UNESCO technical papers
in marine science 65

Methodology for oceanic CO_2 measurements

Final report of
SCOR Working Group 75
Woods Hole, U.S.A.
October 1988

UNESCO 1992

ISSN 0503-4299

Published in 1992
by the United Nations Educational,
Scientific and Cultural Organization
7, place de Fontenoy, 75352 Paris 07 SP

Printed in UNESCO's workshops.

Printed in France

Abstract

This report summarizes the results of the deliberations of the SCOR Working Group 75 on methodology for oceanic CO2 measurements at meetings in Hamburg (1983), Lake Arrowhead (1984), Les Houches (1985) and Woods Hole (1988). It reviews the scientific and technical basis for oceanic studies: measuring equipment, procedures, ocean carbon standards and intercalibration. The report describes the state-of-the-art methodology and recommends a program dedicated to determining the diurnal, seasonal and interannual variability of the oceanic carbon cycle. The framework of a global CO2 survey as an international effort is adopted by JGOFS (Joint Global Ocean Flux Study) in the world hydrographic program of WOCE (World Ocean Circulation Experiment).

Résumé

Le présent rapport représente une synthèse des débats consacrés par le Groupe de travail 75 du SCOR à la méthodologie des mesures du CO^2 dans l'océan lors de ses réunions de Hambourg (1983), Lake Arrowhead (1984), Les Houches (1985) et Woods Hole (1988). Les éléments scientifiques et techniques qui sont à la base des études océaniques sont passés en revue : matériel de mesure, procédures, normes relatives au carbone de l'océan et interétalonnage. Les méthodes les plus récentes sont décrites et un programme permettant de déterminer les variations diurnes, saisonnières et interannuelles du cycle du carbone de l'océan est recommandé. La JGOFS (Etude conjointe des flux océaniques mondiaux) a adopté le cadre d'une étude mondiale sur le CO^2 conçue comme une opération internationale qui sera un élément du programme hydrographique mondial de WOCE (Expérience sur la circulation océanique mondiale).

Resumen

Este informe resume los resultados de las deliberaciones del Grupo de Trabajo 75 del SCOR sobre Metodología para las Mediciones del CO_2 Oceánico que tuvieron lugar en reuniones celebradas en Hamburgo (1983), Lake Arrowhead (1984), Les Houches (1985) y Woods Hole (1988). El informe pasa revista a la base científica y técnica de los estudios oceánicos: equipo de medición, procedimientos, estándares e intercalibración del carbono oceánico. Describe la metodología más avanzada y recomienda un programa dedicado a determinar la variabilidad diurna, estacional e interanual del ciclo del carbono oceánico. El Estudio Mundial Conjunto de los Flujos Oceánicos (JGOFS) adopta dentro del programa hidrográfico de WOCE (Experimento Mundial sobre la Circulación Oceánica) el marco de referencia de una encuesta mundial sobre el CO_2 en calidad de esfuerzo internacional.

Выдержка

В настоящем докладе кратко излагаются результаты обсуждений в Рабочей группе 75 СКОР по методологии измерения содержания CO_2 в океане на заседаниях в Гамбурге (1983 г.), Лэйк Эрроухэде (1984 г.), Ле Уш (1985 г.) и Вудс-Холе (1988 г.). В нем рассматривается научная и техническая основа для океанических исследований: измерительное оборудование, процедуры, нормы содержания углерода в океане и взаимная калибровка. В докладе описывается современная методология и рекомендуется программа, посвященная определению ежедневной, сезонной и межгодовой переменчивости океанического углеродного цикла. Рамки глобального исследования содержания CO_2 в качестве международного мероприятия утверждены СИПМО (Совместное изучение потоков Мирового океана) во всемирной гидрографической программе ВОСЕ (Эксперимент по изучению циркуляции Мирового океана).

خلاصة

يتضمن هذا التقرير ملخصا لنتائج مداولات فريق العمل ٧٥ التابع للجنة العلمية لبحوث المحيطات (سكور) بشأن المنهجية المتعلقة بعمليات قياس ثاني أوكسيد الكربون في المحيطات، وذلك في الاجتماعات التي عقدها في هامبورغ (١٩٨٣) وليك أروهيد (١٩٨٤) ولي أوش (١٩٨٥) وودز هول (١٩٨٨). ويستعرض التقرير الأساس العلمي والتقني للدراسات المحيطية : معدات القياس، والأساليب، والمعايير المتعلقة بكربون المحيطات والمضاهاة. كما يتضمن التقرير وصفا لأحدث منهجية في هذا الصدد ويوصي بتنفيذ برنامج مخصص لتحديد التغير اليومي والفصلي والسنوي في دورة الكربون المحيطي. وقد اعتمدت الدراسة المشتركة لتدفق المحيطات في العالم (JGOFS) الإطار المتعلق باستقصاء عالمي عن ثاني أوكسيد الكربون، كنشاط دولي في إطار البرنامج الهيدروغرافي العالمي التابع للتجربة العالمية بشأن حركة المحيطات (ووس).

摘　要

本报告概述了海洋调查科学委员会（SCOR）第75工作组在汉堡（1983年）、阿罗黑德湖（1984年）、莱苏什（1985年）和伍兹霍尔（1988年）会议上就海洋二氧化碳测量方法进行审议的结果。它审查了各种海洋研究的技术基础：测量设备、程序、海洋碳标准和定标。报告描述了现代化方法并建议了一项专门确定全日、季节和年际海洋碳循环变率的计划。全球二氧化碳调查方案，作为一项国际活动已由全球海洋通量联合研究（JGOFS）在世界海洋环流试验（WOCE）世界水文计划中实施。

TABLE OF CONTENTS

Foreword

SCOR Working Group 75, as indicated by its title, is concerned with the methodology for CO_2 measurements in the world oceans. "Methodology" here signifies the technical aspects of instrumentation, detection, and sampling, the development of standards, and the preparation of data for permanent archiving. To promote adequate sampling of sea water, Working Group 75 has undertaken the design of an oceanographic station network and has proposed the use of ships-of-opportunity to supplement dedicated broad-scale oceanographic expeditions.

Our title singles out CO_2 as the principal chemical compound which links oceanic carbