A. 1973. Organic carbon production on the windward reef flat of Eniwetok Atoll. Limnol. Ocean., 18, 953-961.

SMITH, S.V. 1985. Physical, chemical and biological characteristics of CO_2 gas flux across the air-water interface. Plant Cell and Environ., 8, 387-398.

SMITH, W.O. 1977. The respiration of photosynthetic carbon in eutrophic areas of the ocean. J. Mar. Res., 35, 557-565.

SOROKIN, Y.L. 1971. Bacterial components of oceanic ecosystems. Mar. Biol., 11, 101-105.

SOURNIA, A. 1971. Mesure de la production primaire des oceans par la methods au 14C. In: L'energie nucleaire et ses applications biologiques a Madagascar Tananarive 6 et 7 Mai 1971., 12, 251-267.

STEELE, J.H., FARMER, D.M. & HENDERSON, E.W. 1977. Circulation and temperature structure in large marine enclosures. J. Fish Res. Bd. Can., 34, 1095-1104.

STEEMANN NIELSEN, E. 1952. The use of radioactive carbon (14C) for measuring organic production in the sea. J. Con. Int. Explor. Mer., 18, 117-140.

STEEMANN NIELSEN, E. & JENSEN, E.A. 1957. Primary oceanic production - the autotrophic production of organic matter in the oceans. Galathea Rep., 1, 49-135.

STEEMANN NIELSEN, E. & HANSEN, V.K. 1959. Measurement with the 14C technique of the rates of respiration in natural populations of phytoplankton. Deep Sea Res., 5, 222-233.

STEEMANN NIELSEN, E. 1975. Marine Photosynthesis., pub. Elsevier Press.

STRICKLAND, J.D.H. 1960. Measuring the production of marine phytoplankton. Fish. Res. Bd. Can. Bull., 122.

STRICKLAND, J.D.H. & PARSONS, T.R. 1972. A manual of seawater analysis. Fish. Res. Bd. Can. Bull., 167.

STUMM, W. & MORGAN, J.J. 1981. Aquatic Chemistry: An introduction emphasising chemical equilibria in natural waters., 2nd edn., pub. Wiley & Sons.

SUGIMURA, Y. & SUZUKI, Y. 1988. A high temperature catalytic oxidation method for the determination of non-volatile DOC in seawater by direct injection of a liquid sample. Mar. Chem., 24, 105-131.

SWINNERTON, J.W., LINNENBOM, V.J. & CHECK, C.H. 1962. Determination of dissolved gases in aqueous solutions by gas chromatography. Anal. Chem., 34, 483-485.

SWINNERTON, J.W., LINNENBOM, V.J. & CHECK, C.H. 1964. Determination of Argon and Oxygen by gas chromatography. Anal. Chem., 36, 1669-1671.

SYRETT, P.J. 1956. The assimilation of ammonia and nitrate by nitrogen starved cells of Chlorella vulgaris. III Differences of metabolism dependent on the nature of the nitrogen source. Ibid, 9, 28-36.

TAKAHASHI, T. 1961. Carbon dioxide in the atmosphere and in Atlantic ocean water. J. Geophys. Res., 66, 477-490.

TAKAHASHI, T., WEISS, R.F., CULBERSON, C.H., EDMOND, J.M., HAMMOND, D.E., WONG, C.S., YUAN HUI, L. & BAINBRIDGE, A. 1970. A carbonate chemistry profile at the 1969 Geosecs Intercalibration Station in the eastern Pacific ocean. J. Geophys. Res., 75, 7648-7666.

TAKAHASHI, T. 1980. Carbonate chemistry of the surface waters of the worlds oceans. In: Isotope Marine Chemistry. eds. GOLDBERG, E.D. & HORIBE, Y. & SARUHASHI, K., pub. Uchida Rokakuko Tokyo, 291-326.

TAKAHASHI, T., OLAFSSON, J., BROECKER, W.S., GODDARD, J., CHIPMAN, D.W. & WHITE, J. 1985. Seasonal variability of the carbon nutrient chemistry in the oceans areas west and north of Iceland. Rit. Fisk., 9, 20-36.

TALLING, J.F. 1973. The application of some electrochemical methods to the measurement of photosynthesis and respiration in fresh waters. Freshwat. Biol., 3, 335-362.

TALLING, J.F. 1984. Past and contemporary trends and attitudes in work on primary production. J. Plank. Res., 6, 203-217.

TEAL, J.M. & KANWISHER, J. 1966. The use of pCO_2 for the calculation of biological production with examples from waters off Massachusetts. J. Mar. Res., 24, 4-14.

THOMPSON, T.G. & ANDERSON, D.H. 1940. The determination of the akalinity of seawater. J. Mar. Res., 3, 224-229.

THORPE, S.A. 1969. The effect of horizontal gradients on thermohaline convection. J. Fluid Mech., 38, 375-400.

TIJSSEN, S.B. 1979. Diurnal oxygen rhythmn and primary productivity in the mixed layer of the Atlantic ocean at 20 ^{o}N. Neth. J. Sea Res., 13, 79-84.

TIJSSEN, S.B. & EIJGENRAAM, A. 1982. Primary and community production in the Southern Bight of the North Sea deduced from oxygen concentration variations in the Spring of 1980. Neth. J. Sea Res., 16, 247-259.

TIJSSEN, S.B. & WETSTEYN, F.J. 1984. Diurnal pattern seasonal change and variability of oxygen in the water column of the oyster ground (North Sea) in Spring-Summer 1981. Neth. J. Sea Res., 18, 13-30.

TOLBERT, N.E. 1974. Photorespiration. In: Algal Physiology and Biochemistry, ed. STEWART, W.D.P., pub. Blackwell Oxford, 474-504.

UNESCO. 1987. Thermodynamics of the carbon dioxide system in seawater. Technical Papers in Marine Science, 51.

VAN NEIL, C.B., ALLEN, M.B. & WRIGHT, B.E. 1953. On the photochemical reduction of nitrate by algae. Biochem. Biophys. Acta, 12, 67-74.

VERDUIN, J. 1960. Phytoplankton communities of weatern Lake Erie and the CO_2 and O_2 changes associated with them. Limnol. Ocean., 5, 372-380.

VERDUIN, J. 1975. Photosynthetic rates in Lake Superior. Verh. Int. Verein. Limnol., 19, 134-139.

WATTENBERG. H. 1933. Uber die titrationsalkalinitat und den kalziumkarbonategehalt des meerwassers. Deutsche Atlantische Exped. Meteor, 8, 122-231.

WEICHART, G. 1980. Chemical and primary productivity in Fladen Ground during the first phase of spring phytoplankton bloom. Meteor Forsch-Ergebn A, 22, 79-86.

WEISS, R.F. 1970. The solubility of nitrogen, oxygen and argon in water and seawater. Deep Sea Res., 17, 721-735.

WEISS, R.F & CRAIG, H. 1973. Precise shipboard determination of nitrogen, oxygen, argon and TOC by gas chromatography. Deep Sea Res., 20, 291-303.

WEISS, R.F. 1982.*a* CO_2 effects: research and assessment programme, workshop on oceanic CO_2 standardisation. pub. Miami Univ.

WEISS, R.F. 1981. Determinations of CO_2 and CH_4 by dual catalyst flame ionisation chromatography and N_2O by electron capture chromatography. J. Chrom. Sci., 19, 611-616.

WEISS, R.F. 1982.*b* Seasonal effects of temperature and salinity on the partial pressure of CO_2 in seawater. Nature, 300, 511-513.

WEST, L.E. & ROBINSON, R.J. 1941. Potentiometric analysis of seawater. II Determination of titration alkalinity. J. Mar. Res., 4, 38-45.

WHITFIELD, M. 1975. Electroanalytical chemistry of seawater. In: Chemical Oceanography vol 14 2nd Edn., ed. RILEY, J.P. & SKIRROW, G., pub. Academic Press.

WHITFIELD, M., BUTLER, R.A. & COVINGTON, A.K. 1985. The determination of pH in estuarine waters. Ocean. Acta, 8, 423-432.

WHITTAKER, R.H. & LIKENS, G.E. 1973. Carbon in the biota. In: Carbon and Biosphere, ed. WOODWELL, G.M. & PECAN, E.V., pub. Tech. Inform. Cen. USA Atomic Energy Commission.

WILLIAMS, P.J.LeB. 1975. Biological and chemical aspects of dissolved organic materials in seawater. In: Chemical Oceanography vol 2 2nd Edn., eds. RILEY, J.P & SKIRROW, G., pub. Academic Press.

WILLIAMS, P.J.LeB., RAINE, R.C.T. & BRYAN, J.R. 1979. Agreement between the 14C and oxygen methods of measuring phytoplankton production: reassessment of the photosynthetic quotient. Oceanol. Acta, 2, 411-416.

WILLIAMS, P.J.LeB. & JENKINSON, N.W. 1982. A transportable micro-processor controlled precise Winkler titration suitable for field station and shipboard use. Limnol. Ocean., 27, 576-584.

WILLIAMS, P.J.LeB., HEINEMANN, K., MARRA, J. & PURDIE, D.A. 1983. Comparison of 14C and O_2 measurements of phytoplankton production in oligotrophic waters. Nature, 305, 49-50.

WILLIAMS, P.J.LeB. 1984. A review of measurements of respiration rates of marine phytoplankton populations. In: Heterotrophic activity in the Sea, eds. HOBBIE, J.E. & WILLIAMS, P.J.LeB., pub. Plenum Press, 357-391.

WILLIAMS, P.J.LeB. & ROBERTSON, J.E. 1988. A serious inhibition problem from a Niskin sampler encountered during plankton productivity studies. Limnol. Ocean., (in press).

WOOD, K.G. & VERDUIN, J. 1972. Correlation between TCO_2 and O_2 concentrations in Lake Erie, USA. Arch. Hydrobiol., 71, 1-16.

YENTSCH, C.S. 1974. Some aspects of the enviromental physiology of marine phytoplankton : a second look. Oceanogr. Mar. Biol., 12, 41-75.

ZELITCH, I. 1971. Photosynthesis, photorespiration and plant productivity, pub. Academic Press NY.

APPENDIX No 1

Worked example for the calculation of eddy diffusivity coefficients

The following is a worked example for calculating the value of the eddy diffusivity coefficient at a particular depth and point in time.

Temperature (^{o}C) made from 2/7 0910 h to 2/7 1520 h

Depth	0910 h	1210 h	1520 h
2 m	-	17.59	17.82
3 m	17.17	17.33	17.52
4 m	-	17.26	17.37

Calculation of Kz

Using the following equation (McEwen 1929, Hutchinson 1941)

$$\frac{d\theta}{dT} = \text{radiant energy term} + \frac{d}{dZ} \cdot \left(Kz \cdot \frac{d\theta}{dZ} \right) + Kh \cdot d\theta_h$$

where θ represents temperature change hence $d\theta/dT$ is the observed rate of change of temperature with time

Z represents depth, Kz is the eddy diffusion coefficient that is to be calculated for the vertical axis (z). Kh represents the coefficient for advection in the horizontal plane, θh is the change of temperature in the horizontal axis.

Ignoring the radiant energy input and horizontal advection as being neglible

$$\frac{d\theta}{dT} = \frac{d}{dZ} \cdot \left(Kz \cdot \frac{d\theta}{dZ} \right)$$

Substituting the temperature data given above
The L.H.S. of the equation

$$\frac{d\theta}{dT} = \frac{0.35}{6 \times 3600} = 1.6204 \times 10^{-5} \ ^{o}C \ sec^{-1} \qquad \text{--------(1)}$$

The R.H.S. of the equation

$$\frac{d}{dZ} \cdot \left(Kz \cdot \frac{d\theta}{dZ} \right) = Kz \ \frac{\frac{(17.26 - 17.33)}{100} - \frac{(17.33 - 17.59)}{100}}{100}$$

$$= \frac{Kz \ (0.19)^{o}C}{10000 \ cm^2} \qquad \text{--------(2)}$$

As equation (1) equals equation (2)
then

$$1.6204 \times 10^{-5} = \frac{Kz \ (0.19)}{10000}$$

$Kz = 0.853 \ cm^2/sec$ ($0.31 \ m^2/h$)
at 3 m depth at 1210 h 2/7/86.

APPENDIX No 2

Correction of observed gas fluxes using a given value for Kz

The following is a worked example for correcting the observed flux in gas concentrations at 3 metres depth within the mesocosm. Both O_2 and TCO_2 observed flux for a twelve hour time period will be corrected to provide both an observed and corrected molar ratio for comparison.

The value of Kz used is 0.2 m^2/h

Observed concentrations measured from 9/7/86 0525 h to 9/7/86 1725 h

Depth(m)	TCO_2 (µmol/kg) 0525h	TCO_2 (µmol/kg) 1725h
2m	1273.4 +/- 0.1	1258.7 +/- 1.1
3m	1272.1 +/- 0.5	1255.4 +/- 0.6
4m	1275.0 +/- 0.6	1261.7 +/- 0.5

Depth (m)	O_2 (µmol/kg) 0525h	O_2 (µmol/kg) 1725h
2m	No data	355.6 +/- 0.2
3m	335.4 +/- 0.3	358.4 +/- 0.2
4m	335.0 +/- 0.2	355.8 +/- 0.1

First, diffusion corrections will be made to TCO_2 observed concentrations

A)Corrections to TCO_2 flux measurements

Total change observed in TCO_2 concentration during the sampling period

= - 16.69 +/- 0.781 µmol/kg for a 12 h period
= - 1.39 +/- 0.065 µmol/kg h^{-1}

An estimate of direction and magnitude of flux at any one point in time is a result of the relative gradients operating in and out of the depth being sampled. This flux is given by the following relationship (Hesslein and Quay 1973)

$$\text{Flux} = + Kz \left(d\, TCO_2 / d\, z \right)_{\text{lower}} - Kz \left(d\, TCO_2 / d\, z \right)_{\text{upper}}$$

Where Kz is the eddy diffusion coefficient in the z axis, z is the depth in metres, lower and upper refer to concentrations recorded above and below the depth that is to be corrected. In this instance the depth that is to be corrected is 3 m.

By convention , an increasing concentration with depth is given a positive sign in the calculation.

Calculation

	0525h	1725h
Lower flux	0.2 x 2.89 +/- 0.781	0.2 x 6.28 +/- 0.224
	= 0.578 +/- 0.1562	= 1.256 +/- 0.1562
Upper flux	-0.2 x -1.31 +/- 0.519	-0.2 x -3.25 +/- 1.253
	= 0.262 +/- 0.1038	= 0.650 +/- 0.2506

Mean Lower flux = 0.917 +/- 0.1105
Mean Upper flux = 0.456 +/- 0.1356
Observed flux = - 1.391 +/- 0.0650

Actual flux after correction for physical effects

= - 2.764 +/- 0.187 μmol/kg h^{-1}

B)Corrections to O_2 flux measurements

Total change observed in O_2 concentrations during the sampling period

= 23.09 +/- 0.361 μmol/kg for a 12 h period
= 1.924 +/- 0.003 μmol/kg h^{-1}

Calculation

	0525h	1725h
Lower flux	0.2 x - 0.31 +/- 0.361	0.2 x - 2.68 +/- 0.224
	= - 0.062 +/- 0.072	= - 0.536 +/- 0.0447
Upper flux	No data	- 0.2 x - 2.85 +/- 0.2828
		= - 0.570 +/- 0.0566

Mean Lower flux = - 0.299 +/- 0.0424
Mean Upper flux = - 0.570 +/- 0.0566
Observed flux = 1.924 +/- 0.0030

Actual flux after correction for physical effects

= 2.793 +/- 0.0708 μmol/kg h^{-1}

Using the observed and corrected fluxes for both gases it is possible to calculate a molar ratio for both approaches

Observed molar ratio	Corrected molar ratio
1.924 +/- 0.003	2.793 +/- 0.007
-1.391 +/- 0.065	-2.764 +/- 0.187
= 1.38 +/- 0.068	= 1.01 +/- 0.073

APPENDIX No 3

Calculation of standard error bars for a quotient

The ratio or quotient (Z) can be calculated by the division of two values.

$$\frac{X}{Y} = Z$$

however when the two values possess a standard error it is important to place an error bar on the ratio.

$$\frac{X \pm S.E.x}{Y \pm S.E.y} = Z \pm S.E.z$$

If X and Y are mean values taken from different normal distributions, and the standard deviation of the distributions of both X and Y is much less than the mean.The standard error of the quotient (Z) can be calculated using the following equation

$$S.E.z = \frac{1}{Y^2}\sqrt{Y^2.\ S.E.^2\ x + X^2.\ S.E.^2\ y}$$

(Baird 1962, Faires and Parks 1964, Barford 1967)

APPENDIX No 4

Calculation of gas transfer across the air-sea interface

Gas transfer can be summarised by the following :

$$F = K [P_{atm(g)} - P_{w(g)}] \quad (1)$$

$$K = D . \alpha . h^{-1} \quad (2)$$

where

$P_{atm(g)}$ = Partial pressure of the specific gas in the atmosphere. (units = atm)

$P_{w(g)}$ = Partial pressure of the specific gas in the water. (units = atm)

K = Gas exchange coefficient (units = mol m^{-2} h^{-1} atm^{-1})

F = Gas flux (units = mol m^{-2} h^{-1})

D = Molecular diffusivity (units = m^2 s^{-1})

α = Solubility (units = mol m^{-3} atm^{-1})

h = Surface film thickness (units = m)

Method 1

Following Tijssen and Eijgenraam (1982)

$K = 10^{-6} \cdot W^2$ (where both K and W have units = $m.s^{-1}$)

taking a high observed wind speed ie 45 $km.h^{-1}$ on 13/08/87 1800h

$W = 12.5\ m.s^{-1}$

therefore

$K = 1.5625\ m.s^{-1}$ or $K = 0.5625\ m.h^{-1}$

Observed oxygen concentration = 366.3 $\mu moles.kg^{-1}$
Expected oxygen concentration = 259.1 $\mu moles.kg-1$

This can be approximated to

Observed oxygen concentration = 366.3 $mmoles.m^{-3}$
Expected oxygen concentration = 259.1 $mmoles.m^{-3}$

Actual - Expected = 107.2 $mmoles.m^{-3}$

then the calculated gas flux - F

$F = 0.5625 (107.2) = 60.3\ mmoles\ m^{-2}\ h^{-1}$

Method 2

Following Smith (1985)

$h = 0.072 \times e^{-0.215\ U10}$

taking a high observed wind speed ie 45 km/h on 13/08/87 1800h

U_{10} = 45 km/h or 12.5 m/s

Therefore

$$h = 4.9 \times 10^{-3} \text{ cm or } 4.9 \times 10^{-5} \text{ m}$$

taking $D = 1.8 \times 10^{-9}$ m^2/sec (Broecker and Peng 1974)
and $\alpha = 1.3050$ moles m^{-3} atm^{-1} (Weiss 1970)
with $T = 14\ ^{o}C$

then using

$$K = D \cdot \alpha \cdot h^{-1}$$

$$K = 0.173 \text{ moles } m^{-2}\ h^{-1}\ atm^{-1}$$

If we take the pO_2 atmosphere = 0.2095 atm
and as

$$pO_2 \text{ water} = [\ O_2\ ] /$$

$$= \frac{354.9 \text{ mmoles.m}^{-3}}{1.3050 \times 10^{3} \text{ mmoles.m}^{-3}.\text{atm}^{-1}}$$

$$= 0.2734 \text{ atm}$$

then the calculated gas flux (F)

$$F = 0.173\ (\ -\ 0.062\ )$$

$$\text{Flux} = -\ 0.0107 \text{ moles } m^{-2}\ h^{-1} \quad \text{or} \quad -\ 10.7 \text{ mmoles } m^{-2}\ h^{-1}$$

APPENDIX No. 5

Two tailed T test for results taken from fixing experiments

Long term fixing experiment

Bottles	No. of replicates	Mean	S.D.	S.E.
Zero Time	12	2022.63	2.16	0.623
Unfixed	6	2251.07	2.15	0.878
Fixed	6	2017.69	4.04	1.650

Null hypothesis:
Mean zero time is equal to the mean of the fixed samples
(against an alternative hypothesis that they are not equal)

Value of the T test statistic = 2.80
Probability that incorrect = 3.1 %
Degrees of freedom = 6

Null hypothesis:
Mean zero time is equal to the mean of the unfixed samples
(against an alternative hypothesis that they are not equal)

Value of the T test statistic = -212.11
Probability that incorrect = < 0.01 %
Degrees of freedom = 10

Fixing experiment 8/2/89

Bottles	No. of replicates	Mean	S.D.	S.E.
Zero Time	9	2114.89	2.87	0.956
Unfixed	6	2152.67	1.86	0.759
Fixed Clean	6	2117.24	2.71	1.110
Fixed Unclean	6	2118.29	0.45	0.182

Null hypothesis:
Mean zero time is equal to the mean of the fixed clean samples (against an alternative hypothesis that they are not equal)

Value of the T test statistic = -1.61
Probability that incorrect = 14 %
Degrees of freedom = 11

Null hypothesis:
Mean zero time is equal to the mean of the fixed unclean samples (against an alternative hypothesis that they are not equal)

Value of the T test statistic = -3.49
Probability that incorrect = 0.08 %
Degrees of freedom = 8

Null hypothesis:
Mean zero time is equal to the mean of the unfixed samples (against an alternative hypothesis that they are not equal)

Value of the T test statistic = -30.94
Probability that incorrect = < 0.01 %
Degrees of freedom = 12

Fixing experiment 16/2/89

Bottles	No. of replicates	Mean	S.D.	S.E.
Zero Time	9	2125.51	1.08	0.361
Unfixed Clean	6	2143.51	1.55	0.633
Unfixed Dirty	6	2135.45	0.34	0.139
Fixed Clean	6	2122.40	0.86	0.351
Fixed Unclean	6	2122.26	0.59	0.239

Null hypothesis:
Mean zero time is equal to the mean of the fixed clean samples (against an alternative hypothesis that they are not equal)

Value of the T test statistic = 6.18
Probability that incorrect = < 0.01 %
Degrees of freedom = 12

Null hypothesis:
Mean zero time is equal to the mean of the unfixed clean samples (against an alternative hypothesis that they are not equal)

Value of the T test statistic = - 24.70
Probability that incorrect = < 0.01 %
Degrees of freedom = 8

Null hypothesis:
Mean zero time is equal to the mean of the unfixed dirty samples (against an alternative hypothesis that they are not equal)

Value of the T test statistic = - 25.70
Probability that incorrect = < 0.01 %
Degrees of freedom = 10

DATA APPENDIX

FOR SWEDEN

In vitro incubations

Sweden

INCUBATION 3 1800h 8/07/86 to 05250h 9/07/86

Night incubation - 3m depth

Units = µmol/kg

Mean value given +/- one standard error (Coefficient of variance)

Oxygen	Carbon Dioxide
ZERO	ZERO
R(1)= 339.17	R(1)= 1256.72
R(2)= 338.35	R(2)= 1256.26
R(3)= 337.07	R(3)= 1256.19
R(4)= 338.82	R(4)= 1257.91
Mean = 338.35 +/- 0.46 (0.14%)	Mean = 1256.77 +/- 0.40 (0.03%)
LIGHT	LIGHT
R(1)= 327.24	R(1)= 1267.08
R(2)= 327.37	R(2)= 1268.12
	R(3)= 1267.91
	R(4)= 1268.02
Mean = 327.31 +/- 0.07 (0.02%)	Mean = 1267.78 +/- 0.24 (0.02%)
DARK	DARK
R(1)= 324.60	R(1)= 1269.93
R(2)= 324.26	R(2)= 1269.39
R(3)= 324.46	
R(4)= 325.09	
Mean = 324.60 +/- 0.18 (0.05%)	Mean = 1269.66 +/- 0.27 (0.02%)

Incubation time = 12 h

Gross Production = 2.70 +/- 0.19	Gross Production = 1.88 +/- 0.36
Net Production = -11.05 +/- 0.46	Net Production = -11.01 +/- 0.46
Respiration = 13.75 +/- 0.49	Respiration = 12.89 +/- 0.48

INCUBATION 4 0525h 9/07/86 to 1723h 9/07/86

Day incubation - 3m depth

Units = µmol/kg

Mean value +/- one standard error (Coefficient of variance)

Oxygen	Carbon Dioxide
ZERO	ZERO
R(1)= 315.10	R(1)= 1276.81
R(2)= 314.95	R(2)= 1276.34
R(3)= 315.43	
R(4)= 315.49	
Mean = 315.24 +/- 0.13 (0.04%)	Mean = 1276.58 +/- 0.24 (0.02%)
LIGHT	LIGHT
R(1)= 334.00	R(1)= 1264.91
R(2)= 333.71	R(2)= 1263.79
R(3)= 333.61	
R(4)= 334.32	
Mean = 333.91 +/- 0.16 (0.05%)	Mean = 1264.35 +/- 0.56 (0.06%)
DARK	DARK
R(1)= 306.11	R(1)= 1290.54
R(2)= 306.69	R(2)= 1289.04
R(3)= 306.34	
R(4)= 306.88	
Mean = 306.51 +/- 0.17 (0.06%)	Mean = 1289.79 +/- 0.75 (0.06%)

Incubation time = 12 h

Gross Production = 27.41 +/- 0.24	Gross Production = 25.44 +/- 0.94
Net Production = 18.67 +/- 0.21	Net Production = 12.23 +/- 0.61
Respiration = 8.74 +/- 0.22	Respiration = 13.22 +/- 0.79

INCUBATION 5 1723h 9/07/86 to 05300h 10/07/86
Night incubation - 3m depth

Units = µmol/kg
Mean value given +/- one standard error (Coefficient of variance)

Oxygen	Carbon Dioxide
ZERO	ZERO
R(1)= 347.01	R(1)= 1258.03
R(2)= 347.95	R(2)= 1258.03
R(3)= 347.19	
Mean = 347.38 +/- 0.29 (0.08%)	Mean = 1258.03 +/- 0.00 (0.00%)
LIGHT	LIGHT
R(1)= 337.26	R(1)= 1267.91
R(2)= 338.26	R(2)= 1266.49
R(3)= 337.98	R(3)= 1268.92
R(4)= 337.57	R(4)= 1267.79
Mean = 337.77 +/- 0.22 (0.07%)	Mean = 1267.78 +/- 0.50 (0.04%)
DARK	DARK
R(1)= 334.63	R(1)= 1271.52
R(2)= 335.60	R(2)= 1270.04
R(3)= 334.54	R(3)= 1270.95
R(4)= 334.32	R(4)= 1270.42
Mean = 334.77 +/- 0.28 (0.09%)	Mean = 1270.73 +/- 0.32 (0.03%)

Incubation time = 12 h

Gross Production = 3.00 +/- 0.36	Gross Production = 2.96 +/- 0.59
Net Production = - 9.62 +/- 0.36	Net Production = - 9.75 +/- 0.50
Respiration = 12.61 +/- 0.40	Respiration = 12.70 +/- 0.32

INCUBATION 6 0530h 10/07/86 to 1725h 10/07/86

Day incubation - 3m depth

Units = µmol/kg

Mean Value +/- one standard error (Coefficent of variance)

Oxygen

ZERO

R(1)= 330.37
R(2)= 331.91
R(3)= 330.19
R(4)= 328.97

Mean = 330.36 +/- 0.60 (0.18%)

LIGHT

R(1)= 341.85
R(2)= 340.17
R(3)= 340.85
R(4)= 340.26

Mean = 340.78 +/- 0.39 (0.11%)

DARK

R(1)= 326.64
R(2)= 325.34
R(3)= 323.81
R(4)= 324.13
R(5)= 325.15

Mean = 324.60 +/- 0.18 (0.05%)

Carbon Dioxide

ZERO

R(1)= 1275.72
R(2)= 1273.62
R(3)= 1273.72
R(4)= 1274.42

Mean = 1274.37 +/- 0.48 (0.04%)

LIGHT

R(1)= 1263.01
R(2)= 1262.03

Mean = 1262.52 +/- 0.49 (0.04%)

DARK

R(1)= 1278.88
R(2)= 1277.37
R(3)= 1278.75

Mean = 1278.33 +/- 0.48 (0.04%)

Incubation time = 11 h

Gross Production = 15.77 +/- 0.63
Net Production = 10.42 +/- 0.72
Respiration = 5.35 +/- 0.78

Gross Production = 15.81 +/- 0.69
Net Production = 11.85 +/- 0.69
Respiration = 3.96 +/- 0.68

INCUBATION 7 1725h 10/07/86 to 0520h 11/07/86

Night incubation - 3m depth

Units = µmol/kg

Mean value given +/- one standard error (Coefficient of variance)

Oxygen	Carbon Dioxide
ZERO	ZERO
R(1)= 337.56	R(1)= 1263.07
R(2)= 336.30	R(2)= 1264.10
R(3)= 336.07	R(3)= 1263.01
R(4)= 336.00	R(4)= 1264.44
Mean = 336.48 +/- 0.36 (0.11%)	Mean = 1263.66 +/- 0.36 (0.03%)
LIGHT	LIGHT
R(1)= 330.30	R(1)= 1265.57
R(2)= 328.89	R(2)= 1266.73
R(3)= 329.69	R(3)= 1266.66
R(4)= 329.61	R(4)= 1267.34
R(5)= 329.61	
R(6)= 329.65	
Mean = 329.63 +/- 0.18 (0.06%)	Mean = 1266.58 +/- 0.37 (0.03%)
DARK	DARK
R(1)= 326.80	R(1)= 1269.09
R(2)= 326.86	R(2)= 1268.59
R(3)= 326.34	R(3)= 1268.42
R(4)= 326.73	R(4)= 1268.85
Mean = 326.68 +/- 0.12 (0.04%)	Mean = 1268.74 +/- 0.15 (0.01%)

Incubation time = 12.3 h

Gross Production = 2.94 +/- 0.22	Gross Production = 2.16 +/- 0.40
Net Production = - 6.86 +/- 0.41	Net Production = - 2.92 +/- 0.52
Respiration = 9.80 +/- 0.38	Respiration = 5.08 +/- 0.39

INCUBATION 8 0520h 11/07/86 to 1745h 11/07/86

Day incubation - 3m depth

Units = µmol/kg

Mean value given +/- one standard error (Coefficient of variance)

Oxygen

ZERO

R(1)= 329.39
R(2)= 330.40
R(3)= 328.82
R(4)= 329.26

Mean = 329.47 +/- 0.33 (0.10%)

LIGHT

R(1)= 341.44
R(2)= 341.64
R(3)= 341.52
R(4)= 340.12
R(5)= 339.26

Mean = 340.80 +/- 0.47 (0.14%)

DARK

R(1)= 321.43
R(2)= 320.97
R(3)= 320.89
R(4)= 321.03
R(5)= 320.22

Mean = 320.91 +/- 0.20 (0.06%)

Carbon Dioxide

ZERO

R(1)= 1263.20
R(2)= 1264.73
R(3)= 1264.10

Mean = 1264.01 +/- 0.44 (0.04%)

LIGHT

R(1)= 1256.98
R(2)= 1256.31
R(3)= 1257.37

Mean = 1256.89 +/- 0.31 (0.03%)

DARK

R(1)= 1276.05
R(2)= 1275.05

Mean = 1275.55 +/- 0.50 (0.04%)

Incubation time = 12 h

Gross Production	= 19.89 +/- 0.51	Gross Production	= 18.66 +/- 0.59
Net Production	= 11.33 +/- 0.58	Net Production	= 7.12 +/- 0.54
Respiration	= 8.56 +/- 0.39	Respiration	= 11.54 +/- 0.67

DATA APPENDIX

FOR LOCH EWE

Thermistor data (Channels 1-11)

CHANNEL 1 (DEG C) 2139 237.479200 720.000000

LISTINGS OF HOURLY VALUES

HOUR	0	1	2	3	4	5	6	7	8	9	10	11
DAY	12	13	14	15	16	17	18	19	20	21	22	23
237	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
	13.32	13.42	13.39	13.30	13.32	13.32	13.27	13.23	13.04	12.97	13.01	13.06
238	13.04	13.06	13.06	13.04	13.01	13.01	13.01	13.04	13.06	13.11	13.25	13.39
	13.39	13.32	12.73	12.47	12.56	12.59	12.59	12.59	12.59	12.59	12.59	12.59
239	12.59	12.59	12.59	12.59	12.59	12.59	12.56	12.56	12.66	12.80	12.78	12.94
	13.06	13.35	13.18	13.11	13.04	12.99	12.94	12.92	12.90	12.90	12.85	12.82
240	12.82	12.82	12.82	12.82	12.85	12.85	12.85	12.87	12.92	12.97	13.04	.00
	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00

CHANNEL 2 (DEG C) 2139 237.479200 720.000000

LISTINGS OF HOURLY VALUES

HOUR	0	1	2	3	4	5	6	7	8	9	10	11
DAY	12	13	14	15	16	17	18	19	20	21	22	23
237	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
	13.63	13.68	13.68	13.68	13.73	13.75	13.75	13.73	13.70	13.65	13.61	13.58
238	13.56	13.54	13.54	13.49	13.46	13.46	13.44	13.44	13.44	13.44	13.46	13.54
	13.61	13.63	12.99	12.78	12.82	12.85	12.85	12.87	12.87	12.87	12.87	12.87
239	12.87	12.87	12.87	12.87	12.85	12.85	12.85	12.85	12.87	12.92	12.94	13.01
	13.06	13.13	13.16	13.18	13.20	13.25	13.25	13.27	13.27	13.27	13.25	13.25
240	13.25	13.23	13.23	13.23	13.23	13.20	13.20	13.20	13.20	13.20	13.18	.00
	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00

CHANNEL 3 (DEG C) 2139 237.479200 720.000000

LISTINGS OF HOURLY VALUES

HOUR	0	1	2	3	4	5	6	7	8	9	10	11
DAY	12	13	14	15	16	17	18	19	20	21	22	23
237	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
	13.49	13.54	13.54	13.49	13.49	13.49	13.49	13.49	13.49	13.49	13.49	13.49
238	13.49	13.46	13.44	13.39	13.37	13.37	13.35	13.30	13.30	13.30	13.30	13.35
	13.42	13.46	12.85	12.64	12.68	12.71	12.71	12.73	12.73	12.73	12.73	12.73
239	12.73	12.73	12.73	12.73	12.73	12.71	12.71	12.73	12.73	12.75	12.75	12.82
	12.82	12.87	12.90	12.92	12.92	12.94	12.94	12.97	12.97	12.94	12.92	12.92
240	12.92	12.92	12.92	12.90	12.90	12.90	12.90	12.90	12.90	12.87	12.90	.00
	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00

CHANNEL 4 (DEG C) 2139 237.479200 720.000000

LISTINGS OF HOURLY VALUES

HOUR	0	1	2	3	4	5	6	7	8	9	10	11
DAY	12	13	14	15	16	17	18	19	20	21	22	23
237	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
	13.32	13.35	13.35	13.32	13.35	13.35	13.32	13.30	13.30	13.30	13.27	13.27
238	13.27	13.27	13.30	13.30	13.30	13.27	13.30	13.30	13.32	13.37	13.42	13.44
	13.49	13.49	13.01	12.80	12.82	12.85	12.87	12.90	12.90	12.90	12.90	12.90
239	12.90	12.90	12.90	12.90	12.90	12.87	12.87	12.87	12.90	12.90	12.90	12.97
	12.97	12.97	12.97	12.97	12.99	12.97	12.99	12.97	12.99	12.97	12.97	12.94
240	12.94	12.94	12.94	12.94	12.94	12.92	12.92	12.94	12.94	12.94	12.92	.00
	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00

CHANNEL 5 (DEG C) 2139 237.479200 720.000000

LISTINGS OF HOURLY VALUES

HOUR	0	1	2	3	4	5	6	7	8	9	10	11
DAY	12	13	14	15	16	17	18	19	20	21	22	23
237	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
	12.87	12.90	12.90	12.87	12.87	12.87	12.87	12.85	12.85	12.85	12.82	12.82
238	12.82	12.82	12.85	12.85	12.87	12.87	12.87	12.90	12.92	12.94	12.97	13.01
	13.04	13.06	12.92	12.71	12.71	12.73	12.78	12.80	12.80	12.80	12.82	12.82
239	12.82	12.82	12.82	12.82	12.80	12.80	12.80	12.80	12.80	12.80	12.82	12.85
	12.85	12.85	12.85	12.85	12.85	12.82	12.85	12.82	12.82	12.82	12.80	12.80
240	12.80	12.78	12.78	12.78	12.78	12.75	12.75	12.75	12.73	12.73	12.73	.00
	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00

CHANNEL 6 (DEG C) 2139 237.479200 720.000000

LISTINGS OF HOURLY VALUES

HOUR	0	1	2	3	4	5	6	7	8	9	10	11
DAY	12	13	14	15	16	17	18	19	20	21	22	23
237	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
	12.73	12.73	12.73	12.73	12.73	12.73	12.73	12.71	12.71	12.71	12.71	12.71
238	12.71	12.71	12.71	12.73	12.73	12.73	12.73	12.73	12.73	12.78	12.80	12.82
	12.87	12.87	12.97	12.78	12.80	12.80	12.82	12.82	12.82	12.87	12.90	12.90
239	12.92	12.92	12.92	12.90	12.90	12.90	12.90	12.90	12.90	12.90	12.90	12.90
	12.90	12.90	12.87	12.87	12.87	12.87	12.85	12.82	12.82	12.82	12.82	12.82
240	12.80	12.80	12.78	12.78	12.75	12.75	12.75	12.73	12.73	12.73	12.71	.00
	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00

CHANNEL 7 (DEG C) 2139 237.479200 720.000000

LISTINGS OF HOURLY VALUES

HOUR	0	1	2	3	4	5	6	7	8	9	10	11
DAY	12	13	14	15	16	17	18	19	20	21	22	23
237	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
	12.59	12.61	12.61	12.61	12.59	12.59	12.59	12.59	12.56	12.54	12.54	12.56
238	12.54	12.56	12.54	12.54	12.54	12.54	12.54	12.54	12.56	12.59	12.59	12.61
	12.64	12.66	12.87	12.75	12.75	12.78	12.78	12.78	12.78	12.78	12.78	12.80
239	12.80	12.80	12.80	12.80	12.82	12.87	12.87	12.87	12.87	12.87	12.85	12.82
	12.82	12.82	12.80	12.80	12.80	12.80	12.78	12.78	12.75	12.73	12.73	12.71
240	12.71	12.71	12.71	12.68	12.68	12.68	12.66	12.64	12.64	12.61	12.61	.00
	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00

CHANNEL 8 (DEG C) 2139 237.479200 720.000000

LISTINGS OF HOURLY VALUES

HOUR	0	1	2	3	4	5	6	7	8	9	10	11
DAY	12	13	14	15	16	17	18	19	20	21	22	23
237	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
	12.47	12.47	12.47	12.47	12.47	12.47	12.45	12.45	12.45	12.45	12.45	12.45
238	12.45	12.45	12.45	12.42	12.42	12.42	12.42	12.45	12.42	12.45	12.47	12.47
	12.49	12.49	12.68	12.68	12.68	12.71	12.71	12.71	12.71	12.71	12.73	12.73
239	12.73	12.73	12.73	12.73	12.73	12.73	12.73	12.73	12.73	12.73	12.73	12.73
	12.73	12.73	12.73	12.71	12.68	12.66	12.66	12.64	12.64	12.61	12.61	12.59
240	12.56	12.56	12.56	12.54	12.54	12.54	12.52	12.52	12.49	12.49	12.47	.00
	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00

CHANNEL 9 (DEG C) 2139 237.479200 720.000000

LISTINGS OF HOURLY VALUES

HOUR	0	1	2	3	4	5	6	7	8	9	10	11
DAY	12	13	14	15	16	17	18	19	20	21	22	23
237	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
	12.40	12.40	12.40	12.40	12.40	12.40	12.40	12.38	12.35	12.35	12.35	12.35
238	12.35	12.35	12.35	12.35	12.35	12.35	12.35	12.35	12.35	12.35	12.35	12.38
	12.35	12.38	12.64	12.64	12.64	12.64	12.64	12.66	12.66	12.66	12.66	12.66
239	12.66	12.66	12.66	12.66	12.66	12.66	12.66	12.66	12.66	12.66	12.68	12.66
	12.66	12.66	12.64	12.61	12.61	12.59	12.56	12.54	12.54	12.49	12.49	12.47
240	12.47	12.45	12.45	12.45	12.45	12.40	12.40	12.40	12.38	12.38	12.35	.00
	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00

CHANNEL 10 (DEG C) 2139 237.479200 720.000000

LISTINGS OF HOURLY VALUES

HOUR	0	1	2	3	4	5	6	7	8	9	10	11
DAY	12	13	14	15	16	17	18	19	20	21	22	23
237	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
	12.35	12.35	12.35	12.35	12.35	12.35	12.35	12.33	12.33	12.33	12.31	12.31
238	12.31	12.31	12.31	12.31	12.31	12.31	12.31	12.31	12.31	12.31	12.31	12.33
	12.35	12.33	12.47	12.61	12.61	12.61	12.64	12.64	12.64	12.64	12.64	12.64
239	12.64	12.64	12.61	12.61	12.64	12.61	12.61	12.61	12.64	12.64	12.61	12.64
	12.61	12.61	12.59	12.56	12.54	12.49	12.47	12.45	12.45	12.45	12.45	12.40
240	12.40	12.38	12.35	12.35	12.35	12.35	12.33	12.33	12.31	12.28	12.26	.00
	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00

CHANNEL 11 (DEG C) 2139 237.479200 720.000000

LISTINGS OF HOURLY VALUES

HOUR	0	1	2	3	4	5	6	7	8	9	10	11
DAY	12	13	14	15	16	17	18	19	20	21	22	23
237	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00
	12.21	12.21	12.19	12.19	12.19	12.16	12.16	12.19	12.19	12.16	12.16	12.16
238	12.14	12.16	12.12	12.14	12.12	12.12	12.12	12.12	12.12	12.12	12.12	12.14
	12.14	12.16	12.23	12.45	12.45	12.45	12.45	12.45	12.45	12.45	12.45	12.47
239	12.45	12.45	12.45	12.45	12.45	12.45	12.45	12.45	12.45	12.45	12.45	12.45
	12.42	12.40	12.40	12.35	12.33	12.31	12.26	12.26	12.23	12.23	12.21	12.19
240	12.16	12.16	12.16	12.14	12.16	12.12	12.12	12.12	12.09	12.07	12.05	.00
	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00	.00

SOLAR ENERGY Kipp and Zonen Solarimeter

August 1987

Date	0600h	0800h	1000h	1200h	1400h	1600h	1800h	2000h	2200h
13/8/87	0	4	7	18	48	67	14	4	0
14/8/87	1	9	28	17	29	16	21	7	1
15/8/87	0	6	16	38	22	32	14	3	0
16/8/87	0	7	10	30	32	40	33	10	2
17/8/87	0	5	42	82	70	106	58	18	0
18/8/87	0	4	22	42	64	48	40	15	1
19/8/87	0	8	34	92	73	34	13	6	1
20/8/87	0	3	9	18	13	17	7	4	0
21/8/87	0	13	30	25	66	102	80	38	1
22/8/87	0	10	40	70	89	99	66	19	0
23/8/87	0	2	10	29	38	51	40	10	1
24/8/87	0	13	48	77	103	106	72	26	1
25/8/87	0	4	19	44	28	20	-	-	-

units = gcal cm^{-2}

Two hourly values

SOLAR ENERGY Kipp and Zonen Solarimeter

August 1987

Date	0600h	0800h	1000h	1200h	1400h	1600h	1800h	2000h	2200h
13/8/87	0.00	2.73	4.77	12.27	32.71	45.66	9.54	2.73	0.00
14/8/87	0.68	6.13	19.08	11.59	19.76	10.90	14.31	4.77	0.68
15/8/87	0.00	4.09	10.90	25.90	14.99	21.81	9.54	2.04	0.00
16/8/87	0.00	4.77	6.82	20.44	21.81	27.26	22.49	6.82	1.36
17/8/87	0.00	3.41	28.62	55.88	47.70	72.23	39.53	12.27	0.00
18/8/87	0.00	2.73	14.99	28.62	43.61	32.71	27.26	10.22	0.68
19/8/87	0.00	5.45	23.17	62.70	49.75	23.17	8.86	4.09	0.68
20/8/87	0.00	2.04	6.13	12.27	8.86	11.59	4.77	2.73	0.00
21/8/87	0.00	8.86	20.44	17.04	44.98	69.51	54.52	25.90	0.68
22/8/87	0.00	6.81	27.26	47.70	60.65	67.47	44.98	12.95	0.00
23/8/87	0.00	1.36	6.81	19.76	25.90	34.76	27.26	6.81	0.68
24/8/87	0.00	8.86	32.71	52.47	88.59	72.24	49.07	17.72	0.68
25/8/87	0.00	2.73	12.95	29.99	19.08	13.63	-	-	-

units = quanta cm^2 s^{-1} x 10^{15}

Two hourly values

CHLOROPHYLL A (MG/M^3)

CODE	CHLOROPHYLL A	PHAEOPHYTIN
335 16/08/87 1m	15.641	1.562
273 16/08/87 2m	14.406	0.553
140 16/08/87 3m	8.041	0.934
117 16/08/87 4m	2.915	6.869
488 16/08/87 5m	7.732	0.776
1m 14/08/87	10.217	1.470
4m 14/08/87	9.423	1.469
5m 14/08/87	6.586	1.701
6m 14/08/87	6.527	1.034
Inc 3 Zero	7.982	0.572
Inc 4 Zero	7.203	0.276
204 19/08/87 1m	10.187	0.496
488 19/08/87 2m	11.201	0.392
335 19/08/87 3m	8.982	0.680
421 19/08/87 4m	10.025	0.820
Inc 6 Zero	2.598	0.515
Inc 6 Light	2.267	0.472
Inc 6 Dark	1.855	0.548
109 20/08/87 1m	6.277	1.062
107 20/08/87 5m	6.703	0.870
553 20/08/87 10m	3.643	0.570
840 Inc 5 Zero	7.438	0.555
842 Inc 5 Dark	7.100	0.753
841 Inc 5 Light	3.864	0.255
848 Inc 4 Light	7.585	0.549
849 Inc 4 Dark	5.410	0.793
560 Inc 7 Zero	10.290	1.584
561 Inc 7 Light	10.643	1.371
562 Inc 7 Dark	10.261	1.847

In situ measurements

Loch Ewe

INSITU 1 - 8

12/08/87 to 14/08/87

OXYGEN (µmol/kg)

MEAN VALUE +/- ONE STANDARD ERROR

DEPTH (metres)	12/08/87 1800h	13/08/87 0005h	13/08/87 0815h	13/08/87 1215h	13/08/87 1830h	14/08/87 0030h	14/08/87 0615h	14/08/87 1745h
1m	368.48 +/- 0.98	365.34 +/- 0.24	350.65 +/- 1.18	351.65 +/- 0.56	366.34 +/- 0.39	352.84 +/- 0.04	342.42 +/- 0.24	368.94 +/- 0.34
3m	350.37 +/- 0.35	348.49 +/- 1.83	349.95 +/- 0.12	352.14 +/- 0.24	359.94 +/- 0.16			
4m	336.13 +/- 0.27	323.68 +/- 0.54	335.34 +/- 0.35	329.92 +/- 0.36	348.61 +/- 0.09	335.18 +/- 0.68	338.03 +/- 0.13	341.69 +/- 0.24
5m	317.31 +/- 0.20	321.52 +/- 0.63	315.89 +/- 0.16	320.13 +/- 0.10	326.04 +/- 0.13	307.60 +/- 0.39	333.63 +/- 0.20	331.56 +/- 0.23
6m						329.89 +/- 0.16	310.09 +/- 0.19	309.71 +/- 0.12

INSITU 1 - 8

12/08/87 to 14/08/87

CARBON DIOXIDE (µmol/kg)

MEAN VALUE +/- ONE STANDARD ERROR

DEPTH (metres)	12/08/87 1800h	13/08/87 0005h	13/08/87 0815h	13/08/87 1215h	13/08/87 1830h	14/08/87 0030h	14/08/87 0615h	14/08/87 1745h
1m	1579.99 +/- 0.07	1580.03 +/- 0.88	1575.09 +/- 0.15	1572.42 +/- 1.79	1562.11 +/- 0.05	1576.52 +/- 1.02	1582.61 +/- 0.18	1624.70 +/- 1.26
3m	1765.45 +/- 1.95	1714.45 +/- 1.03	1715.11 +/- 0.82	1720.35 +/- 0.69	1734.93 +/- 0.73			
4m	1838.60 +/- 0.59	1866.83 +/- 0.76	1817.96 +/- 0.80	1851.75 +/- 0.83	1869.73 +/- 0.60	1835.62 +/- 1.44	1808.20	1838.70 +/- 0.15
5m	1889.27 +/- 0.14	1878.95 +/- 0.13	1884.72 +/- 1.04	1868.14 +/- 0.17	1800.97 +/- 0.20	1874.21 +/- 0.14	1817.31 +/- 0.47	1850.25 +/- 0.02
6m						1912.97 +/- 1.71	1895.85	1903.45 +/- 1.89

INSITU 9 - 12
17/08/87 to 20/08/87

OXYGEN (µmol/kg)

MEAN VALUE +/- ONE STANDARD ERROR

DEPTH (metres)	17/08/87 1630h Postmix 1	18/08/87 0800h Postmix 2	18/08/87 1700h	19/08/87 0615h	19/08/87 1830h	20/08/87 0615h
1m	329.32	318.38 +/- 0.14	347.67 +/- 0.62	337.76 +/- 0.13	363.29 +/- 0.09	354.92 +/- 0.44
2m	329.15	322.08 +/- 0.01	345.26 +/- 0.38	338.68 +/- 0.28	360.91 +/- 0.26	352.91 +/- 1.64
3m	328.85	323.47 +/- 0.13	343.19 +/- 0.41	339.02 +/- 0.45	354.80 +/- 0.20	351.39 +/- 0.22
4m	328.75	324.40 +/- 0.04	342.06 +/- 0.20	337.37 +/- 0.00	353.31 +/- 0.26	347.43 +/- 0.06
5m		323.63	336.66 +/- 0.26	331.70 +/- 0.65	343.95 +/- 0.13	340.58 +/- 0.48
6m	322.69	317.43	324.88 +/- 0.70	318.23	323.67 +/- 0.11	326.02 +/- 1.69
8m	307.58					
10m	289.05					

INSITU 9 - 12

18/08/87 to 20/08/87

CARBON DIOXIDE (µmol/kg)

MEAN +/- ONE STANDARD ERROR

DEPTH (metres)	18/08/87 1700hrs	19/08/87 0615hrs	19/08/87 1830hrs	20/08/87 0615hrs
1m	1819.59 +/- 1.56	1827.41 +/- 0.96	1805.36 +/- 0.38	1800.79 +/- 0.50
2m	1821.17 +/- 0.28	1827.33 +/- 0.48	1808.58 +/- 0.96	1812.52 +/- 0.36
3m	1825.83 +/- 0.00	1829.25 +/- 0.00	1816.43 +/- 0.33	1819.38 +/- 0.15
4m	1827.50 +/- 0.50	1834.03 +/- 0.08	1817.99 +/- 0.94	1826.63 +/- 0.23
5m	1834.76 +/- 0.55	1838.49 +/- 1.19	1830.34 +/- 0.75	1834.15 +/- 0.05
6m	1853.01 +/- 0.70	1884.42 +/-0.06	1856.66 +/- 1.50	1853.70 +/- 0.25

INSITU 13 - 18
21/08/87 to 24/08/87

CARBON DIOXIDE (µmol/kg)

MEAN VALUE +/- ONE STANDARD ERROR

DEPTH (metres)	21/08/87 1600h	22/08/87 0600h	22/08/87 1730h	23/08/87 0645h	23/08/87 1615h	24/08/87 0615h
1m	1771.46 +/- 0.12	1782.16 +/- 1.44	1795.12 +/- 0.21	1782.84* +/- 1.76	17147.35 +/- 0.55	1789.35 +/- 0.16
2m	1815.54 +/- 0.47	1825.46 +/- 1.84	1825.83 +/- 0.23	1828.43 +/- 0.30	1776.47 +/- 0.45	1813.41 +/- 0.52
3m	1835.97 +/- 1.91	1835.91 +/- 0.50	1852.24 +/- 1.05	1864.50 +/- 0.36	1857.93 +/- 0.91	1855.58 +/- 1/05
4m	1857.33 +/- 0.32	1897.42 +/- 0.49	1877.14 +/- 0.30	1885.13 +/- 0.82	1883.60 +/- 0.67	1908.50 +/- 0.75
5m	1868.51 +/- 0.98	1908.30 +/- 0.65	1898.66 +/- 0.57	1901.20 +/- 1.09	1896.86 +/- 0.56	1908.50 +/- 1.39
6m	1864.67 +/- 0.11	1906.88 +/- 0.94	1915.44 +/- 1.23	1915.07 +/- 0.41	1905.53 +/- 1.71	1913.14 +/- 0.36

INSITU 13 - 18
20/08/87 to 24/08/87

OXYGEN (μmol/kg)

MEAN VALUE +/- ONE STANDARD ERROR

DEPTH (metres)	20/08/87 1800h Postmix	21/08/87 1600h	22/08/87 0600h	22/08/87 1730h	23/08/87 0645h	23/08/87 1615h	24/08/87 0615h
1m	301.55	326.56 +/- 0.32	328.11 +/- 0.23	366.73 +/- 0.38	352.20 +/- 0.14	393.25 +/- 0.44	348.35 +/- 0.34
2m	300.90	322.43 +/- 0.27	318.13 +/- 0.31	351.85 +/- 1.04	337.15 +/- 0.40	375.40 +/- 0.16	337.78 +/- 0.08
3m	300.59	317.34 +/- 0.06	313.13 +/- 0.79	335.86 +/- 0.23	319.73 +/- 0.19	326.04 +/- 0.28	322.05 +/- 0.24
4m	301.43	309.51 +/- 0.13	304.19 +/- 0.19	319.70 +/- 0.78	310.82 +/- 0.04	311.24 +/- 0.49	307.98 +/- 0.15
5m	300.21	300.86 +/- 0.28	295.37 +/- 0.71	305.34 +/- 0.13	301.38 +/- 0.25	298.68 +/- 0.06	291.13 +/- 0.15
6m	299.46	299.92 +/- 0.07	295.76 +/- 0.82	291.80 +/- 0.18	291.70 +/- 0.44	290.77 +/- 0.27	287.04 +/- 0.25
9m	290.61						
12.5m	274.51						

In vitro incubations

Loch Ewe

INCUBATION 1 1820hrs 12/08/87 to 0730hrs 13/08/87
Night incubation - 3m depth

Units = µmol/kg
Mean value given +/- one standard error (Coefficient of variance)

Oxygen	Carbon Dioxide
ZERO	ZERO
R(1)= 299.08	R(1)= 1799.56
R(2)= 299.49	R(2)= 1798.08
R(3)= 299.57	
R(4)= 299.82	
Mean = 299.49 +/- 0.15 (0.05%)	Mean = 1798.82 +/- 0.74 (0.04%)
LIGHT	LIGHT
R(1)= 296.90	R(1)= 1799.60
R(2)= 297.45	R(2)= 1798.05
R(3)= 295.68	
R(4)= 295.79	
Mean = 296.46 +/- 0.43 (0.15%)	Mean = 1798.83 +/- 0.78 (0.04%)
DARK	DARK
R(1)= 295.56	R(1)= 1800.21
R(2)= 295.53	R(2)= 1799.45
R(3)= 295.47	
R(4)= 294.90	
Mean = 295.37 +/- 0.16 (0.05%)	Mean = 1799.83 +/- 0.38 (0.02%)

Incubation time = 13.2 hrs

Gross Production = 1.09 +/- 0.46	Gross Production = - 1.01 +/- 0.86
Net Production = - 3.04 +/- 0.46	Net Production = 0.01 +/- 1.07
Respiration = 4.13 +/- 0.22	Respiration = - 1.01 +/- 0.83

INCUBATION 2 0730hrs 13/08/87 to 1904hrs 13/08/87
Day incubation - 3m depth

Units = µmol/kg
Mean value given +/- one standard error (Coefficient of variance)

Oxygen	Carbon Dioxide
ZERO	ZERO
R(1)= 320.22	R(1)= 1840.59
R(2)= 319.73	R(2)= 1840.10
R(3)= 320.22	
R(4)= 318.11	
Mean = 319.57 +/- 0.50 (0.16%)	Mean = 1840.35 +/- 0.25 (0.01%)
LIGHT	LIGHT
R(1)= 302.73	R(1)= 1825.06
R(2)= 302.30	R(2)= 1824.23
Mean = 302.52 +/- 0.22 (0.07%)	Mean = 1824.65 +/- 0.42 (0.02%)
DARK	DARK
R(1)= 311.52	R(1)= 1828.01
R(2)= 304.52	R(2)= 1825.13
R(3)= 308.50	R(3)= 1821.10
Mean = 308.18 +/- 2.03 (0.66%)	Mean = 1824.75 +/- 2.00 (0.11%)

Incubation time = 11.5 hrs

Gross Production = - 5.67 +/- 2.04	Gross Production = - 0.10 +/- 2.05
Net Production = - 17.05 +/- 0.54	Net Production = - 15.70 +/- 0.48
Respiration = 11.39 +/- 2.09	Respiration = - 15.60 +/- 2.02

INCUBATION 3 1755hrs 18/08/87 to 0655hrs 19/08/87
Night incubation - 3m depth

Units = µmol/kg
Mean value given +/- one standard error (Coefficient of variance)

Oxygen	Carbon Dioxide
ZERO	ZERO
R(1)= 320.88	R(1)= 1828.30
R(2)= 321.00	R(2)= 1827.03
R(3)= 320.17	
R(4)= 322.56	
Mean = 321.15 +/- 0.50 (0.16%)	Mean = 1827.67 +/- 0.24 (0.04%)
LIGHT	LIGHT
R(1)= 317.11	R(1)= 1832.81
R(2)= 317.78	R(2)= 1833.74
R(3)= 318.18	
R(4)= 318.11	
Mean = 317.80 +/- 0.24 (0.08%)	Mean = 1833.28 +/- 0.47 (0.03%)
DARK	DARK
R(1)= 315.93	R(1)= 1835.05
R(2)= 315.75	R(2)= 1834.69
R(3)= 316.27	
R(4)= 316.00	
Mean = 315.99 +/- 0.11 (0.03%)	Mean = 1834.07 +/- 0.18 (0.01%)

Incubation time = 13 hrs

Gross Production = 1.81 +/- 0.27	Gross Production = - 1.60 +/- 0.49
Net Production = - 3.36 +/- 0.56	Net Production = 5.61 +/- 0.79
Respiration = 5.17 +/- 0.52	Respiration = - 7.21 +/- 0.66

INCUBATION 4 0650hrs 19/08/87 to 1920hrs 19/08/87

Day incubation - 3m depth

Units = µmol/kg

Mean value given +/- one standard error (Coefficient of variance)

Oxygen	Carbon Dioxide
ZERO	ZERO
R(1)= 302.61	R(1)= 1826.22
R(2)= 302.45	R(2)= 1824.92
R(3)= 302.82	
R(4)= 302.07	
Mean = 302.49 +/- 0.16 (0.05%)	Mean = 1825.6 +/- 0.65 (0.04%)
LIGHT	LIGHT
R(1)= 314.61	R(1)= 1824.60
R(2)= 313.37	R(2)= 1821.70
R(3)= 315.74	
R(4)= 313.66	
Mean = 314.35 +/- 0.54 (0.17%)	Mean = 1823.2 +/- 1.45 (0.08%)
DARK	DARK
R(1)= 296.47	R(1)= 1836.07
R(2)= 296.59	R(2)= 1835.60
R(3)= 295.26	
R(4)= 295.63	
Mean = 295.99 +/- 0.32 (0.11%)	Mean = 1835.80 +/- 0.24 (0.01%)

Incubation Time = 12.5 hrs

Gross Production = 18.36 +/- 0.63	Gross Production = -12.69 +/- 1.47
Net Production = 11.86 +/- 0.56	Net Production = - 2.42 +/- 1.59
Respiration = 6.50 +/- 0.36	Respiration = -10.27 +/- 0.69

INCUBATION 5 1900hrs 19/08/87 to 0650hrs 20/08/87
Night incubation - 3m depth

Units = µmol/kg
Mean value given +/- one standard error (Coefficient of variance)

Oxygen	Carbon Dioxide
ZERO	ZERO
R(1)= 320.46	R(1)= 1816.44
R(2)= 321.44	R(2)= 1814.39
Mean = 320.95 +/- 0.49 (0.15%)	Mean = 1815.42 +/- 1.03 (0.06%)
LIGHT	LIGHT
R(1)= 322.21	R(1)= 1818.79
R(2)= 322.93	R(2)= 1820.38
Mean = 322.57 +/- 0.36 (0.11%)	Mean = 1819.59 +/- 0.80 (0.04%)
DARK	DARK
R(1)= 320.25	R(1)= 1820.42
R(2)= 320.36	R(2)= 1820.08
R(3)= 319.37	
Mean = 319.99 +/- 0.31 (0.10%)	Mean = 1820.25 +/- 0.17 (0.01%)

Incubation time = 11.83 hrs

Gross Production = 2.58 +/- 0.48	Gross Production = - 0.67 +/- 0.81
Net Production = 1.62 +/- 0.61	Net Production = 4.17 +/- 1.30
Respiration = 0.96 +/- 0.58	Respiration = - 4.84 +/- 1.04

INCUBATION 6 1645hrs 20/08/87 to 1900hrs 21/08/87
Artificial Daylight - 8m depth

Units = µmol/kg
Mean value given +/- one standard error (Coefficient of variance)

Oxygen	Carbon Dioxide
ZERO	ZERO
R(1)= 247.50	R(1)= 1933.99
R(2)= 247.39	R(2)= 1934.73
R(3)= 247.29	R(3)= 1934.52
Mean = 247.39 +/- 0.06 (0.03%)	Mean = 1934.40 +/- 0.22 (0.01%)
LIGHT	LIGHT
R(1)= 247.59	R(1)= 1932.30
R(2)= 248.84	R(2)= 1931.47
R(3)= 249.36	
Mean = 248.60 +/- 0.53 (0.21%)	Mean = 1931.90 +/- 0.42 (0.02%)
DARK	DARK
R(1)= 241.23	R(1)= 1947.36
R(2)= 241.27	R(2)= 1947.89
R(3)= 241.38	
Mean = 241.29 +/- 0.04 (0.02%)	Mean = 1947.63 +/- 0.27 (0.01%)

Incubation time = 26.25 hrs

Gross production = 7.30 +/- 0.53	Gross Production = -15.48 +/- 0.42
Net Production = 1.20 +/- 0.53	Net Production = - 2.53 +/- 0.47
Respiration = 6.10 +/- 0.08	Respiration = -12.95 +/- 0.22

INCUBATION 7 0700hrs 23/08/87 to 1900hrs 23/08/87

Day incubation - 3m depth

Units = µmol/kg

Mean value given +/- one standard error (Coefficient of variance)

Oxygen	Carbon Dioxide
ZERO	ZERO
R(1)= 316.16	R(1)= 1853.80
R(2)= 315.10	R(2)= 1850.70
R(3)= 315.30	
R(4)= 315.03	
Mean = 315.40 +/- 0.26 (0.08%)	Mean = 1852.25 +/- 1.55 (0.08%)
LIGHT	LIGHT
R(1)= 323.59	R(1)= 1844.90
R(2)= 322.66	R(2)= 1847.30
R(3)= 326.12	
R(4)= 328.87	
Mean = 325.31 +/- 1.39 (0.43%)	Mean = 1846.10 +/- 1.20 (0.05%)
DARK	DARK
R(1)= 300.23	R(1)= 1862.13
R(2)= 302.09	R(2)= 1863.90
R(3)= 304.46	
R(4)= 304.22	
Mean = 302.75 +/- 0.99 (0.33%)	Mean = 1863.02 +/- 0.89 (0.05%)

Incubation time = 12 hrs

Gross Production = 22.56 +/- 1.71	Gross Production = -16.92 +/- 1.49
Net Production = 9.91 +/- 1.42	Net Production = - 6.15 +/- 1.96
Respiration = 12.65 +/- 1.03	Respiration = -10.77 +/- 1.79

INCUBATION 8 1820hrs 23/08/87 to 0620hrs 24/08/87
Night incubation - 3m depth

Units = µmol/kg
Mean value given +/- one standard error (Coefficient of variance)

Oxygen	Carbon Dioxide
ZERO	ZERO
R(1)= 286.68	R(1)= 1851.31
R(2)= 286.51	R(2)= 1851.90
R(3)= 286.86	
R(4)= 286.94	
Mean = 286.75 +/- 0.10 (0.03%)	Mean = 1851.60 +/- 0.30 (0.02%)
LIGHT	LIGHT
R(1)= 276.26	R(1)= 1861.03
R(2)= 276.24	R(2)= 1860.58
R(3)= 277.01	
R(4)= 276.43	
Mean = 276.49 +/- 0.18 (0.07%)	Mean = 1860.81 +/- 0.23 (0.01%)
DARK	DARK
R(1)= 274.44	R(1)= 1862.79
R(2)= 274.46	R(2)= 1861.78
R(3)= 274.60	
R(4)= 274.22	
Mean = 274.43 +/- 0.08 (0.03%)	Mean = 1862.29 +/- 0.51 (0.03%)

Incubation time = 12 hrs

Gross Production = 2.06 +/- 0.20	Gross Production = -1.48 +/- 0.55
Net Production = -10.26 +/- 0.20	Net Production = 9.20 +/- 0.37
Respiration = 12.32 +/- 0.12	Respiration = -10.68 +/- 0.59

DATA APPENDIX

CHALLENGER CRUISE

DATA APPENDIX

Challenger Cruise

Surface measurements
(Complete cruise)

T°C	S‰	TCO_2	SE	Chl.	Tr.	Attn.	Long.	Lat.
7.41	34.75	2057.78	0.76	1.67	79	0.94	64.70	-6.87
7.10	34.77	2069.16	0.78	1.06	78	0.99	64.93	-6.62
7.04	34.76	2069.44	0.40	-99.00	80	0.89	64.98	-6.48
7.44	34.79	2061.10	1.24	-99.00	77	1.05	64.83	-6.35
8.17	35.04	2055.61	0.26	5.30	66	1.66	61.90	-6.70
8.88	35.11	-99.00	-99.00	-99.00	68	1.54	62.13	-6.13
9.27	35.15	2026.14	1.30	-99.00	65	1.72	62.30	-5.85
9.28	35.12	2060.35	1.49	1.80	78	0.99	62.48	-5.45
9.38	35.15	2088.29	0.43	0.63	84	0.70	62.87	-4.72
9.38	35.16	2087.94	1.42	-99.00	84	0.70	63.07	-4.40
9.57	35.11	2067.93	0.68	-99.00	76	1.10	63.47	-3.07
9.68	35.11	2068.01	1.14	1.10	77	1.05	63.08	-2.73
10.36	35.02	2063.47	0.97	0.85	78	0.99	62.87	-2.55
9.36	35.04	2060.04	0.57	1.32	76	1.10	62.62	-2.50
9.88	35.16	2073.32	1.31	1.24	77	1.05	62.27	-2.45
10.14	35.16	2071.87	0.33	1.16	78	0.99	61.97	-2.53
10.41	35.19	2073.46	1.02	0.85	81	0.84	61.67	-2.48
10.56	35.24	2067.06	0.46	0.59	80	0.89	61.00	-1.43
10.50	35.25	2070.44	1.10	0.41	83	0.75	61.00	-2.40
10.58	35.25	2067.07	0.78	0.86	78	0.99	61.00	-3.08
10.63	35.29	2068.37	1.20	0.69	81	0.84	60.58	-3.67
10.50	35.28	2073.88	1.04	0.51	82	0.79	61.00	-4.33
10.86	35.24	2066.90	1.32	0.55	81	0.84	59.83	-10.03
11.09	35.14	2033.66	0.43	1.77	70	1.43	59.85	-10.40
11.01	35.19	2049.21	0.77	-99.00	74	1.20	59.85	-11.08
10.99	35.20	2042.23	1.82	1.46	71	1.37	59.88	-11.97
11.26	35.05	2044.87	0.52	1.49	73	1.26	59.88	-12.17
10.52	35.16	2064.03	1.02	0.93	77	1.05	59.67	-12.37

Missing value = -99.00

T°C : Temperature
S‰ : Salinity
TCO_2 : Units µmol/kg
SE : Standard error (µmol/kg)
Chl. : Chlorophyll a (mg/m^3)
Tr. : Percentage transmission
Attn. : Attenuation ($metres^{-1}$)
Long. : Longitude
Lat. : Latitude

T°C	S‰	TCO_2	SE	Chl.	Tr.	Attn.	Long.	Lat.
10.69	35.08	2064.56	1.31	1.20	83	0.75	57.00	-19.48
11.04	35.15	2064.62	0.66	0.66	69	1.48	57.18	-20.02
11.03	34.99	2054.36	0.84	1.25	79	0.94	57.93	-19.98
10.94	35.00	2060.65	1.98	-99.00	82	0.79	58.40	-20.13
10.84	34.99	2054.82	1.14	-99.00	80	0.89	58.25	-19.98
10.88	35.02	2061.48	0.81	1.27	77	1.05	58.23	-19.73
10.76	35.06	2068.40	0.97	0.60	81	0.84	58.47	-19.45
10.81	35.05	2065.21	1.07	0.77	80	0.89	58.65	-19.18
10.80	35.07	2064.75	0.13	0.78	78	0.99	58.85	-18.92
11.06	34.93	2044.57	0.37	-99.00	76	1.10	58.43	-17.98
11.39	35.06	2034.08	1.17	-99.00	70	1.43	59.67	-17.67
10.87	35.03	2028.43	0.99	-99.00	70	1.43	59.85	-17.48
10.73	35.08	2042.82	1.10	1.69	76	1.10	60.03	-17.07
10.95	35.07	2046.72	0.35	1.50	76	1.10	60.00	-16.53
10.41	35.01	2053.54	0.45	1.35	77	1.05	59.98	-15.90
11.05	34.89	2053.90	1.03	-99.00	82	0.79	59.53	-15.13
11.40	34.81	2042.87	0.63	-99.00	81	0.84	59.63	-15.05
11.31	34.92	2032.24	0.64	1.86	72	1.31	59.83	-14.90
10.71	35.09	2059.40	0.40	1.08	77	1.05	60.30	-14.55
10.41	35.11	2052.29	1.27	1.02	78	0.99	60.57	-14.38
10.64	35.11	2054.62	0.15	0.98	77	1.05	60.87	-13.80
10.57	35.10	2055.32	0.75	-99.00	78	0.99	60.80	-13.68
10.95	35.25	2058.02	0.50	-99.00	70	1.43	59.85	-12.05
11.22	35.24	2064.31	0.92	1.44	70	1.43	59.85	-12.05
11.27	35.31	2068.26	0.19	1.07	74	1.20	59.63	-11.95
10.96	35.25	-99.00	-99.00	1.78	67	1.60	59.55	-11.28
11.10	35.25	2068.56	0.87	1.34	72	1.31	59.78	-11.12
11.01	35.21	2060.87	0.98	0.91	74	1.20	59.95	-10.97
10.49	35.43	2062.10	1.96	0.91	73	1.26	60.25	-10.67
9.98	34.98	2081.83	0.86	0.88	71	1.37	61.00	-9.28
9.14	34.93	2090.80	1.10	0.90	76	1.10	61.00	-8.75
9.07	35.18	2090.83	0.18	0.85	76	1.10	61.07	-8.20
9.16	35.21	2089.11	-99.00	0.90	73	1.26	61.25	-7.98
8.27	35.08	2083.42	1.27	-99.00	70	1.43	61.73	-7.42
8.48	35.09	2041.42	1.16	1.47	64	1.79	61.97	-7.82
8.72	35.09	2038.54	0.46	2.01	75	1.15	63.53	-7.92
8.76	35.10	2080.97	0.14	1.14	78	0.99	63.80	-7.68
7.44	34.79	-99.00	-99.00	-99.00	78	0.99	64.08	-7.43
6.61	34.62	2036.83	0.69	-99.00	80	0.89	64.18	-7.33
6.78	34.69	2053.53	0.96	-99.00	82	0.79	64.33	-7.20
6.74	34.67	2052.30	1.19	-99.00	82	0.79	64.50	-7.05
6.68	34.65	2043.64	0.33	-99.00	82	0.79	64.58	-6.97

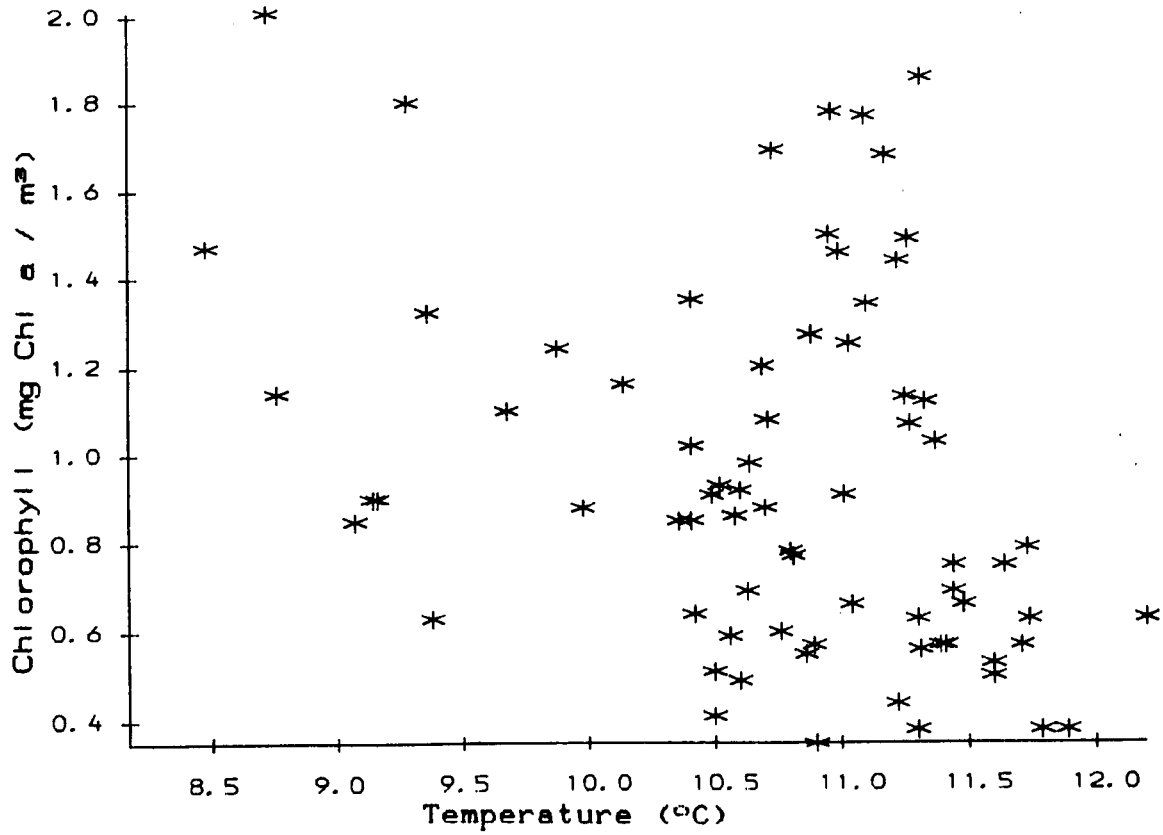
Missing value = -99.00

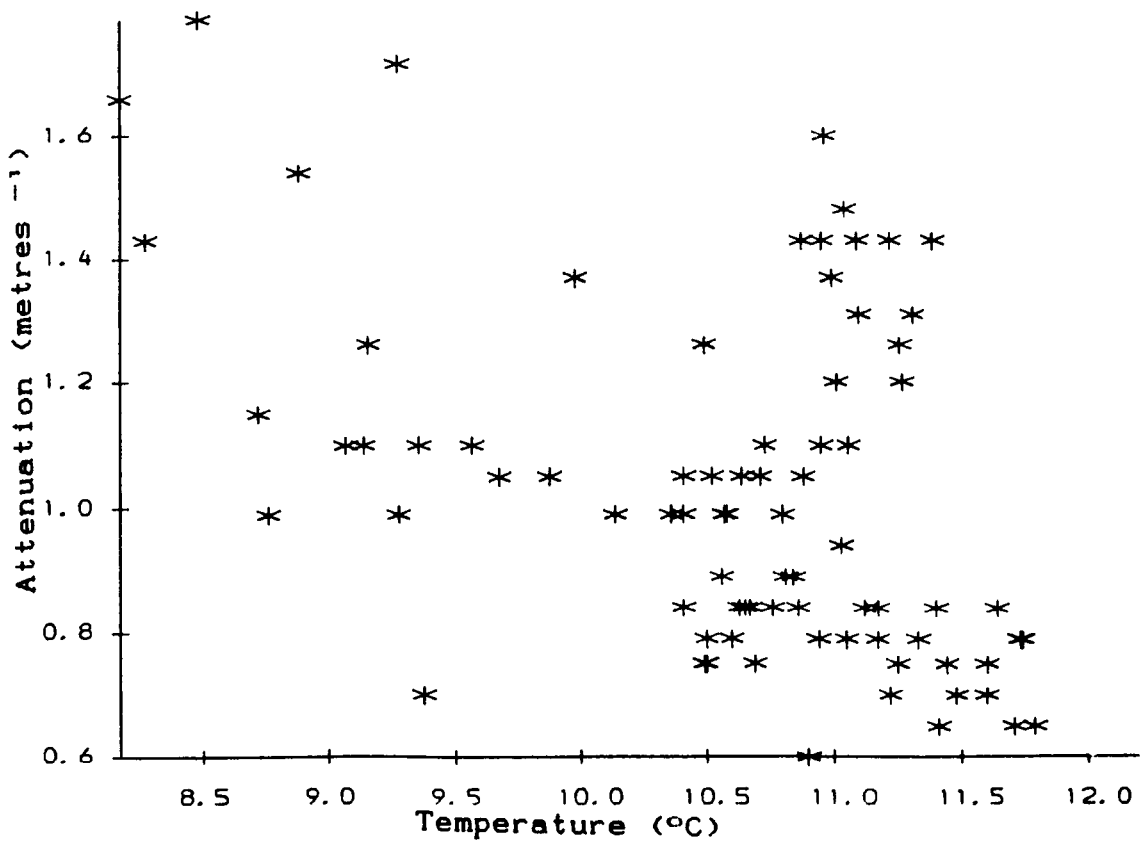
T°C : Temperature
S‰ : Salinity
TCO_2 : Units µmol/kg
SE : Standard error (µmol/kg)
Chl. : Chlorophyll a (mg/m^3)
Tr. : Percentage transmission
Attn. : Attenuation ($metres^{-1}$)
Long. : Longitude
Lat. : Latitude

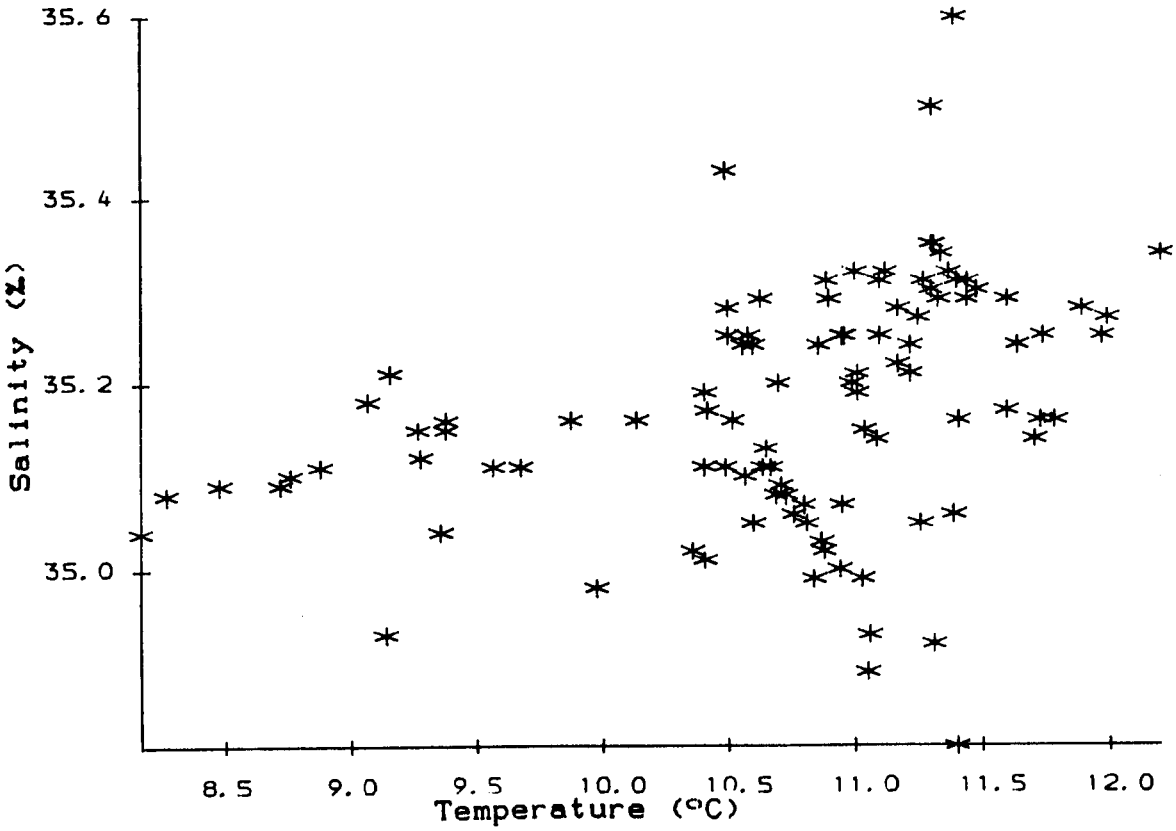
T°C	S‰	TCO_2	SE	Chl.	Tr.	Attn.	Long.	Lat.
11.12	35.32	2079.71	0.04	-99.00	81	0.84	55.03	-10.10
11.17	35.28	2077.93	1.21	1.68	82	0.79	54.97	-10.53
11.25	35.27	2075.62	0.75	1.13	83	0.75	54.97	-10.83
11.33	35.29	2071.85	1.76	1.12	82	0.79	54.95	-11.17
11.17	35.22	2078.11	2.66	-99.00	81	0.84	54.90	-11.60
11.41	35.16	2081.10	1.39	0.57	85	0.65	54.85	-11.75
11.79	35.16	2077.71	2.14	0.38	85	0.65	54.82	-12.00
11.22	35.21	2081.68	0.83	0.44	84	0.70	54.78	-12.50
10.90	35.29	2087.58	0.37	0.35	86	0.60	54.78	-12.75
11.48	35.30	2078.18	0.73	0.66	84	0.70	54.75	-13.00
11.44	35.31	2077.26	0.59	0.75	83	0.75	54.73	-13.33
11.60	35.29	2077.09	0.44	0.53	84	0.70	54.70	-13.63
11.60	35.17	2077.22	0.33	0.50	83	0.75	54.67	-13.92
11.71	35.14	2079.74	0.73	0.57	85	0.65	54.63	-14.32
11.73	35.16	2074.67	0.83	0.79	82	0.79	54.57	-14.85
11.64	35.24	2080.18	1.23	0.75	81	0.84	54.50	-15.22
11.74	35.25	2074.74	0.29	0.63	82	0.79	54.46	-15.57
11.97	35.25	2064.08	0.91	-99.00	-99	-99.00	54.37	-16.48
11.89	35.28	2059.75	0.57	0.38	-99	-99.00	54.42	-16.42
11.99	35.27	2063.67	0.77	-99.00	-99	-99.00	54.52	-16.27
11.34	35.34	2076.58	0.49	-99.00	-99	-99.00	55.43	-15.15
12.20	35.34	2063.97	0.55	0.63	-99	-99.00	55.50	-14.90
11.30	35.30	2079.84	0.36	-99.00	-99	-99.00	55.60	-14.67
11.30	35.35	2081.66	0.58	0.38	-99	-99.00	55.75	-14.18
10.89	35.31	2086.71	0.96	0.57	-99	-99.00	55.88	-13.87
11.39	35.60	2083.22	0.05	0.57	-99	-99.00	56.00	-13.52
11.40	35.31	2084.24	1.41	-99.00	-99	-99.00	56.08	-13.27
11.00	35.32	2075.54	0.81	-99.00	-99	-99.00	56.53	-12.08
11.30	35.50	2076.56	0.55	0.63	-99	-99.00	56.62	-12.65
11.44	35.29	2074.71	0.59	0.69	-99	-99.00	56.68	-13.08
11.31	35.35	2079.83	0.84	0.56	-99	-99.00	56.75	-13.50
11.37	35.32	2071.79	0.72	1.03	-99	-99.00	56.80	-13.80
11.10	35.31	2078.33	1.11	-99.00	-99	-99.00	56.85	-14.08
10.70	35.20	2074.39	1.07	0.88	-99	-99.00	56.87	-14.17
10.42	35.17	2077.08	0.82	0.64	-99	-99.00	56.93	-14.65
10.60	35.24	2080.23	1.22	0.49	-99	-99.00	57.00	-15.05
10.67	35.11	2042.96	0.15	-99.00	81	0.84	57.52	-17.47
10.65	35.13	-99.00	-99.00	-99.00	81	0.84	57.37	-18.08
10.60	35.05	2058.24	1.31	0.92	82	0.79	57.28	-18.37
10.49	35.11	2061.17	1.35	-99.00	83	0.75	57.23	-18.50

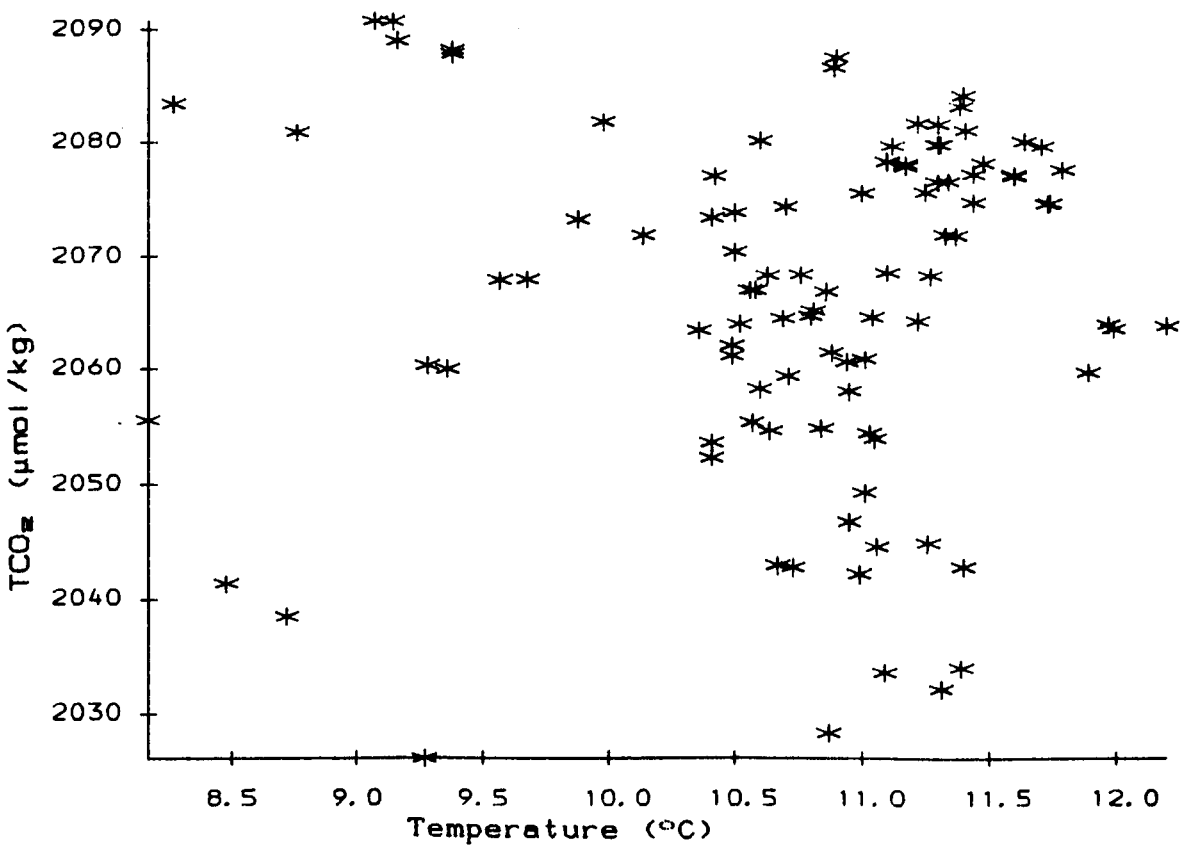
Missing value = -99.00

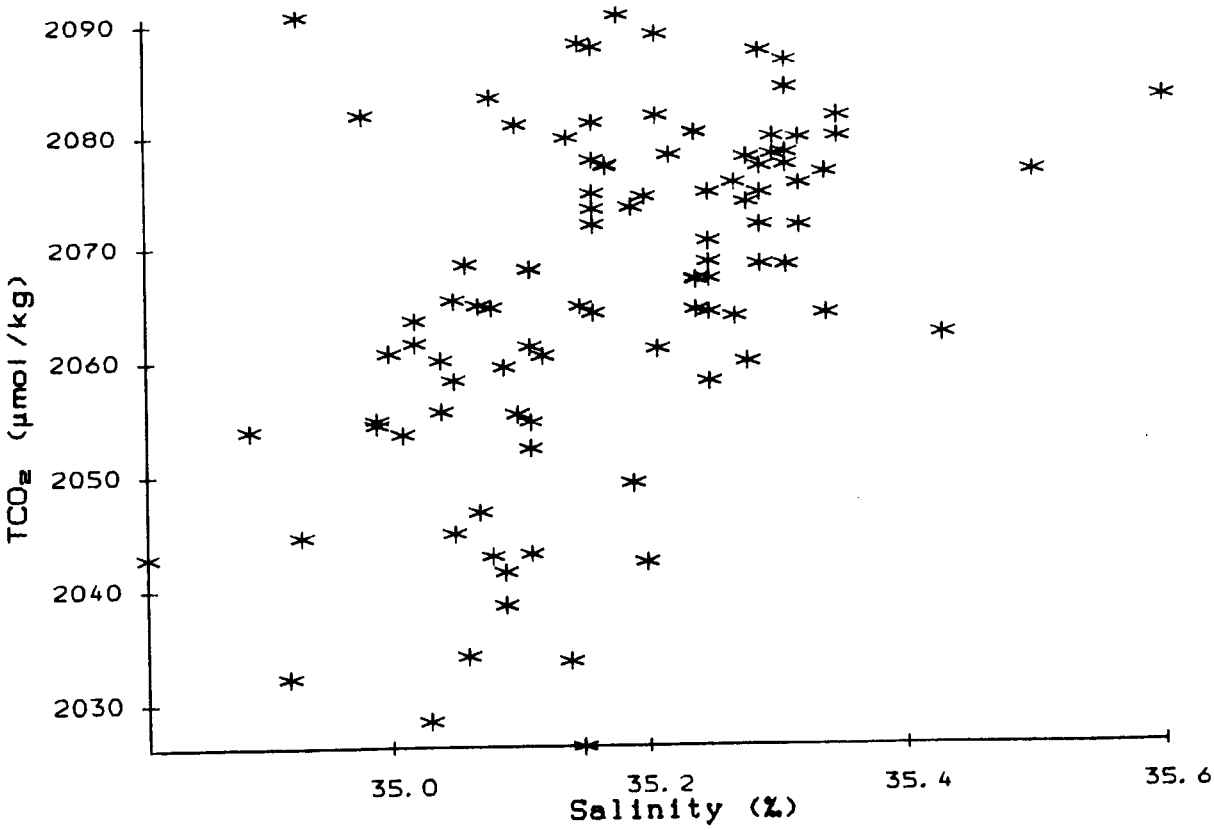
T°C : Temperature
S‰ : Salinity
TCO_2 : Units µmol/kg
SE : Standard error (µmol/kg)
Chl. : Chlorophyll a (mg/m^3)
Tr. : Percentage transmission
Attn. : Attenuation ($metres^{-1}$)
Long. : Longitude

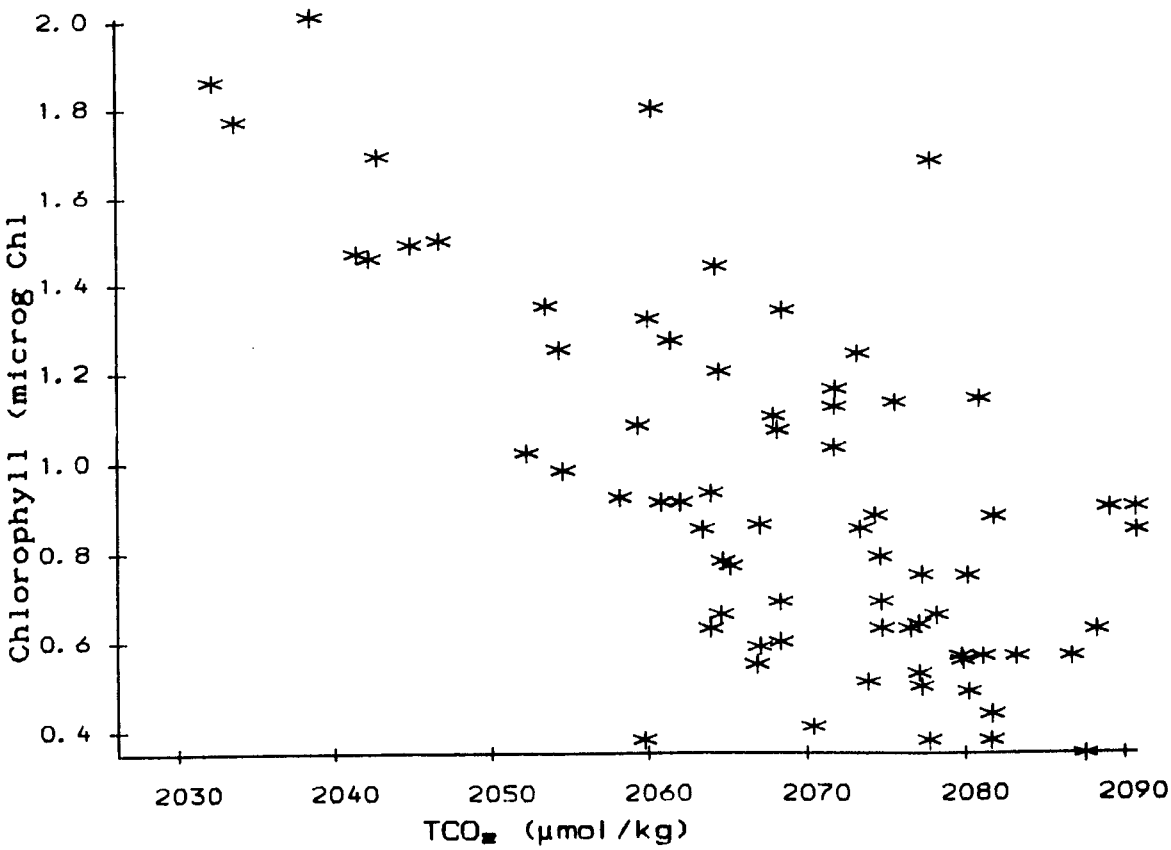

Chlorophyll (mg Chl a / m³)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
Temperature (°C)

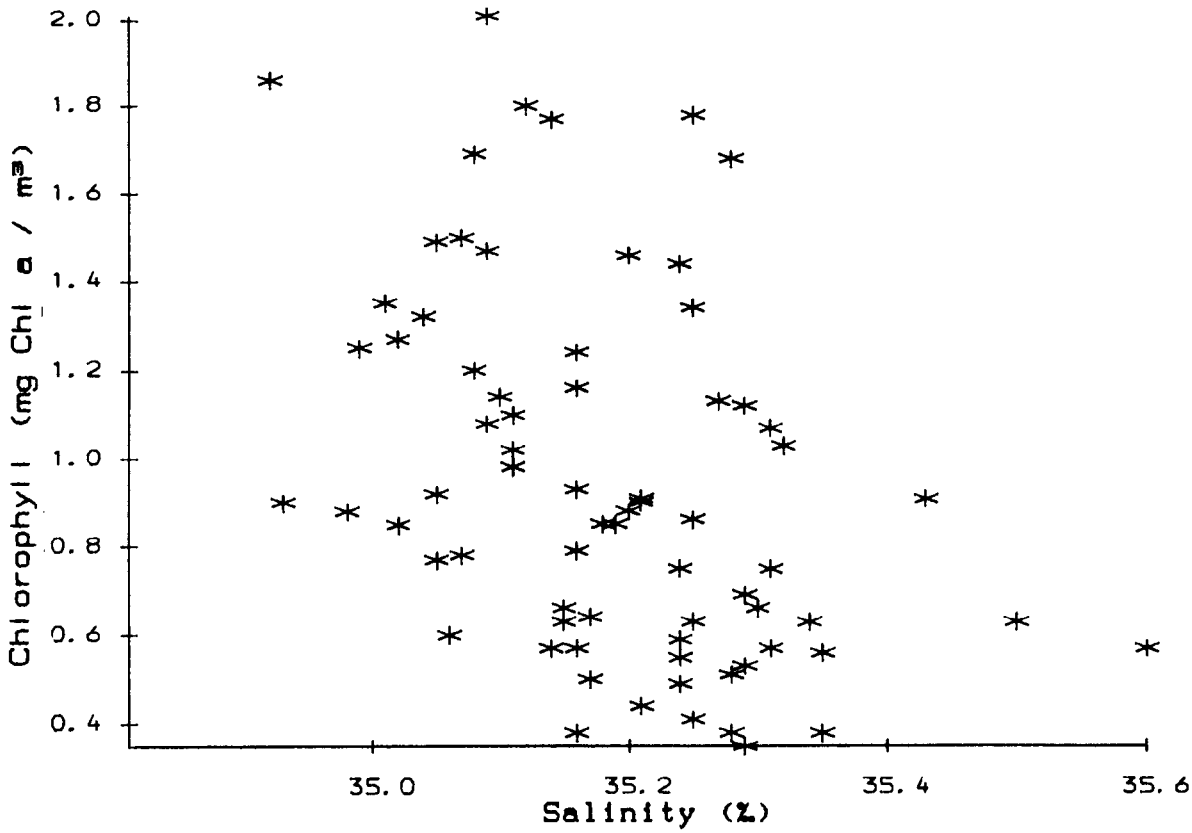

Attenuation (metres⁻¹)
1.6
1.4
1.2
1.0
0.8
0.6
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
Temperature (°C)

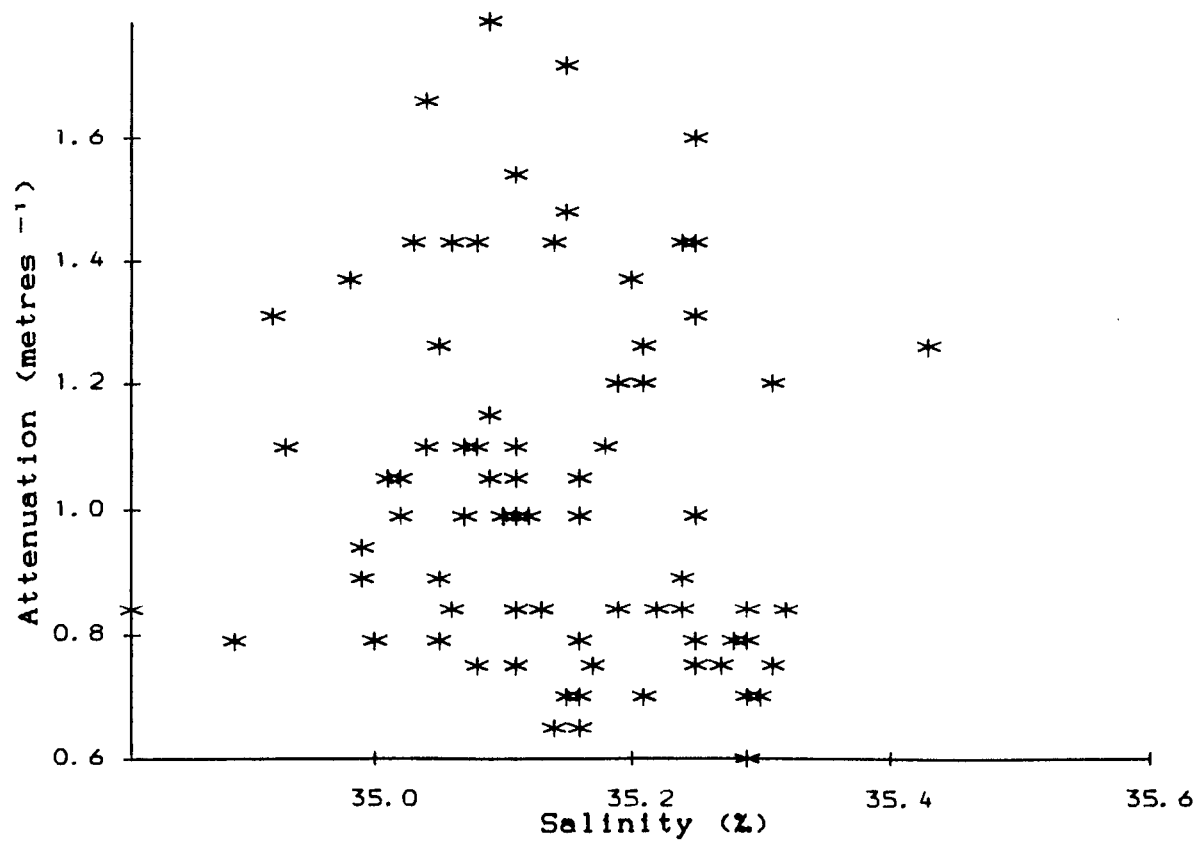

35.6
35.4
35.2
35.0
Salinity (‰)
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
Temperature (°C)

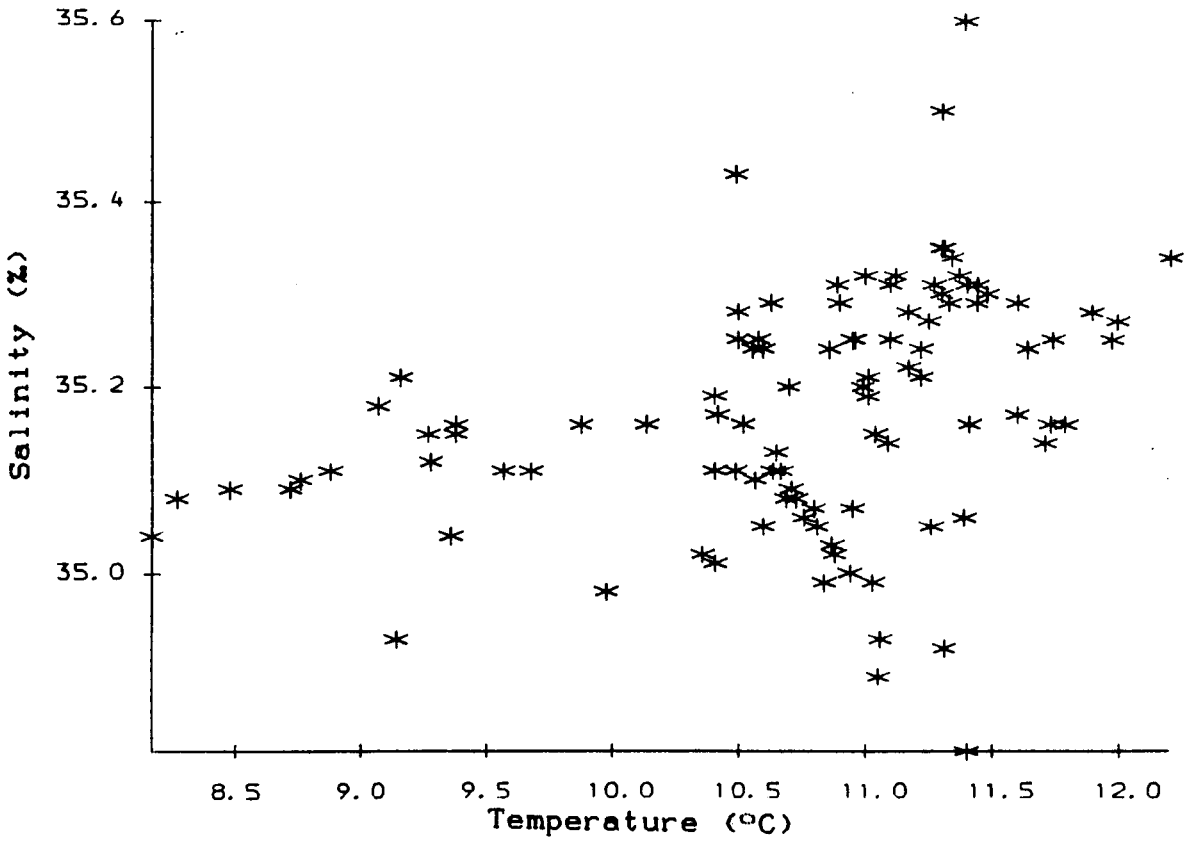

2090
2080
2070
2060
2050
2040
2030
TCO2 (µmol/kg)
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
Temperature (°C)

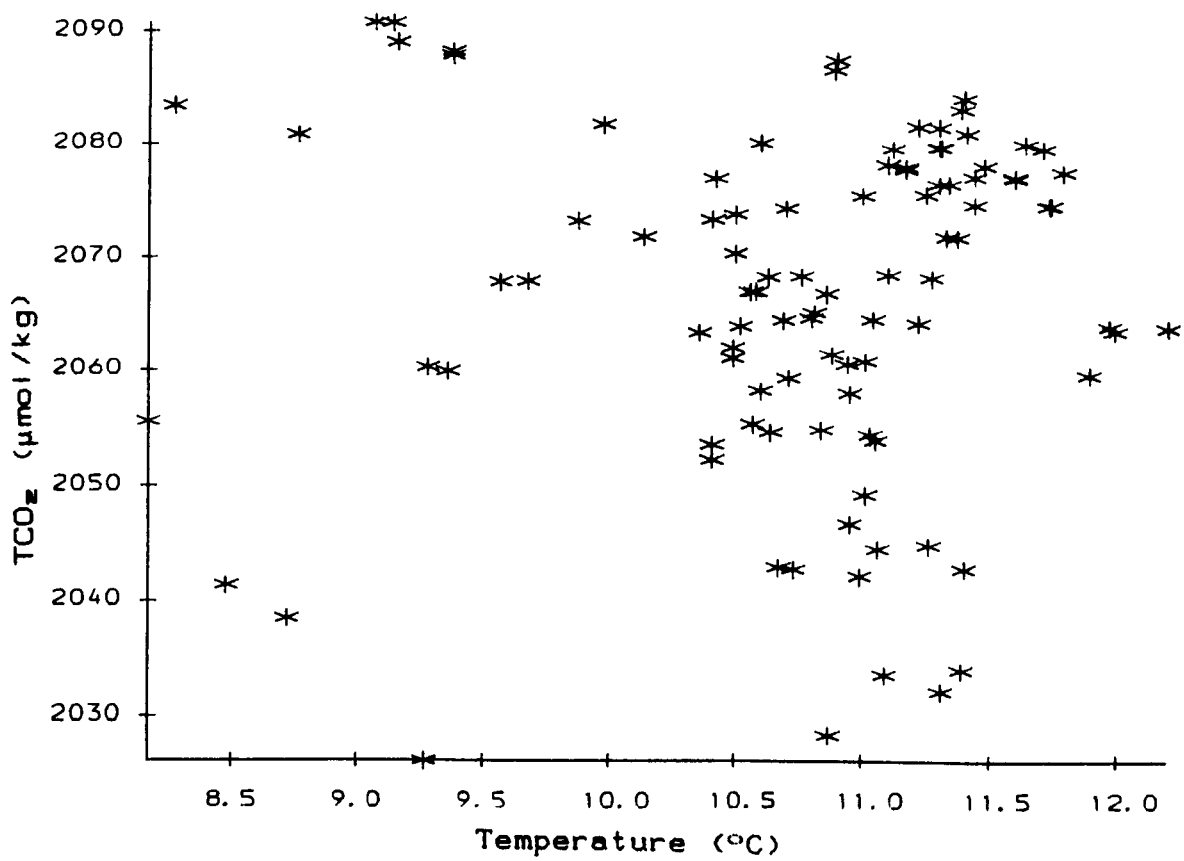

2090
2080
2070
2060
2050
2040
2030
TCO2 (µmol/kg)
35.0
35.2
35.4
35.6
Salinity (%)

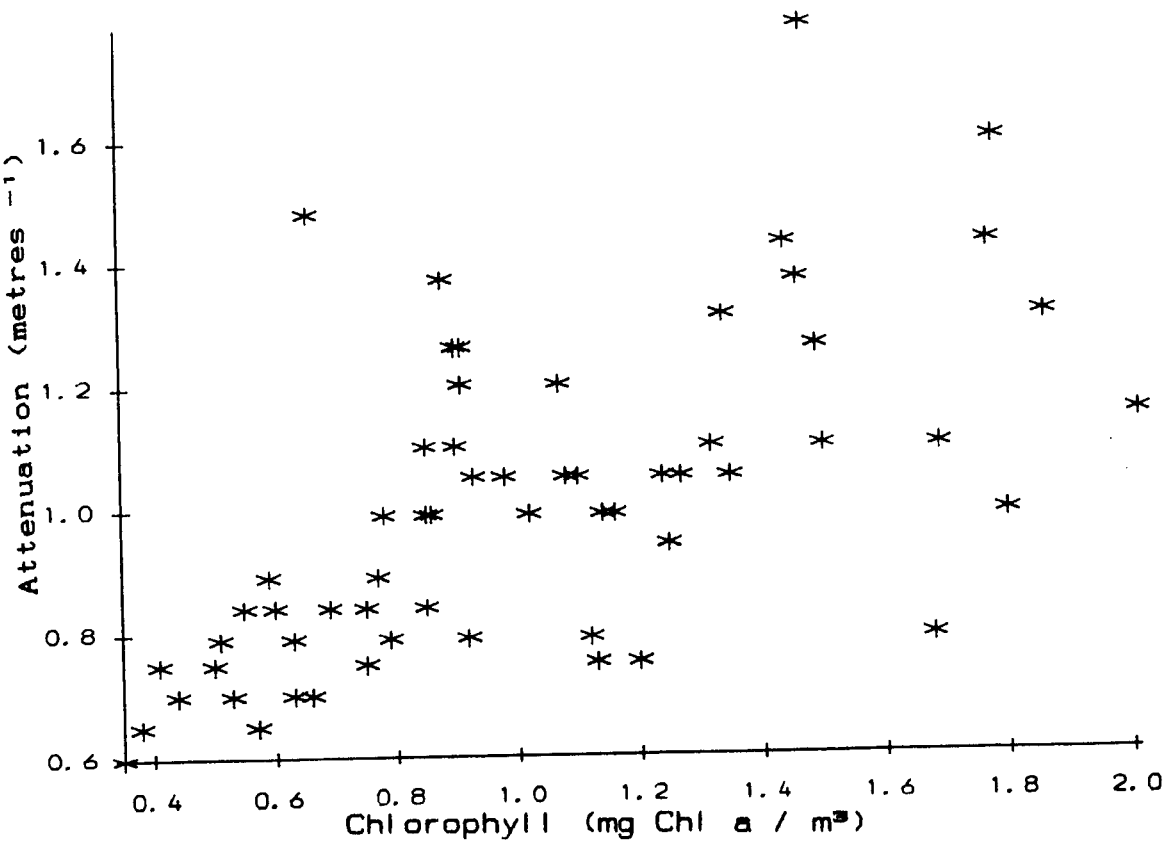

2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
Chlorophyll (microg Chl
2030
2040
2050
2060
2070
2080
2090
TCO2 (µmol/kg)

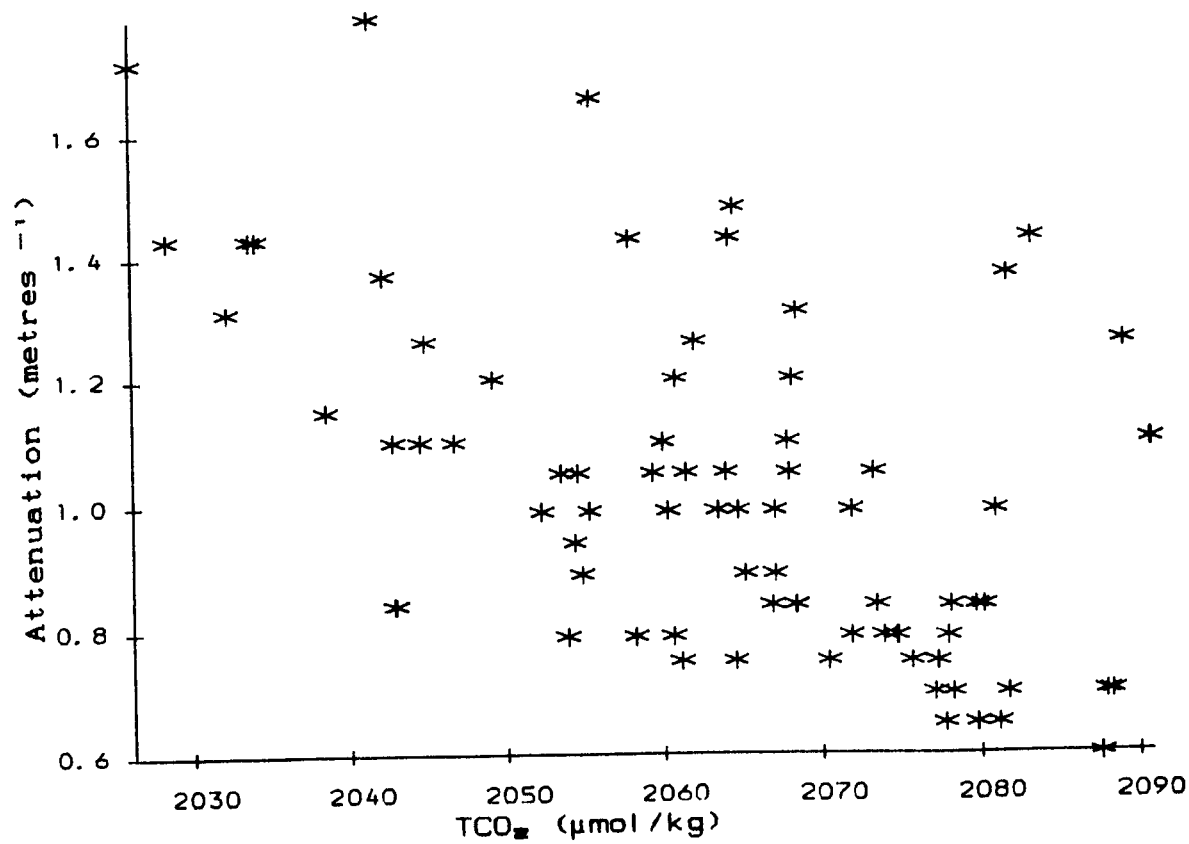

Chlorophyll (mg Chl a / m³)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
35.0
35.2
35.4
35.6
Salinity (‰)


Attenuation (metres⁻¹)
1.6
1.4
1.2
1.0
0.8
0.6
35.0
35.2
35.4
35.6
Salinity (‰)


35.6
35.4
35.2
35.0
Salinity (‰)
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
Temperature (°C)


2090
2080
2070
2060
2050
2040
2030
TCO2 (µmol/kg)
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
Temperature (°C)


Attenuation (metres $^{-1}$)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Chlorophyll (mg Chl a / m^3)


Attenuation (metres $^{-1}$)
1.6
1.4
1.2
1.0
0.8
0.6
2030
2040
2050
2060
2070
2080
2090
TCO_2 (µmol /kg)

DATA APPENDIX

Challenger Cruise

Surface measurements (Rockall)

T°C	S‰	TCO_2	SE	Chl.	Tr.	Attn.	Long.	Lat.
10.60	35.05	2058.24	1.31	0.92	82	0.79	57.28	-18.37
10.49	35.11	2061.17	1.35	-99.00	83	0.75	57.23	-18.50
10.69	35.08	2064.56	1.31	1.20	83	0.75	57.00	-19.48
11.04	35.15	2064.62	0.66	0.66	69	1.48	57.18	-20.02
11.03	34.99	2054.36	0.84	1.25	79	0.94	57.93	-19.98
10.94	35.00	2060.65	1.98	-99.00	82	0.79	58.40	-20.13
10.84	34.99	2054.82	1.14	-99.00	80	0.89	58.25	-19.98
10.88	35.02	2061.48	0.81	1.27	77	1.05	58.23	-19.73
10.76	35.06	2068.40	0.97	0.60	81	0.84	58.47	-19.45
10.81	35.05	2065.21	1.07	0.77	80	0.89	58.65	-19.18
10.80	35.07	2064.75	0.13	0.78	78	0.99	58.85	-18.92
11.06	34.93	2044.57	0.37	-99.00	76	1.10	58.43	-17.98
11.39	35.06	2034.08	1.17	-99.00	70	1.43	59.67	-17.67
10.87	35.03	2028.43	0.99	-99.00	70	1.43	59.85	-17.48
10.73	35.08	2042.82	1.10	1.69	76	1.10	60.03	-17.07
10.95	35.07	2046.72	0.35	1.50	76	1.10	60.00	-16.53
10.41	35.01	2053.54	0.45	1.35	77	1.05	59.98	-15.90
11.05	34.89	2053.90	1.03	-99.00	82	0.79	59.53	-15.13
11.40	34.81	2042.87	0.63	-99.00	81	0.84	59.63	-15.05
11.31	34.92	2032.24	0.64	1.86	72	1.31	59.83	-14.90
10.71	35.09	2059.40	0.40	1.08	77	1.05	60.30	-14.55
10.41	35.11	2052.29	1.27	1.02	78	0.99	60.57	-14.38
10.64	35.11	2054.62	0.15	0.98	77	1.05	60.87	-13.80
10.57	35.10	2055.32	0.75	-99.00	78	0.99	60.80	-13.68
10.95	35.25	2058.02	0.50	-99.00	70	1.43	59.85	-12.05
11.22	35.24	2064.31	0.92	1.44	70	1.43	59.85	-12.05
11.27	35.31	2068.26	0.19	1.07	74	1.20	59.63	-11.95
10.96	35.25	-99.00	-99.00	1.78	67	1.60	59.55	-11.28
11.10	35.25	2068.56	0.87	1.34	72	1.31	59.78	-11.12
11.01	35.21	2060.87	0.98	0.91	74	1.20	59.95	-10.97
10.49	35.43	2062.10	1.96	0.91	73	1.26	60.25	-10.67
10.86	35.24	2066.90	1.32	0.55	81	0.84	59.83	-10.03
11.09	35.14	2033.66	0.43	1.77	70	1.43	59.85	-10.40
11.01	35.19	2049.21	0.77	-99.00	74	1.20	59.85	-11.08
10.99	35.20	2042.23	1.82	1.46	71	1.37	59.88	-11.97
11.26	35.05	2044.87	0.52	1.49	73	1.26	59.88	-12.17
10.52	35.16	2064.03	1.02	0.93	77	1.05	59.67	-12.37

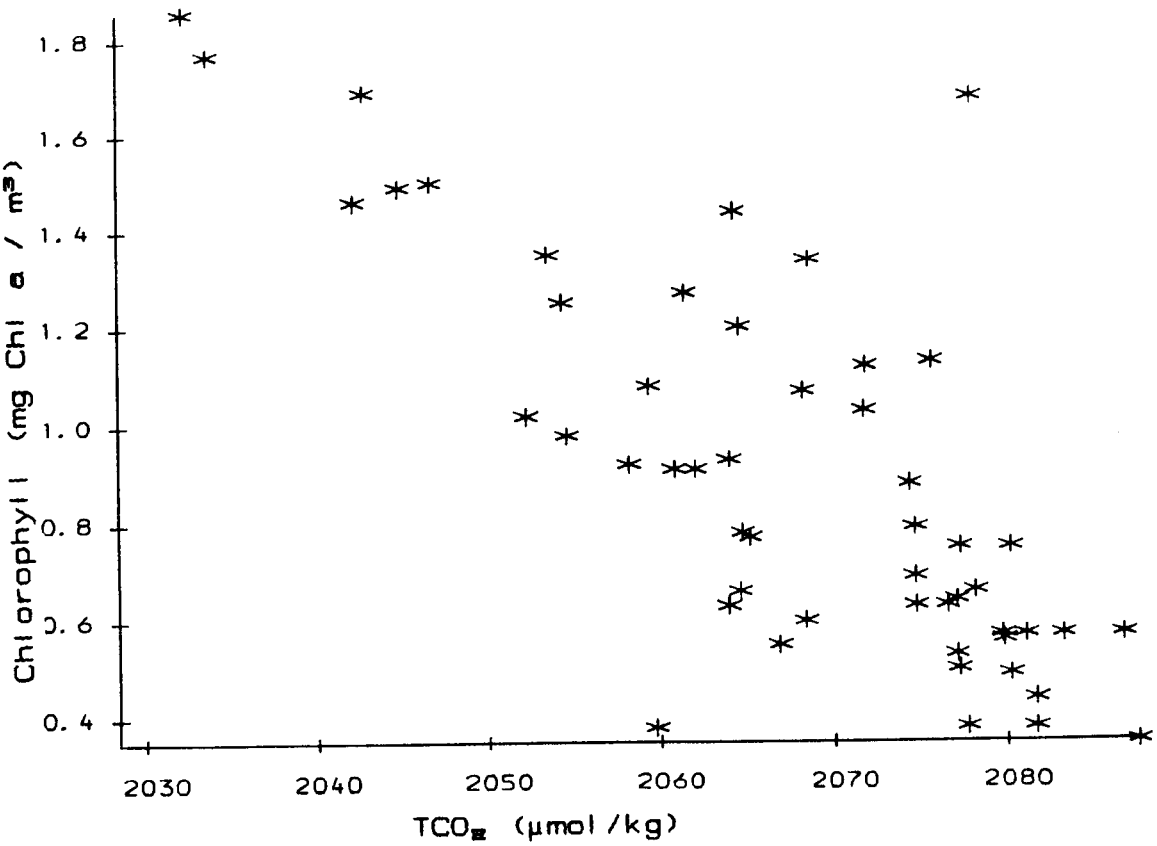
Missing value = -99.00

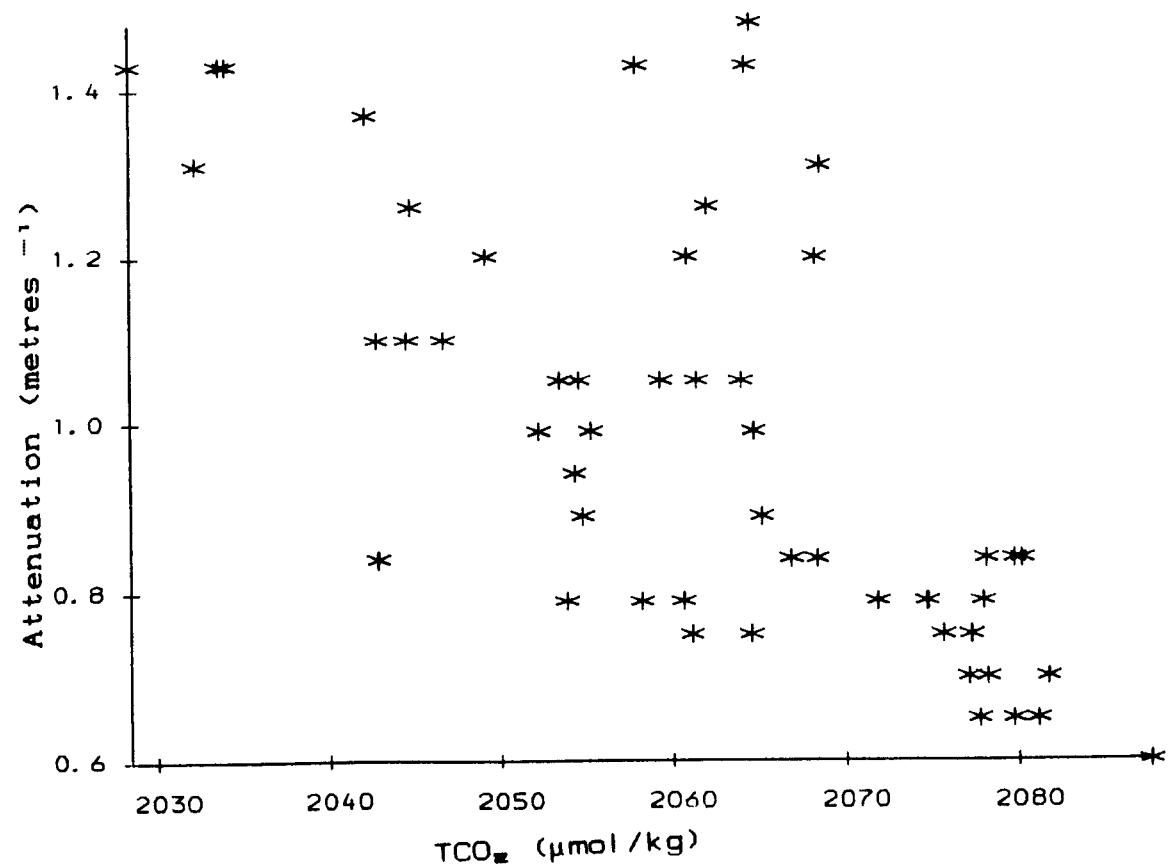
T°C : Temperature
S‰ : Salinity
TCO_2 : Units µmol/kg
SE : Standard error (µmol/kg)
Chl. : Chlorophyll a (mg/m^3)
Tr. : Percentage transmission
Attn. : Attenuation ($metres^{-1}$)
Long. : Longitude
Lat. : Latitude

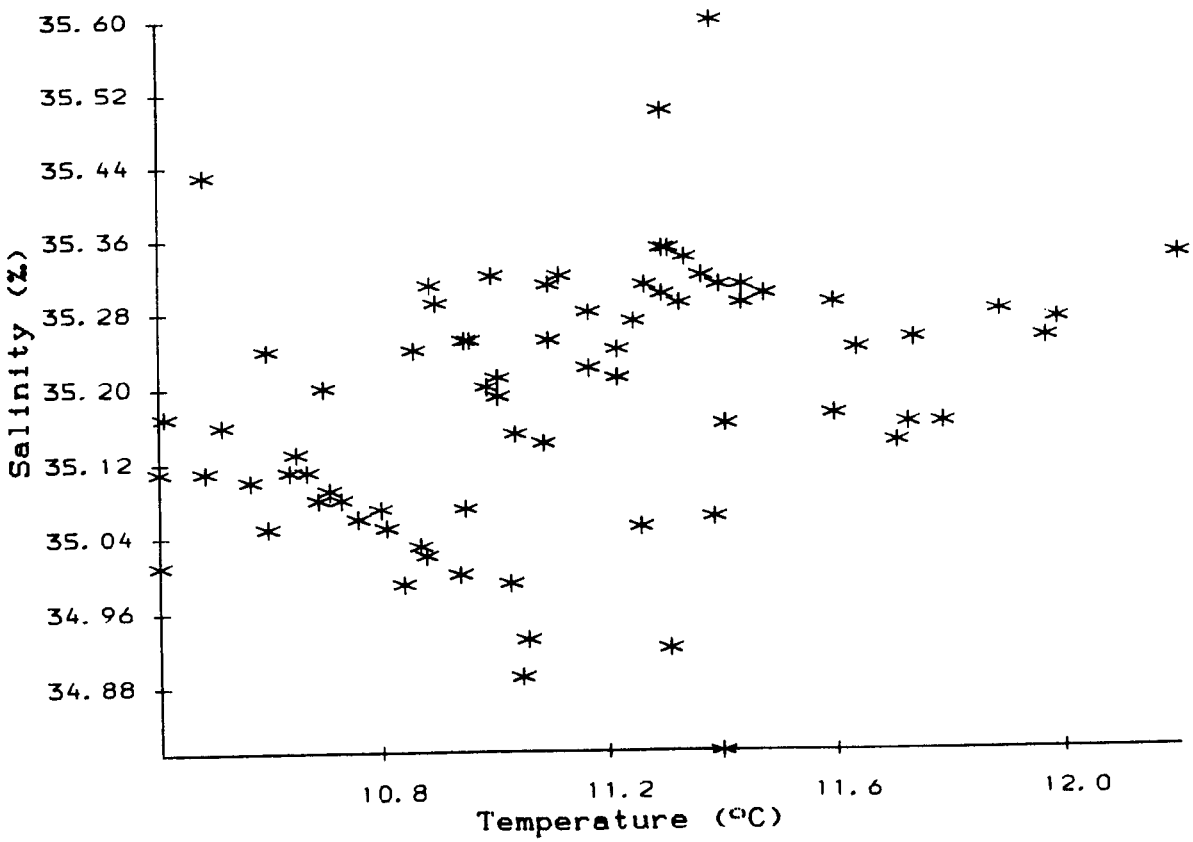
T°C	S‰	TCO_2	SE	Chl.	Tr.	Attn.	Long.	Lat.
11.12	35.32	2079.71	0.04	-99.00	81	0.84	55.03	-10.10
11.17	35.28	2077.93	1.21	1.68	82	0.79	54.97	-10.53
11.25	35.27	2075.62	0.75	1.13	83	0.75	54.97	-10.83
11.33	35.29	2071.85	1.76	1.12	82	0.79	54.95	-11.17
11.17	35.22	2078.11	2.66	-99.00	81	0.84	54.90	-11.60
11.41	35.16	2081.10	1.39	0.57	85	0.65	54.85	-11.75
11.79	35.16	2077.71	2.14	0.38	85	0.65	54.82	-12.00
11.22	35.21	2081.68	0.83	0.44	84	0.70	54.78	-12.50
10.90	35.29	2087.58	0.37	0.35	86	0.60	54.78	-12.75
11.48	35.30	2078.18	0.73	0.66	84	0.70	54.75	-13.00
11.44	35.31	2077.26	0.59	0.75	83	0.75	54.73	-13.33
11.60	35.29	2077.09	0.44	0.53	84	0.70	54.70	-13.63
11.60	35.17	2077.22	0.33	0.50	83	0.75	54.67	-13.92
11.71	35.14	2079.74	0.73	0.57	85	0.65	54.63	-14.32
11.73	35.16	2074.67	0.83	0.79	82	0.79	54.57	-14.85
11.64	35.24	2080.18	1.23	0.75	81	0.84	54.50	-15.22
11.74	35.25	2074.74	0.29	0.63	82	0.79	54.46	-15.57
11.97	35.25	2064.08	0.91	-99.00	-99	-99.00	54.37	-16.48
11.89	35.28	2059.75	0.57	0.38	-99	-99.00	54.42	-16.42
11.99	35.27	2063.67	0.77	-99.00	-99	-99.00	54.52	-16.27
11.34	35.34	2076.58	0.49	-99.00	-99	-99.00	55.43	-15.15
12.20	35.34	2063.97	0.55	0.63	-99	-99.00	55.50	-14.90
11.30	35.30	2079.84	0.36	-99.00	-99	-99.00	55.60	-14.67
11.30	35.35	2081.66	0.58	0.38	-99	-99.00	55.75	-14.18
10.89	35.31	2086.71	0.96	0.57	-99	-99.00	55.88	-13.87
11.39	35.60	2083.22	0.05	0.57	-99	-99.00	56.00	-13.52
11.40	35.31	2084.24	1.41	-99.00	-99	-99.00	56.08	-13.27
11.00	35.32	2075.54	0.81	-99.00	-99	-99.00	56.53	-12.08
11.30	35.50	2076.56	0.55	0.63	-99	-99.00	56.62	-12.65
11.44	35.29	2074.71	0.59	0.69	-99	-99.00	56.68	-13.08
11.31	35.35	2079.83	0.84	0.56	-99	-99.00	56.75	-13.50
11.37	35.32	2071.79	0.72	1.03	-99	-99.00	56.80	-13.80
11.10	35.31	2078.33	1.11	-99.00	-99	-99.00	56.85	-14.08
10.70	35.20	2074.39	1.07	0.88	-99	-99.00	56.87	-14.17
10.42	35.17	2077.08	0.82	0.64	-99	-99.00	56.93	-14.65
10.60	35.24	2080.23	1.22	0.49	-99	-99.00	57.00	-15.05
10.67	35.11	2042.96	0.15	-99.00	81	0.84	57.52	-17.47
10.65	35.13	-99.00	-99.00	-99.00	81	0.84	57.37	-18.08

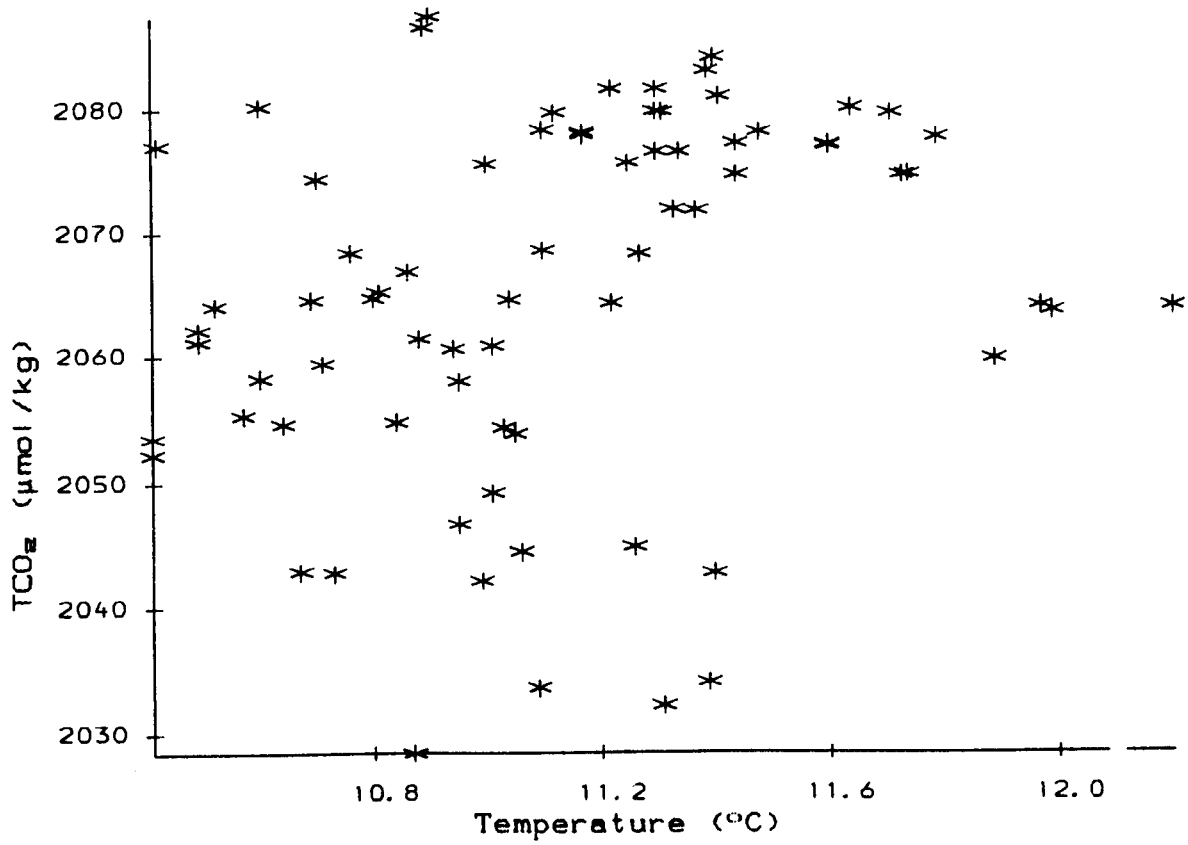
Missing value = -99.00

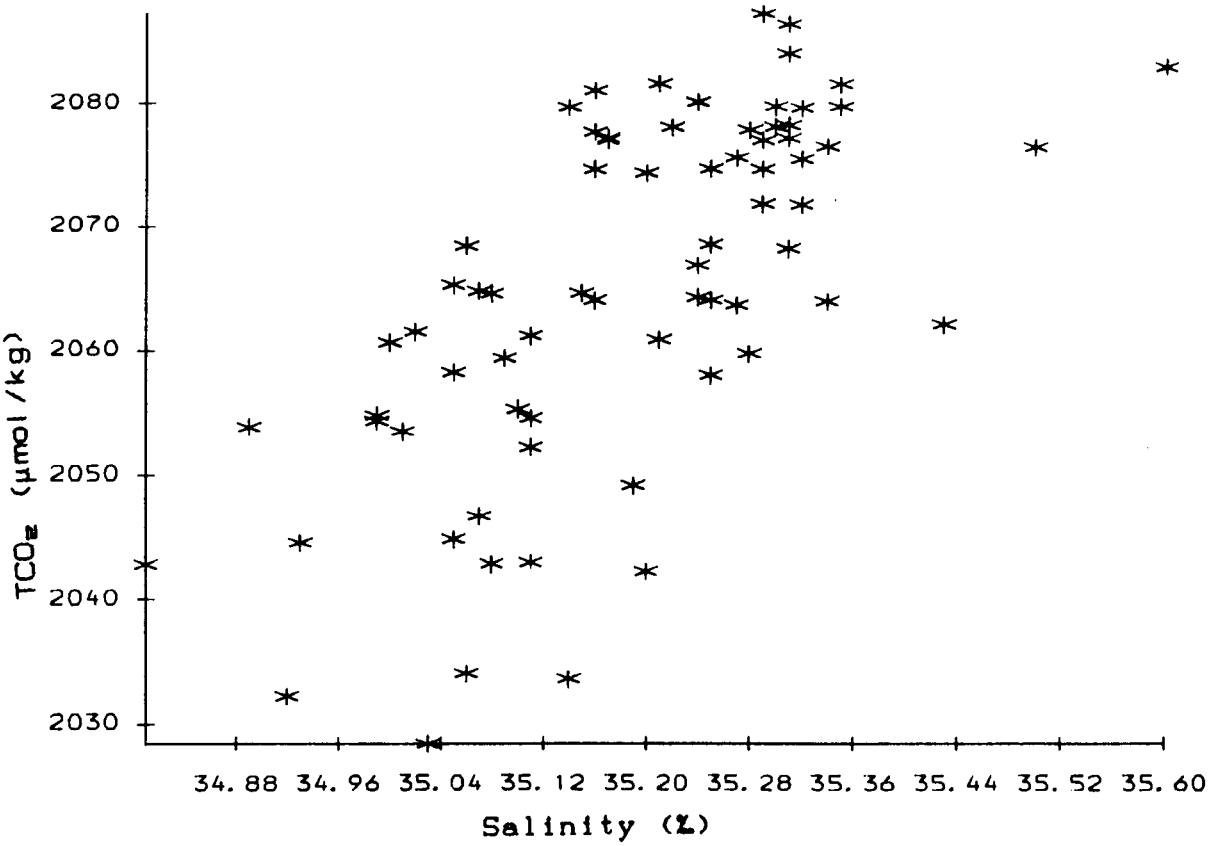
T°C : Temperature
S‰ : Salinity
TCO_2 : Units µmol/kg
SE : Standard error (µmol/kg)
Chl. : Chlorophyll a (mg/m^3)
Tr. : Percentage transmission
Attn. : Attenuation ($metres^{-1}$)
Long. : Longitude
Lat. : Latitude

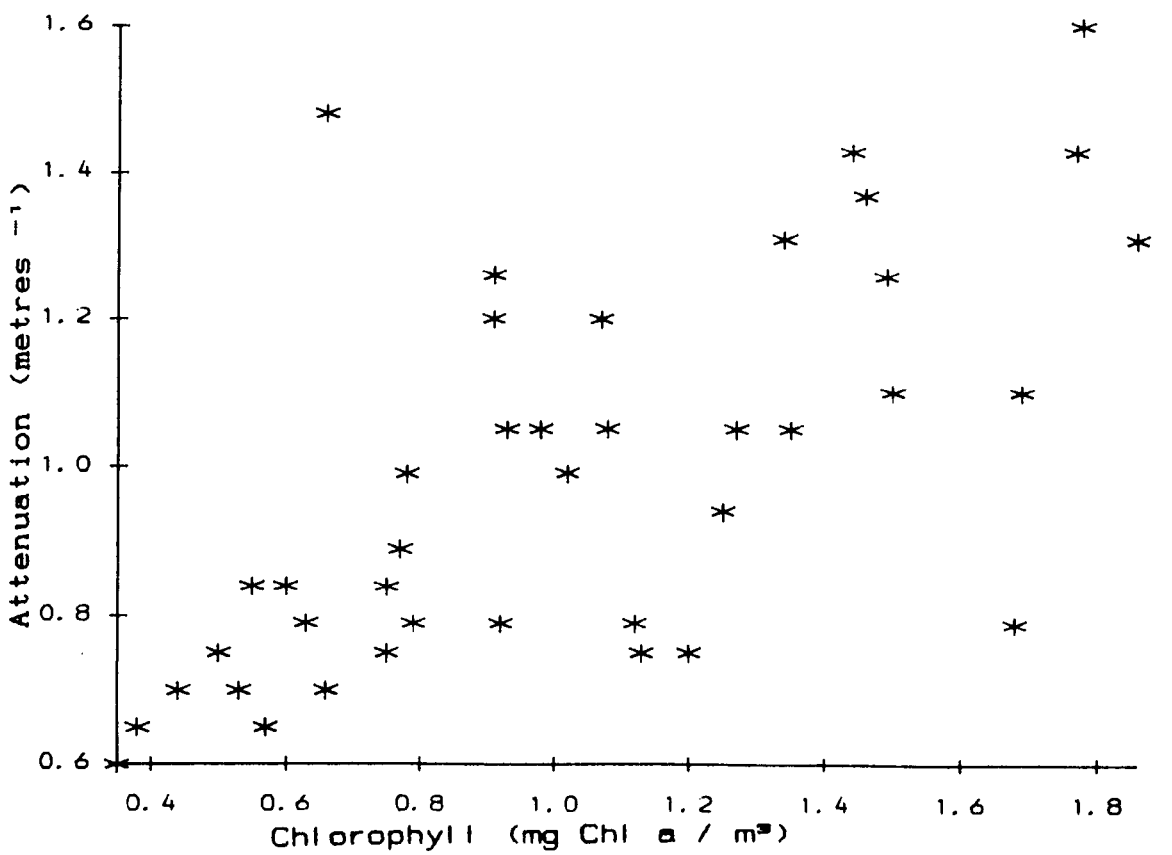

Chlorophyll (mg Chl a / m³)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
2030
2040
2050
2060
2070
2080
TCO₂ (µmol/kg)

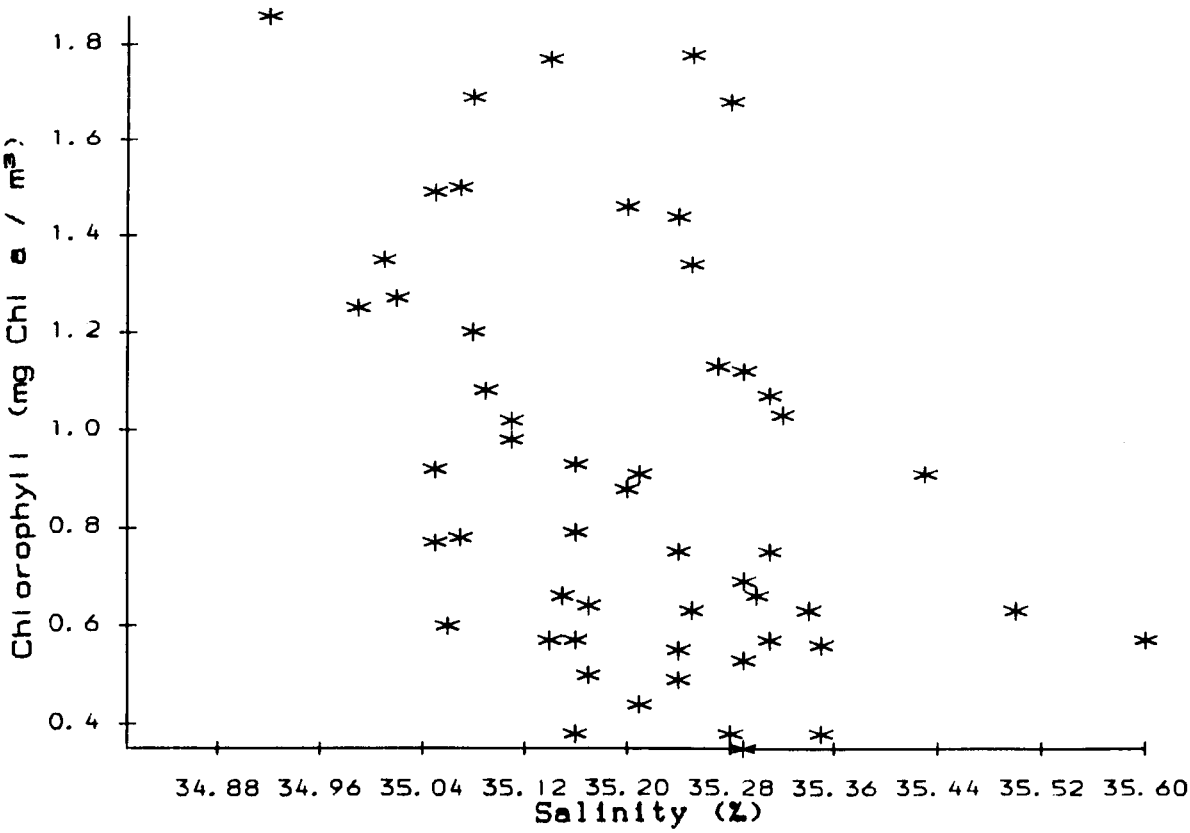

Attenuation (metres⁻¹)
1.4
1.2
1.0
0.8
0.6
2030
2040
2050
2060
2070
2080
TCO₂ (µmol/kg)

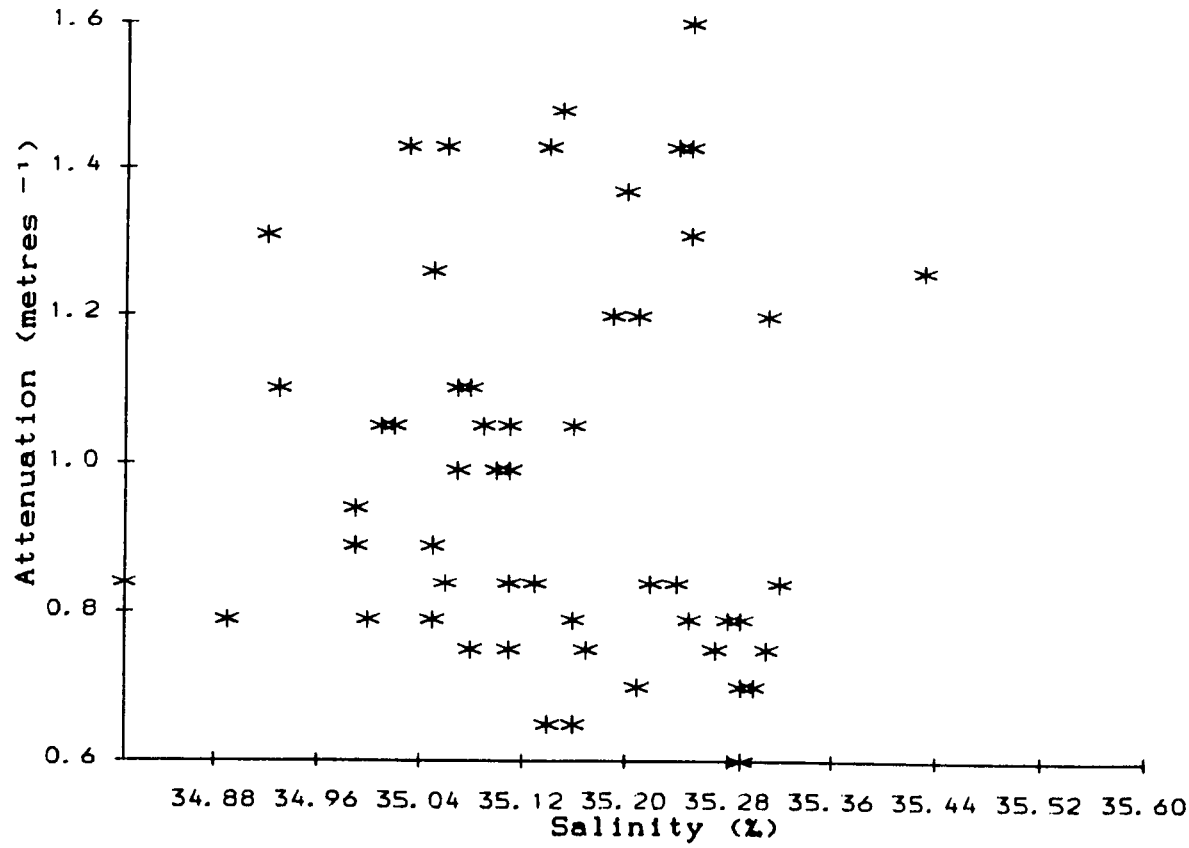

35.60
35.52
35.44
35.36
35.28
35.20
35.12
35.04
34.96
34.88
Salinity (‰)
10.8
11.2
11.6
12.0
Temperature (°C)

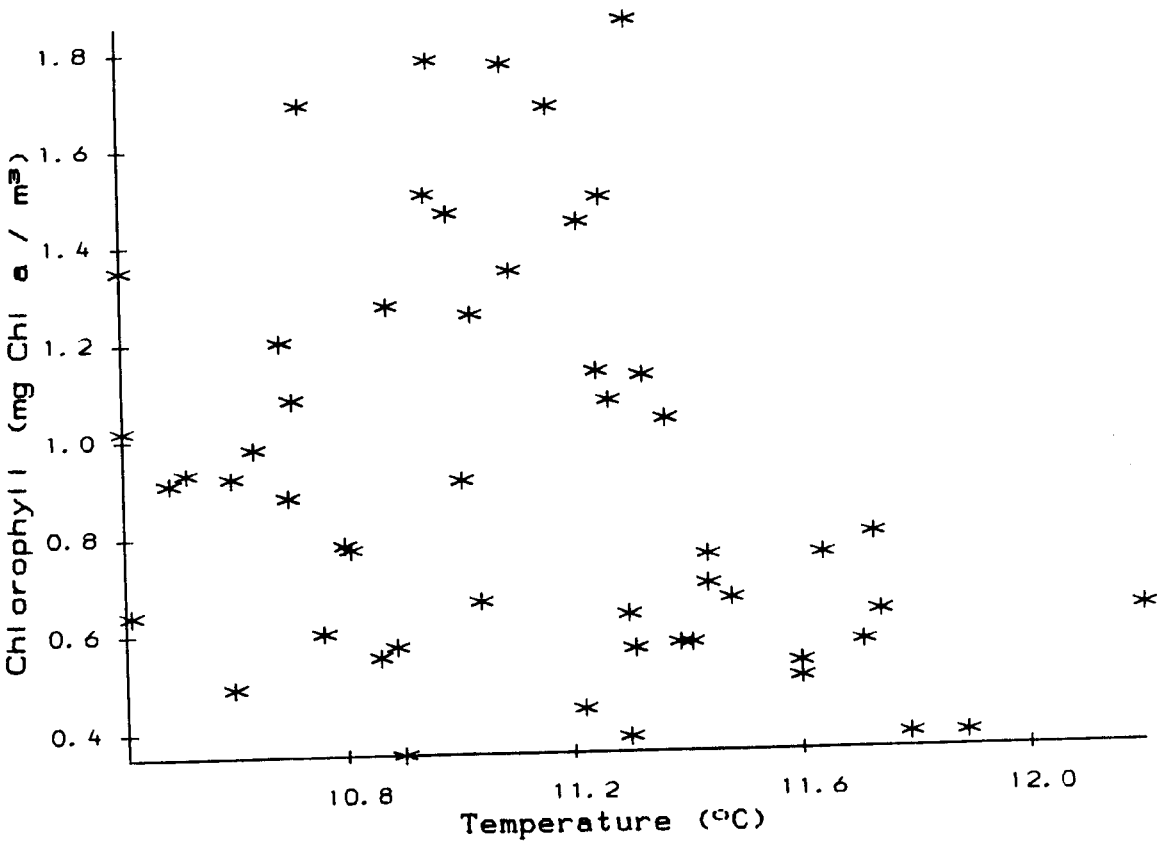

2080
2070
2060
2050
2040
2030
TCO2 (µmol/kg)
10.8
11.2
11.6
12.0
Temperature (°C)

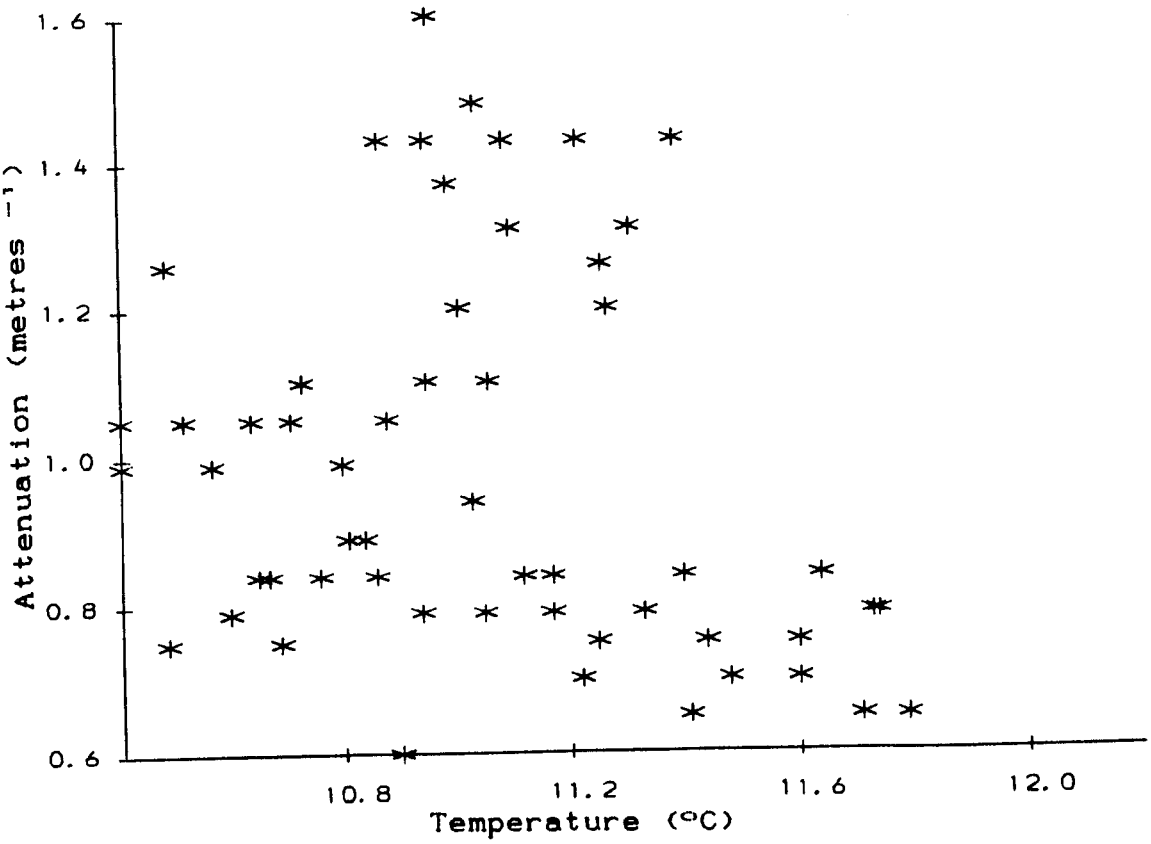

2080
2070
2060
2050
2040
2030
TCO2 (µmol/kg)
34.88 34.96 35.04 35.12 35.20 35.28 35.36 35.44 35.52 35.60
Salinity (‰)


1.6
1.4
1.2
1.0
0.8
0.6
Attenuation (metres⁻¹)
0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8
Chlorophyll (mg Chl a / m³)


Chlorophyll (mg Chl a / m³)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
34.88 34.96 35.04 35.12 35.20 35.28 35.36 35.44 35.52 35.60
Salinity (‰)


Attenuation (metres⁻¹)
1.6
1.4
1.2
1.0
0.8
0.6
34.88 34.96 35.04 35.12 35.20 35.28 35.36 35.44 35.52 35.60
Salinity (‰)


Chlorophyll (mg Chl a / m³)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
10.8
11.2
11.6
12.0
Temperature (°C)


Attenuation (metres⁻¹)
1.6
1.4
1.2
1.0
0.8
0.6
10.8
11.2
11.6
12.0
Temperature (°C)

DATA APPENDIX

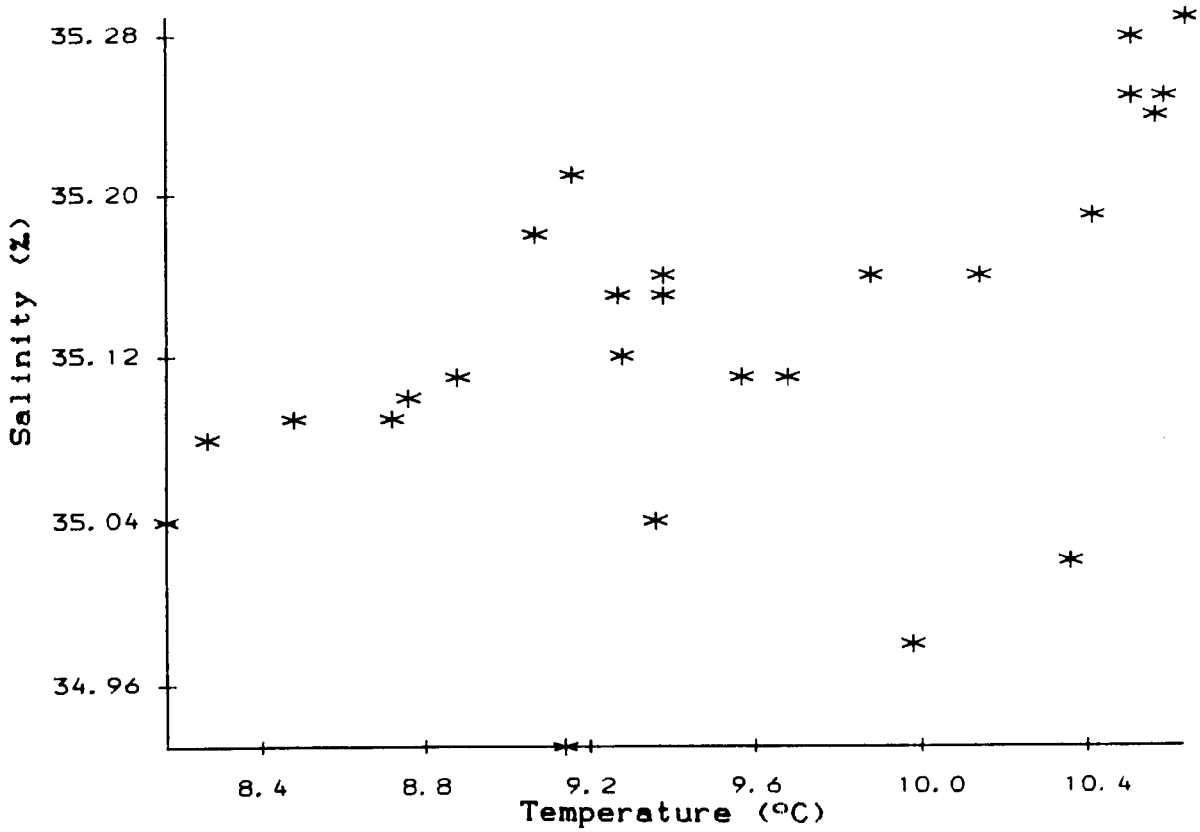
Challenger Cruise

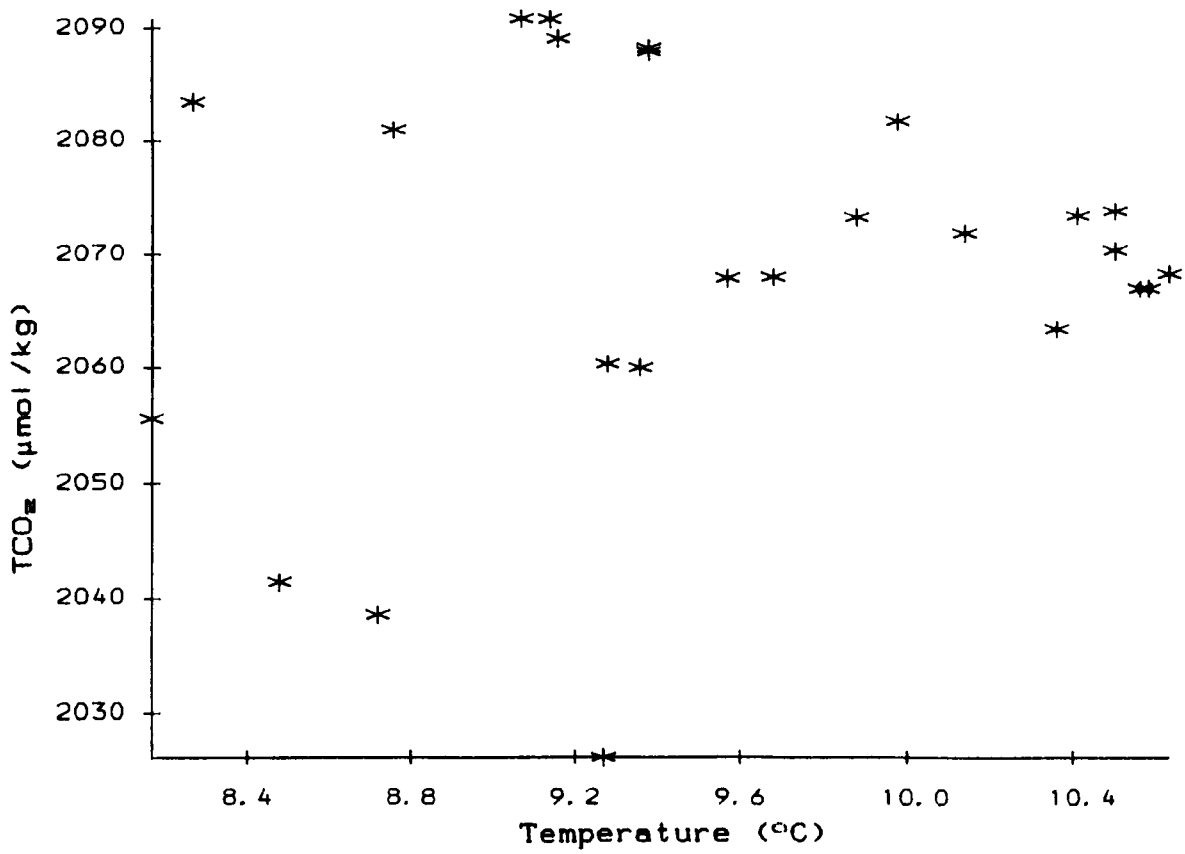
Surface measurements (Faroes)

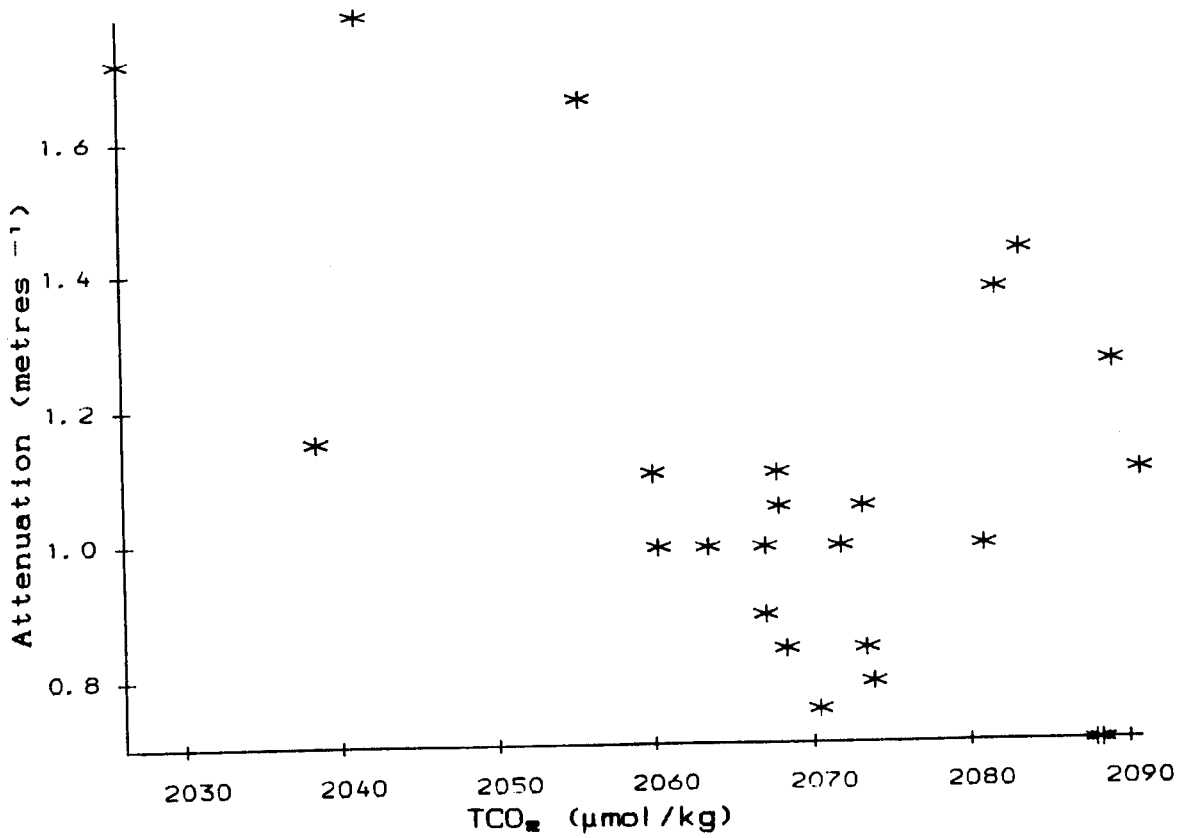
T°C	S‰	TCO_2	SE	Chl.	Tr.	Attn.	Long.	Lat.
9.98	34.98	2081.83	0.86	0.88	71	1.37	61.00	-9.28
9.14	34.93	2090.80	1.10	0.90	76	1.10	61.00	-8.75
9.07	35.18	2090.83	0.18	0.85	76	1.10	61.07	-8.20
9.16	35.21	2089.11	-99.00	0.90	73	1.26	61.25	-7.98
8.27	35.08	2083.42	1.27	-99.00	70	1.43	61.73	-7.42
8.48	35.09	2041.42	1.16	1.47	64	1.79	61.97	-7.82
8.72	35.09	2038.54	0.46	2.01	75	1.15	63.53	-7.92
8.76	35.10	2080.97	0.14	1.14	78	0.99	63.80	-7.68
8.17	35.04	2055.61	0.26	-99.00	66	1.66	61.90	-6.70
8.88	35.11	-99.00	-99.00	-99.00	68	1.54	62.13	-6.13
9.27	35.15	2026.14	1.30	-99.00	65	1.72	62.30	-5.85
9.28	35.12	2060.35	1.49	1.80	78	0.99	62.48	-5.45
9.38	35.15	2088.29	0.43	0.63	84	0.70	62.87	-4.72
9.38	35.16	2087.94	1.42	-99.00	84	0.70	63.07	-4.40
9.57	35.11	2067.93	0.68	-99.00	76	1.10	63.47	-3.07
9.68	35.11	2068.01	1.14	1.10	77	1.05	63.08	-2.73
10.36	35.02	2063.47	0.97	0.85	78	0.99	62.87	-2.55
9.36	35.04	2060.04	0.57	1.32	76	1.10	62.62	-2.50
9.88	35.16	2073.32	1.31	1.24	77	1.05	62.27	-2.45
10.14	35.16	2071.87	0.33	1.16	78	0.99	61.97	-2.53
10.41	35.19	2073.46	1.02	0.85	81	0.84	61.67	-2.48
10.56	35.24	2067.06	0.46	0.59	80	0.89	61.00	-1.43
10.50	35.25	2070.44	1.10	0.41	83	0.75	61.00	-2.40
10.58	35.25	2067.07	0.78	0.86	78	0.99	61.00	-3.08
10.63	35.29	2068.37	1.20	0.69	81	0.84	60.58	-3.67
10.50	35.28	2073.88	1.04	0.51	82	0.79	61.00	-4.33

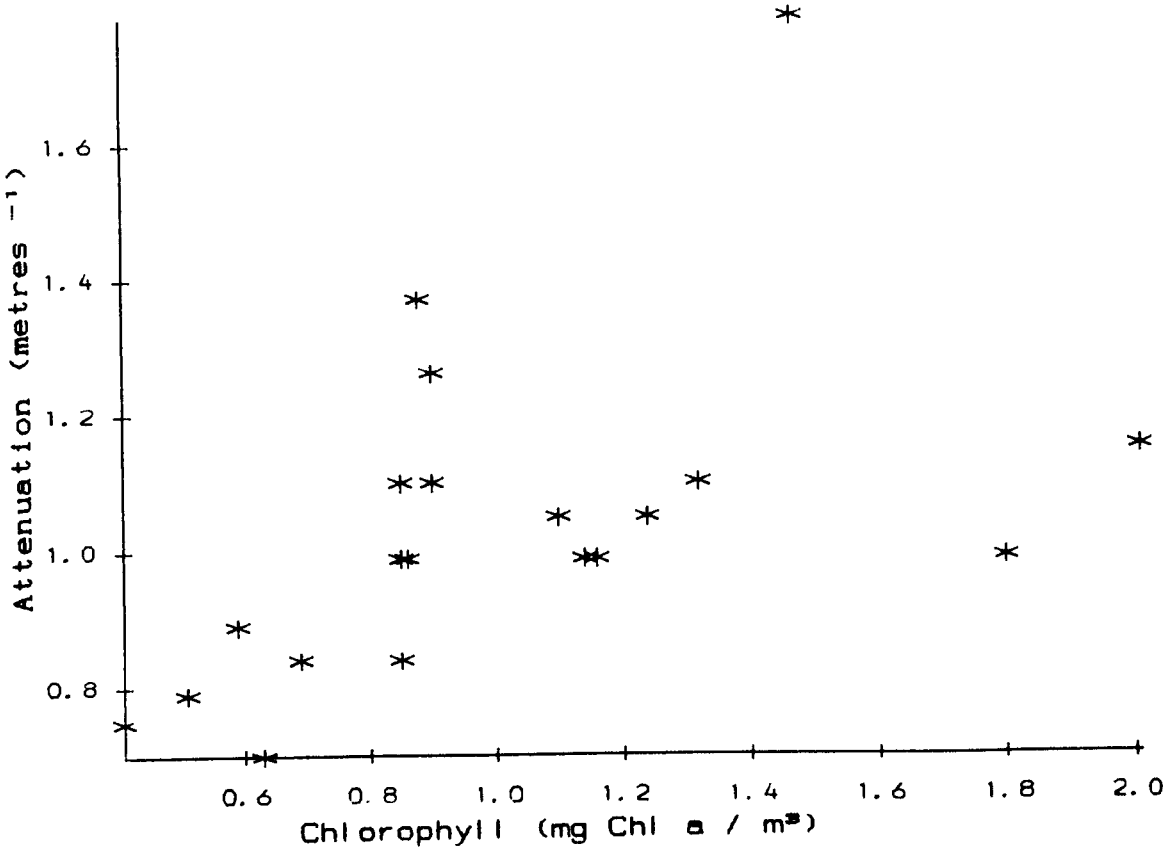
Missing value = -99.00

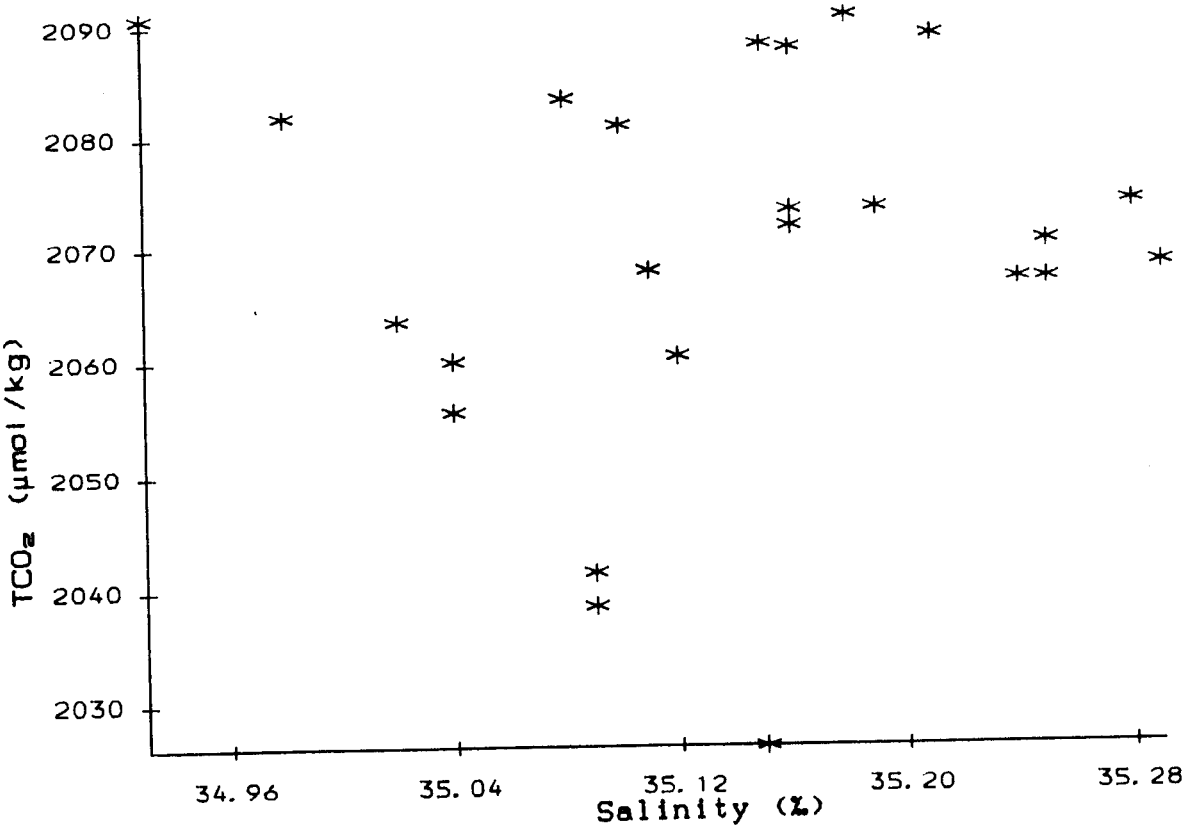
T°C : Temperature
S‰ : Salinity
TCO_2 : Units µmol/kg
SE : Standard error (µmol/kg)
Chl. : Chlorophyll a (mg/m^3)
Tr. : Percentage transmission
Attn. : Attenuation ($metres^{-1}$)
Long. : Longitude
Lat. : Latitude

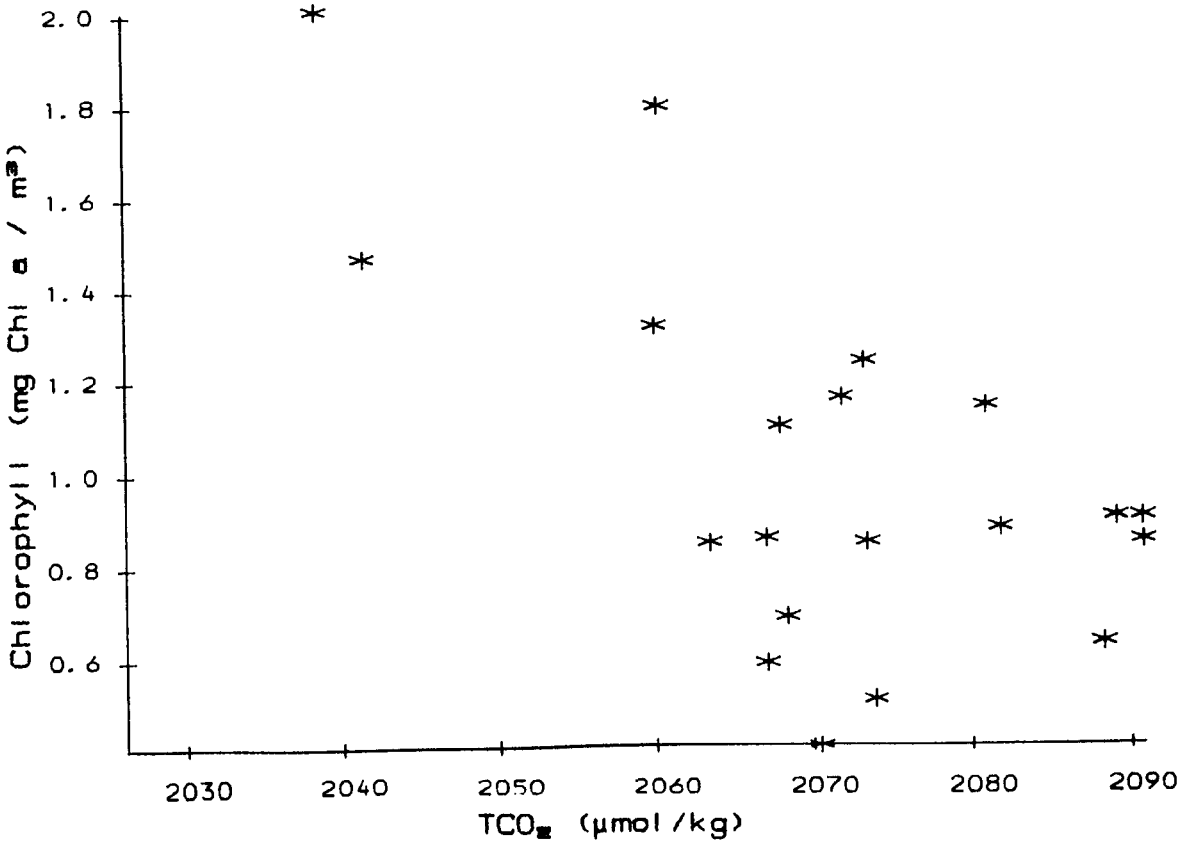

35.28
35.20
35.12
35.04
34.96
Salinity (‰)
8.4
8.8
9.2
9.6
10.0
10.4
Temperature (°C)

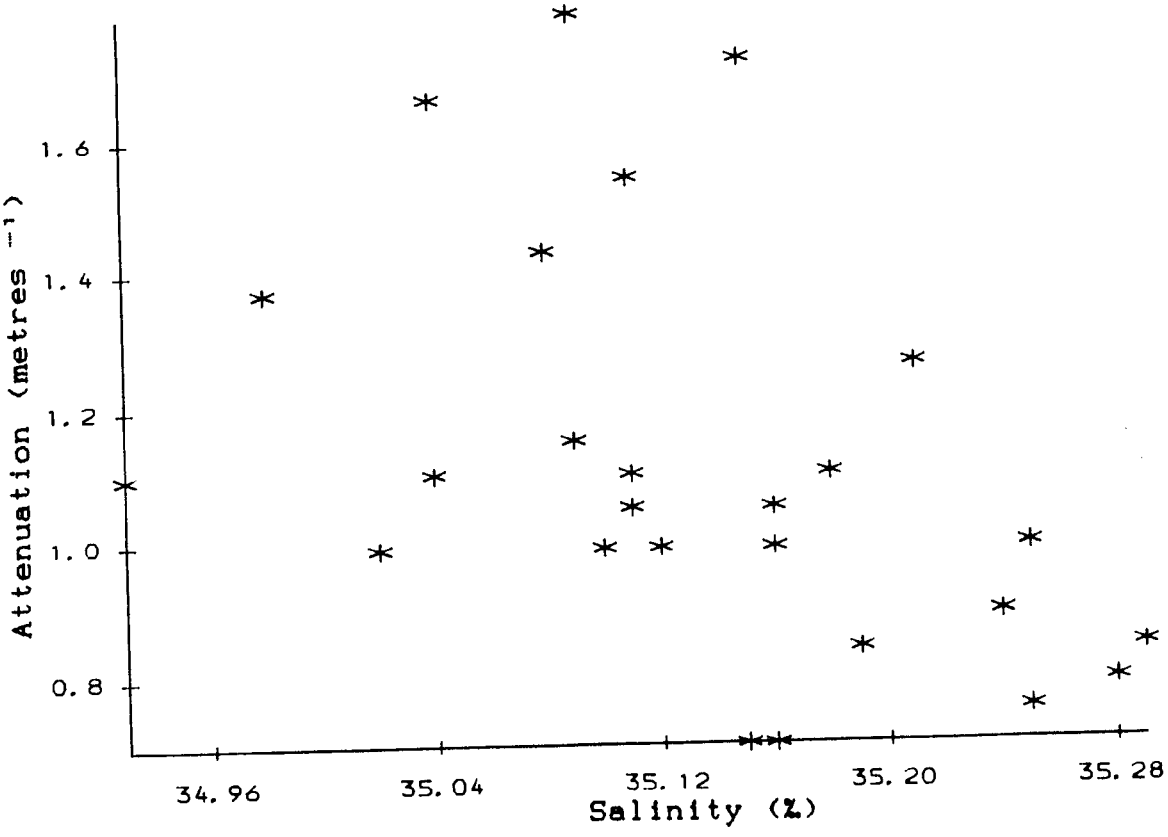

2090
2080
2070
2060
2050
2040
2030
TCO2 (µmol/kg)
8.4
8.8
9.2
9.6
10.0
10.4
Temperature (°C)

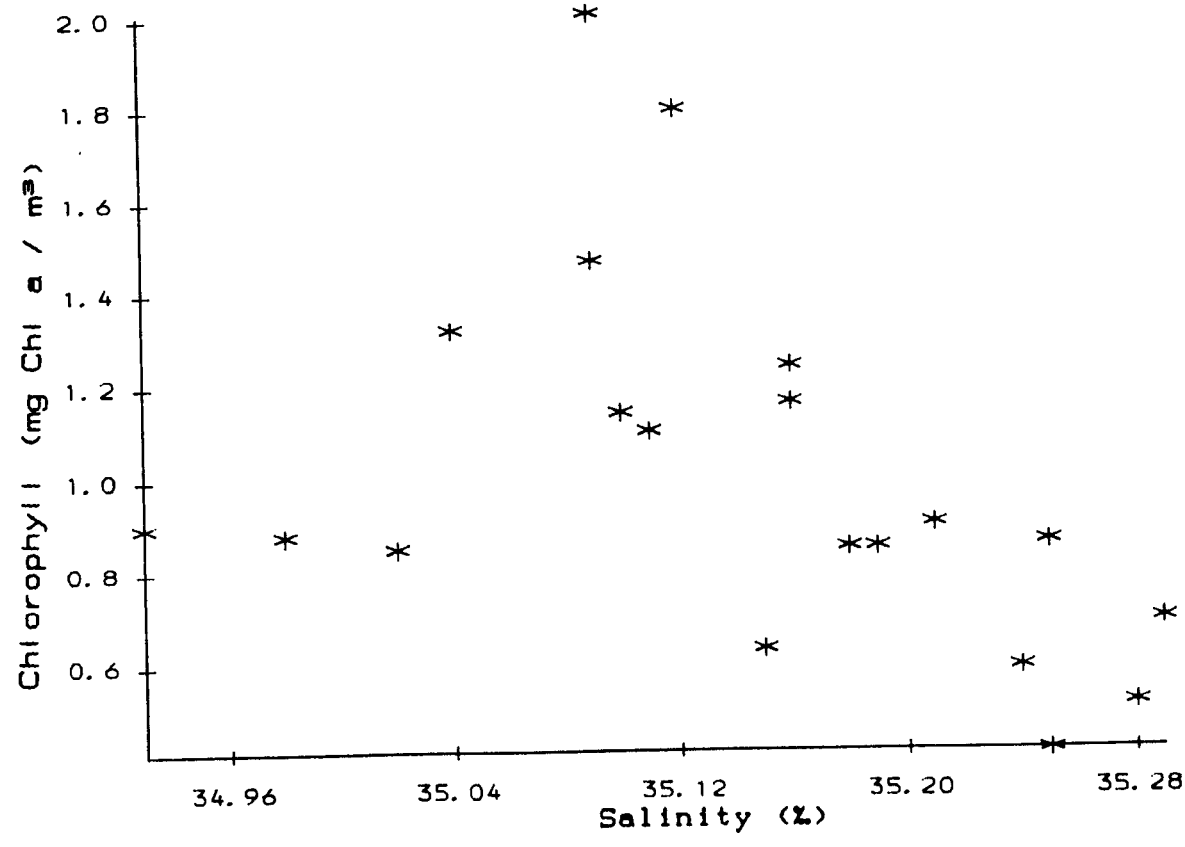

Attenuation (metres $^{-1}$)
1.6
1.4
1.2
1.0
0.8
2030
2040
2050
2060
2070
2080
2090
TCO_2 (µmol/kg)

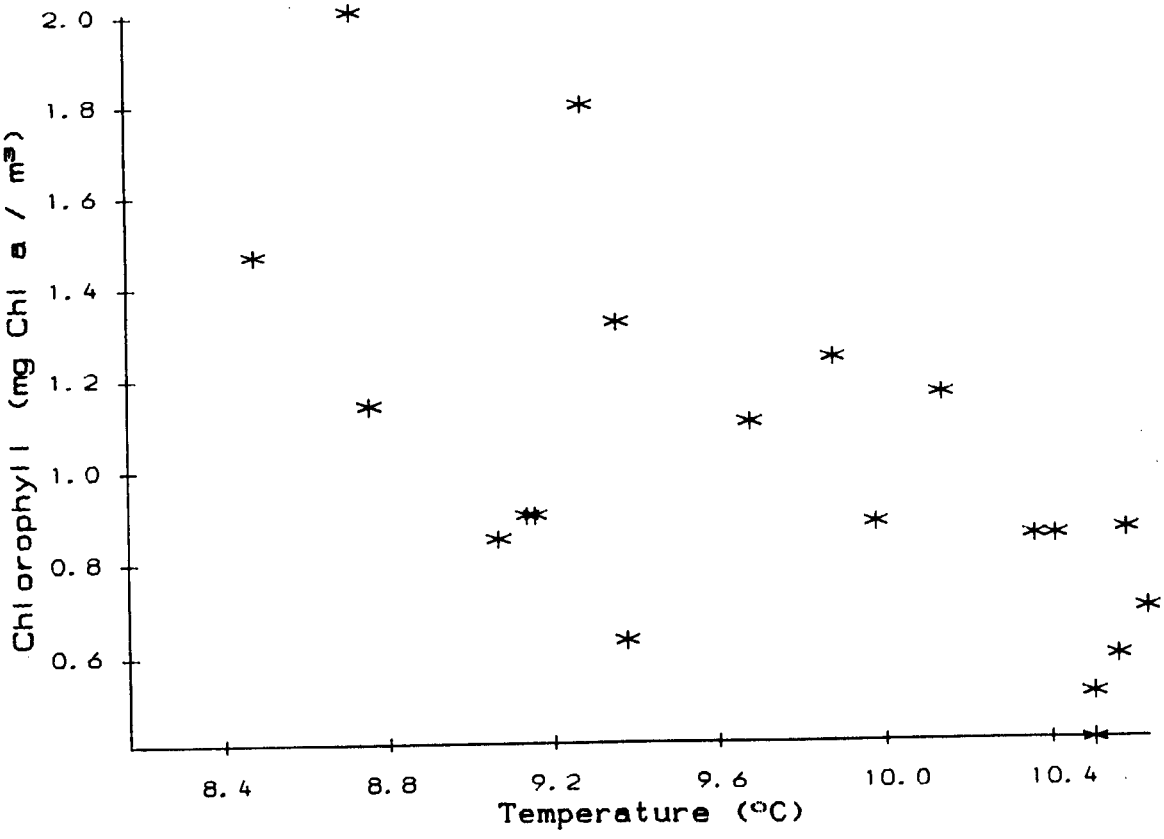

Attenuation (metres $^{-1}$)
1.6
1.4
1.2
1.0
0.8
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Chlorophyll (mg Chl a / m^3)

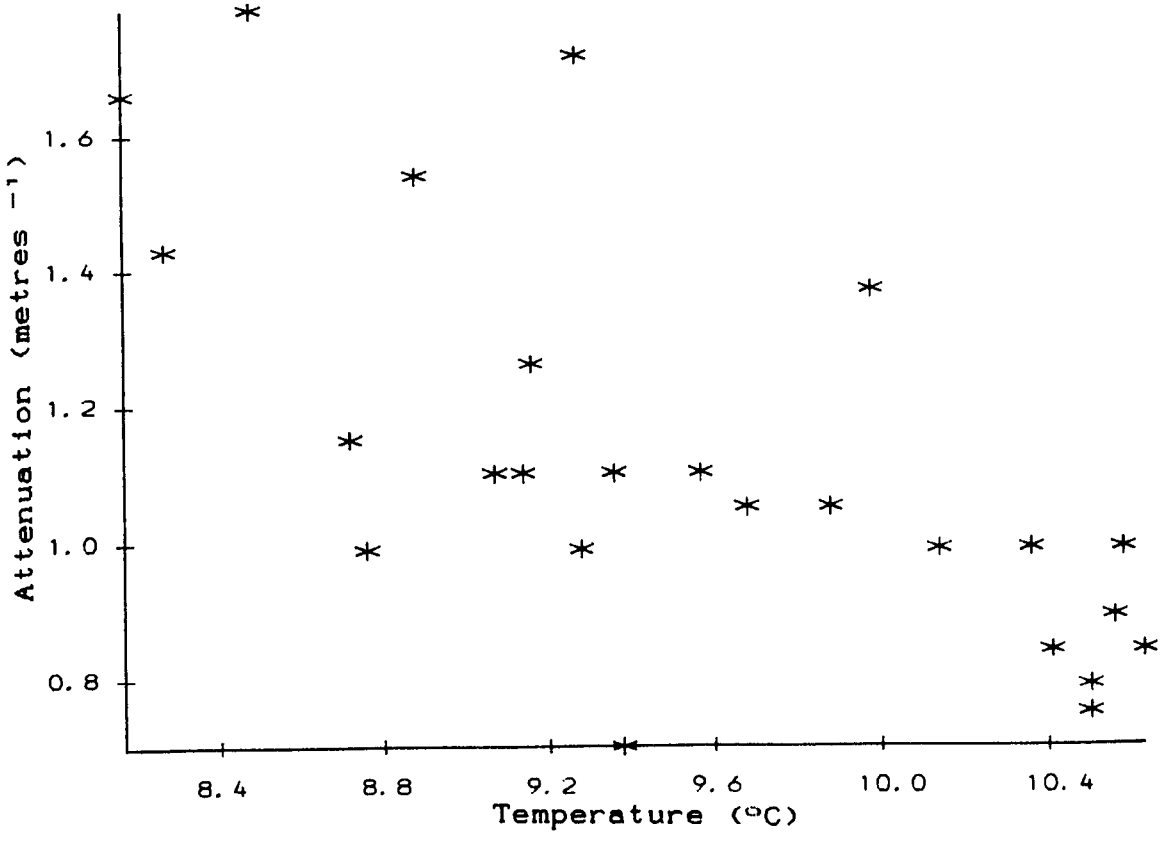

2090
2080
2070
2060
2050
2040
2030
TCO_2 (µmol/kg)
34.96
35.04
35.12
35.20
35.28
Salinity (‰)


2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
Chlorophyll (mg Chl a / m³)
2030
2040
2050
2060
2070
2080
2090
TCO_2 (µmol/kg)


Attenuation (metres $^{-1}$)
1.6
1.4
1.2
1.0
0.8
34.96
35.04
35.12
35.20
35.28
Salinity (%)


Chlorophyll (mg Chl a / m^3)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
34.96
35.04
35.12
35.20
35.28
Salinity (%)


Chlorophyll (mg Chl a / m³)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
8.4
8.8
9.2
9.6
10.0
10.4
Temperature (°C)


Attenuation (metres⁻¹)
1.6
1.4
1.2
1.0
0.8
8.4
8.8
9.2
9.6
10.0
10.4
Temperature (°C)

DATA APPENDIX

Challenger Cruise

Surface measurements (Front)

T°C	S‰	TCO_2	SE	Chl.	Tr.	Attn.	Long.	Lat.
7.44	34.79	-99.00	-99.00	-99.00	78	0.99	64.08	-7.43
6.61	34.62	2036.83	0.69	-99.00	80	0.89	64.18	-7.33
6.78	34.69	2053.53	0.96	-99.00	82	0.79	64.33	-7.20
6.74	34.67	2052.30	1.19	-99.00	82	0.79	64.50	-7.05
6.68	34.65	2043.64	0.33	-99.00	82	0.79	64.58	-6.97
7.41	34.75	2057.78	0.76	1.67	79	0.94	64.70	-6.87
7.10	34.77	2069.16	0.78	1.06	78	0.99	64.93	-6.62
7.04	34.76	2069.44	0.40	-99.00	80	0.89	64.98	-6.48
7.44	34.79	2061.10	1.24	-99.00	77	1.05	64.83	-6.35

Missing value = -99.00

T°C : Temperature
S‰ : Salinity
TCO_2 : Units µmol/kg
SE : Standard error (µmol/kg)
Chl. : Chlorophyll a (mg/m^3)
Tr. : Percentage transmission
Attn. : Attenuation ($metres^{-1}$)
Long. : Longitude
Lat. : Latitude

TITLE

A serious inhibition problem from a Niskin sampler encountered during plankton productivity studies.

RUNNING TITLE

Contamination and plankton photosynthesis

by P.J. leB Williams & J.I.Robertson

School of Ocean Sciences

Marine Science Laboratory

University College of North Wales

Bangor

Gwynedd LL59 5EY

Accepted by Limnology & Oceanography 12 December 1988

ABSTRACT

Low photosynthetic rates and reductions in chlorophyll concentrations were observed during incubations of samples taken with a 30-litre Niskin sampler, during productivity studies of oligotrophic waters in the Indian Ocean. By contrast there appeared to be no effect on community respiration. The rates of photosynthesis were 5-10 fold greater in samples taken with Teflon-lined 10-litre GoFlo bottles, and there was no systematic loss of chlorophyll. The central rubber cord of the Niskin sampler was identified as a potent source of contamination.

Introduction

The magnitude of the rate of primary production in the oceans has been disputed (see e.g. Sorokin, 1971; Sieburth, 1977; Gieskes *et al.*, 1979; Weichart, 1980; Shulenberger and Reid, 1981; Jenkins, 1982). Discussion and concern initially centred on the ^{14}C technique, however research into its methodology and interpretation has led to a consensus that there is no evidence of persistent and gross errors, unique to the ^{14}C technique, in the measurement of gross production (Fitzwater *et al.*, 1982; Williams *et al.*, 1983; Smith *et al.*, 1984; Bender *et al.*, 1988). Davies and Williams (1984) made a comparison of *in vitro* and *in situ* photosynthetic rates and found agreement between the two, suggesting that *in vitro* methods themselves can be regarded as satisfactory. However, their study concerned a temperate, coastal population, whereas discrepancies between the methods of measuring production are regarded to be more a feature of oceanic communities. Thus to some extent the question of the accuracy of ocean productivity measurements remains open.

The possibility of introducing toxic metal or organic contaminants via sample collection has been recognised for some time. Carpenter and Lively (1980) and Fitzwater *et al.* (1982) strongly recommend the use of clean techniques for productivity sampling, especially in oligotrophic situations where ambient metal concentrations may be low.

During a recent cruise in an oligotrophic area of the Indian Ocean we were forced by circumstances to sample with 30-litre Niskin water bottles. We observed low photosynthetic rates and also low chlorophyll-normalized photosynthetic rates. These most likely would have been accepted as typical of the area, were it not for evident and extensive loss of chlorophyll during the incubation (see Table 1; Stations B5, B10, B12). A series of experiments were undertaken in order to investigate the loss of chlorophyll and low photosynthetic rates.

Methods

Except for one experiment, all photosynthetic rates were measured by the oxygen technique (Williams & Jenkinson, 1982). The basic procedure was to fill a clean polyethylene container (60 litre) with water sampled using a 30-litre Niskin bottle. The resulting sample was well mixed and kept in the dark, prior to dispensing into nominally 125 cm^3 borosilicate glass bottles. For all transfers silicone tubing was used and care taken to avoid excessive agitation and bubbling. All glassware and silicone tubing had been cleaned initially by soaking overnight with cold 10% 'Decon' (Decon Laboratories Ltd, Conway St, Hove BN3 3LY, a proprietary decontaminating reagent), rinsed five times with distilled water, followed by a further soaking overnight with 10% HCl and three final rinses with distilled water. Once used, the bottles were left between experiments containing the titrated sample, prior to use, they were rinsed in hot water and twice in seawater (c.f. Williams and Jenkinson, 1982). When setting up the incubation, the bottles were flushed with at least three times their volume of sample and they were filled in an order that prevented bias. Eight replicates were used for zero times, light and dark samples. Typically one set of samples was incubated from dawn to dusk and a second set to the following dawn. Before dawn, all bottles were placed in a deck incubator in the earlier experiments, the incubator was cooled with flowing surface seawater. Dark bottles were placed in black polyethylene bags within the same incubator. Neutral density screens and a cooler-circulator were used when attempting to mimic *in situ* irradiance and temperature. Temperature control was maintained within 2°C. Oxygen concentrations were determined using an automatic Winkler titration described by Williams and Jenkinson (1982). Chlorophyll concentrations of initial and incubated samples were determined by fluorometry on acetone extracts of particulate matter collected on Whatman GF/F filters.

The ^{14}C measurements were made as follows. Identical samples to those used for the oxygen flux measurements were spiked with a solution containing c.4.5 μC: (167 kBq) of $NaH^{14}CO_3$. The isotope, purchased from Amersham International (Berks, England) was not subjected to any purification. The samples were incubated along with the oxygen samples. At the end of the incubation the samples were filtered at c.300 mbar vacuum through a 25mm diameter 0.45μm Nucleopore filter. The samples were counted by liquid scintillation technique using Aquasol as a fluor, quench corrections being made. Dark bottles were incubated along with the light bottles and the radioactivity taken up in the dark subtracted from that taken up in the light bottles. The radioactivity in the dark bottles was 1/3 of the light bottles.

Results and Discussion

Table 1 gives three examples (Stations B5, B10, B12) of samples showing low photosynthetic rates plus rapid and extensive loss of chlorophyll in the light, with significantly less chlorophyll loss in the dark. An examination of fluorescence profiles from CTD casts showed no evidence of an *in situ* diurnal change in chlorophyll levels, thus it was presumed that the decreases in chlorophyll concentrations were a consequence of the sampling and/or incubation procedure. A number of causes were considered and tested; (1) nutrient exhaustion; (2) incubation conditions; (3) bottle effects; and (4) sampling procedure.

1) Nutrient exhaustion. *In vitro* incubations prevent the replenishment of nutrients by vertical diffusion. To see if this was a cause of the chlorophyll loss, a sample was enriched (7.5% v/v) with water taken from the deep nutrient maximum. The sample was allowed to stand overnight

and then the photosynthetic and respiration rate was determined. Both chlorophyll loss and low rates of photosynthesis continued to be observed (Table 1; B14), this nutrient exhaustion was not seen to be the prime cause of the observed effect.

2) Poor incubation conditions. By using natural density screens and a water cooler we were able to approximate the ambient irradiance and temperature. We were also able to confirm that the lid of the Perspex incubator would have attenuated near-UV radiation. We were not, however, able to reproduce light quality, and in order to eliminate this as an uncertainty, we incubated in vitro samples at their appropriate depths in situ from a drifting array. The loss of chlorophyll and low photosynthetic rates remained (Table 1; Stations B16, B18), and accordingly we concluded that the incubation conditions were not the root of the problem.

3) Bottle effects. In order to examine the effect of the bottles and cleaning procedures, an experiment was set up to follow the loss of chlorophyll in different types and sizes of container. In addition we extended our conventional cleaning technique by giving the bottles an extra overnight soaking in acidified seawater. No unique effect of bottle size or container material was observed, nor did the additional cleaning reduce the effect. Substantial loss of chlorophyll in the light was still recorded in all cases (Table 2).

4) Sampling. We were left with the possibility that the contamination was occurring during the sampling step. Accordingly a rosette sampler was set up with 10-litre GoFlo bottles and water compared with a similar sample collected with the 30-litre Niskin. The samples were incubated in clean 2-litre polycarbonate containers on deck. The samples collected

with the GoFlo bottles showed less chlorophyll reduction compared with those collected with a Niskin sampler (Table 3). Similarly, a set of samples collected with the GoFlo bottles (Table 4) gave much higher photosynthetic rates than previous samples taken with Niskin samplers. The chlorophyll-normalized photosynthetic rates in these samples ranged from 0.28-1.23 μmoles O_2 μg $Chla^{-1}$ hr^{-1} (equivalent to 2-10 μgC Chl_a^{-1} hr^{-1}). Although the chlorophyll data were erratic, the marked loss in the light was no longer evident.

To confirm the toxic effect of the Niskin sampler, a 30-litre sample was taken with the GoFlo bottles, mixed in a polyethylene container, half of which was transferred to a Niskin bottle for approximately 30 min. From the two subsamples, duplicate sets of bottles were started in a deck incubator at approximately 0600 h. At 0730, 1200 and 1900 h, bottles were removed and innoculated with 4.5 μCi (167kB_q) $NaH^{14}CO_3$ and incubated for 2 h under constant light (200 μE m^{-2} sec^{-1}). Table 5 (Station B24) shows a decrease in the photosynthetic rate preceding what appears to be an accelerating loss of chlorophyll in the samples exposed to the Niskin bottle, whereas in the control sample neither the chlorophyll nor the photosynthetic rates showed any systematic decrease.

Finally, in an attempt to locate the source of contamination associated with the Niskin sampler, we incubated a piece of the central rubber cord (10 cm) for 20 min in a 5 litre polythene container, using water sampled with the GoFlo bottles. The cord was then removed and the sample, plus a control, incubated on deck. There was a marked loss of chlorophyll in the sample which came into contact with the rubber tubing (Table 5; Station B23), confirming it as a source of contamination.

Previous workers (e.g. Marra & Heinemann, 1987; Chavez & Barber, 1987) have reported a reduction in the photosynthetic rate in samples taken with Niskin samplers. In the case of Chavez and Barber, the reduction in rate was tenfold, i.e. the same magnitude as we observed. This contrasts with Cullen et al. (1986) who, using in vivo fluorescence as an indicator, inferred no inhibition in a set of samples taken from a station in the eastern tropical Pacific. Thus we may expect the effect to be variable. Marra and Heinemann (1987), although they observed the inhibition, were not able to pinpoint its source. Our experiments would suggest that the rubber cord is a potent source of contamination, but they do not eliminate others, e.g. the "O" ring and the walls of the vessel etc. The Niskin bottles came from the NERC Research Vessel Support pool of equipment and as a consequence we have little knowledge of their history. The mechanism of the contamination is far from clear. The chlorophyll loss is evidently light dependent, but the effect does not extend to phaeophytin, nor is phaeophytin the product. The last perhaps is not surprising. The limited time courses we have suggest an accelerating loss of chlorophyll, reminiscent of free radical reactions.

An interesting and important question is to what extent were other components or aspects of the microplankton affected by the contamination. There is no obvious difference between the respiration rates obtained from water taken by the two samplers (c.f. Tables 1 and 3). However, one can argue that since the effect appears to be lightinduced, one might not expect the inhibition processes to occur in the respiration samples which are incubated in the dark. However, we routinely incubated a set of replicates, first in the light for 12 hours, followed by a 12 hour dark incubation.

Thus we are able to determine a respiration rate that follows a 12 hour exposure to the light. These thus would have been subject to whatever process inhibited photosynthesis (no overnight recovery of chlorophyll was noted). These respiration rates are indicated as Resp 12LD in Tables 1 and 4. When compared with the equivalent rate (Resp 12) observed in samples not exposed to light, there are differences, although they are not systematic. We also collected samples with the Niskin bottles for large-volume, long-term, ondeck incubations. These samples were incubated in the light and chlorophyll, ^{14}C-uptake and bacterial and protozoan numbers were monitored over a period of several days. Whereas the chlorophyll concentrations and the ^{14}C determined photosynthetic rates declined dramatically, the heterotrophic micro-organisms increased in abundance (J. King, pers. comm.). This result suggests that the contamination problem may not extend to the microheterotrophs in this instance. Toxic effects of tubing have also been reported by Price et al. (1986). They examined latex, Tygon and silicone, but unfortunately not neoprene tubing. Their experiments were over longer timescales. They found latex rubber to be particularly and persistently toxic to marine algae and in this case the bacterial activity of seawater samples. The results seem to suggest that the mechanism of toxicity is different in the cases of latex and neoprene, which is not surprising.

Our general findings are in line with the conclusions of Marra and Heinemann (1984, 1987), that given normal good practice (clean glassware etc.) the problem of contamination in oligotrophic waters lies more with the sampling than the incubation step. Our results suggest that unless clean sampling techniques are adopted, low photosynthetic rates and photosynthetic indices have to be treated with caution, if not suspicion, and when encountered it would be prudent to measure chlorophyll both at the beginning and the end of the incubation to check for adverse effects. It appears (present

work, Williams unpub., Williams et al., 1983; Williams and Jenkinson, 1982; Marra & Heinemann, 1987; Laws et al., 1987) that when clean techniques are used it is not uncommon to encounter photosynthetic indices close to or above the "theoretical maximum" as defined by Falkowski (1981). This contrasts with our previous notions of oligotrophic communities, gained from observations made prior to our understanding of the need for clean sampling techniques. We do not know to what extent the earlier lower rates were a consequence of contamination effects, but it is obviously important that in future every effort should be made to avoid biases due to contamination. In the case of Niskin bottles, if it is not possible to replace them, it would be essential to replace the central cord if neoprene or latex rubber with silicone or epoxy-coated stainless steel springs, and the neoprene "O" rings with their silicone equivalents.

Acknowledgements

We wish to acknowledge the skilled help of the officers and crew of the RRS "Charles Darwin" and the opportunity afforded us by Professor Simpson and Dr Barton to participate in the cruise, and the NERC through the Research Award GR3/5549. J.I.R. was supported by a NERC postgraduate training award.

P. J. le B. Williams

J. I. Robertson

School of Ocean Sciences,

University College of North Wales,

Bangor,

North Wales,

U.K.

Submitted October 1988

REFERENCES

Bender, M., Grande, K., Johnson, K., Marra, J., Williams, P.J.leB., Sieburth, J., Pilson, M., Langdon, C., Hitchcock, G., Orchardo, J., Hunt, C., Donaghay, P. & Heinemann, K., 1987. A comparison of four methods for determining planktonic community production. Limnol. Ocean., 32, 1085-1099.

Carpenter, E.J. & Lively, J.S., 1980. Review of estimates of algal growth using ^{14}C tracer techniques. Brookhaven Symp. Biol., 31, 161-178. pub. Plenum Press.

Chavez, F.P. & Barber, R.T., 1987. An estimate of new production in the equatorial Pacific. Deep Sea Res., 34, 1229-1245.

Cullen, J.J., Zhur, M. & Pierson, D.C., 1986. A technique to assess the harmful effects of sampling and containment for determination of primary production. Limnol. Ocean., 31, 1364-1373.

Davies, J.M. and Williams, P.J.leB., 1984. Verification of ^{14}C and O_2 derived primary organic production measurements using an enclosed ecosystem. J. Plank. Res., 457-473.

Falkowski, P.G., 1981. Light-shade adaption and assimilation numbers. J. Plank. Res., 3, 203-216.

Fitzwater, S.E., Knauer, G.A. & Martin, J.H., 1982. Metal contamination and its effects on primary production measurements. Limnol. Ocean., 27, 544-551.

Gieskes, W.W.C., Kraay, G.W. and Baars, M.A., 1979. Current ^{14}C methods for measuring primary production - gross underestimates in oceanic waters. Neth. J. Sea Res., 13, 58-78.

Jackson, R.H., Williams, P.J.leB., & JOINT, I.R. Freshwater phytoplankton in the low salinity region of the river Tamar estuary. Est. Wast. Shelf Sci., Vol 25, 1987, 299-311.

Jenkins, W.J., 1982. Oxygen utilisation rates in N. Atlantic subtropical gyre and primary production in oligotrophic systems. Nature, 300, 246-248.

Laws, E.A., DiTullio, G.R. & Redalje, D.G., 1987. High phytoplankton growth and production rates in the North Pacific subtropical gyre. Limnol. Ocean., 32, 905-919.

Marra, J. and Heinemann, K.R., 1984. A comparison between non-contaminating and conventional incubation procedures in primary production measurements. Limnol. Ocean., 29, 389-392.

Marra, J. and Heinemann, K.R., 1987. Primary production in the North Pacific Central gyre - some new measurements based on ^{14}C. Deep Sea Res., 34, 1821-1830.

Price, N.M., Harrison, P.J., Landry, M.R., Azam, F and Hall, K.J.F. 1986. Toxic effect of latex and Tygon tubing on phytoplankton, zooplankton and bacteria. Mar. Ecol. Prog. Ser. 34, 41-49.

Shulenberger, E. and Reid, J.L., 1981. The Pacific shallow oxygen maximum, deep chlorophyll maximum and primary productivity, reconsidered. Deep Sea Res., 28, 901-919.

Sieburth, J.McN., 1977. International Helgoland Symposium: Conveners report on the informal session on biomass and productivity of micro-organisms in planktonic ecosystems. Helgo. wiss. Meer., 30, 697-704.

Smith, R.E.H., Geider, R.J. and Platt, T., 1984. Microplankton productivity in the oligotrophic ocean. Nature, 311, 252-254.

Sorokin, Y.L., 1971. Bacterial components of oceanic ecosystems. Mar. Biol., 11, 101-105.

Weichart, G., 1980. Chemical changes and primary production in Fladen Ground during the first phase of a spring phytoplankton bloom. Meteor Forsch-Ergebn., A. 22, 79-86.

Williams, P.J.leB., and Jenkinson, N.W. 1982. A transportable microprocessor controlled precise Winkler titration suitable for field station and shipboard use. Limnol. Ocean., 27, 576-584.

Williams, P.J.leB., Heinemann, K., Marra, J. and Purdie, D.A., 1983. Comparison of ^{14}C and O_2 measurements of phytoplankton production in oligotrohic waters. Nature, 305, 49-50.

TABLE 1 Chlorophyll concentrations and oxygen-derived photosynthetic and respiration rates in samples taken with a Niskin sampler: the original effect and that of various incubation conditions.

Sample & depth	Incubation conditions	Pigment analyses ($\mu g\ l^{-1}$)			Oxygen flux measurements ($\mu moles\ l^{-1} 12hr^{-1}$)	Photo. index ($\mu moles\ \mu g^{-1} hr^{-1}$)
		Chl Ohr (Pu Ohr)	Chl 12hrD (Pu 12hrD)	Chl 12hrL (Pu 12hrL)	Photo. 12hr Resp. 12hr Resp. 12hrLD	
B5 60m	Deck, in vitro	0.225 (0.138)	0.131 (0.116)	0.000 (0.029)	-0.02±0.053 0.36±0.080 0.74±0.043	- -
B10 55m	Deck, in vitro	0.311 (0.141)	0.341 (0.155)	0.044 (0.081)	0.59±0.109 0.95±0.089 0.82±0.120	0.190 (1.90)
B12 40m	Deck, in vitro	0.350 (0.250)	0.272 (0.139)	0.006* (0.035)*	0.15±0.122 1.15±0.110 0.62±0.120	0.042 (0.42)
B14 55m supplemented with 7.5%v/v deep water	Deck, in vitro	0.277 (0.277)	0.280 (0.224)	0.070 (0.147)	0.21±0.094 1.19±0.068 0.49±0.092	0.076 (0.76)
B16 60m	In situ, in vitro	0.467 (0.326)	0.415 (0.267)	0.259 (0.200)	0.15±0.070 0.02±0.066 0.45±0.082	0.032 (0.32)
B18 50m	In situ, in vitro	0.386 (0.213)	0.332 (0.206)	0.026 (0.053)	0.09±0.075 0.71±0.129 0.75±0.082	0.023 (0.23)

Chl Ohr, Chl 12 hr, Ph Ohr & Ph 12 hr, refer to the chlorophyll$_a$ and phaeophytin concentrations, at zero time and after 12 hours incubation. L & D refer to light and dark incubation.

Photo. 12hr and Resp. 24 hr refer to the 12hr-determined photosynthetic rates and the 24hr-determined respiration rate. Resp. 12hrLD refers to 12 hour dark respiration rates determined on a sample previously incubated for 12 hours in the light.

Photo. index is the photosynthetic index, i.e. the chlorophyll-normalized photosynthetic rate as $\mu moles\ O_2\ \mu gChl_a^{-1} hr^{-1}$, calculated using the initial chlorophyll value assuming a 10 hour light period. The values in parentheses are calculated rates as $\mu gC\ \mu gChl_a\ hr^{-1}$, assuming a P.Q. of 1.2

* 24 hr value, no data available for 12 hr sample.

TABLE 2 Effect of container on chlorophyll loss

Container	Length of Exposure (hr)	% remaining at end of incubation	
		Light incubation	Dark incubation
Polythene bags (5 litre)	6	77	86
	12	36	78
Polycarbonate bottles (2 litre)	6	78	86
	12	39	81
Acid cleaned oxygen bottles	6	76	86
	12	39	76
"Uncleaned" oxygen bottles	6	78	86
	12	37	78

TABLE 3 Effect of sampler on chlorophyll loss

Sampler	Length of Exposure (hr)	% remaining at end of incubation	
		Light incubation	Dark incubation
Niskin	6	47	56
	12	34	83
GoFlo	6	70	65
	12	74	69

TABLE 4 Chlorophyll changes during incubation and oxygen derived photosynthetic rates in samples taken with a GoFlo sampler

Sample & depth	Incubation conditions	Pigment analyses ($\mu g\ l^{-1}$)			Oxygen flux measurements ($\mu moles\ l^{-1} 12hr^{-1}$)	Photo index ($\mu moles\ ug^{-1} hr^{-1}$)
		Chl 0hr (Ph 0hr)	Chl 12hrD (Ph 12hrD)	Chl 12hrL (Ph 12hrL)	Photo. 12 hr Resp. 12 hr Resp. 12hrLD	
B22 29m	Deck, in vitro	0.213 (0.106)	0.119 (0.079)	0.332 (0.133)	2.63±0.063 0.68±0.075 0.35±0.024	1.23 (12.3)
B21 68m	Deck, in vitro	0.504 (0.231)	0.319 (0.252)	0.525* (0.347)	1.40±0.024 0.59±0.031 0.80±0.131	0.28 (2.8)
B21 90m	Deck, in vitro	0.326 (0.266)	0.294 (0.310)	0.252 (0.399)	0.97±0.135 0.49±0.069 0.89±0.057	0.298 (3.0)

* See Table 1 for units and details

TABLE 5 Examination of the source of contamination

	Length of exposure to day light (hr)	Chl a ($\mu g l^{-1}$)	$^{14}CO_2$ fixation rate ($\mu gC\ l^{-1}\ hr^{-1}$)	Photo.* index
B24 GoFlo	1.5	0.273	0.31 0.04	0.112(1.12)
	6	0.378	0.62 0.11	0.225(2.25)
	13	0.268	0.24 0.05	0.086(0.86)
B24 Niskin	1.5	0.231	0.04 0.06	
	6	0.189	0.10 0.05	0.041(0.41)
	13	0.009	0.07 0.05	0.028(0.28)
B23 Polythene bag with rubber cord (5 litre)	0	0.295	.....No Data.....	
	12	0.046	.....No Data.....	
B23 Polythene bag without rubber cord (5 litre)	0	0.277	.....No Data.....	
	12	0.216	.....No Data.....	

*Units as Table 1. Sample B23 was taken with a GoFlo sampler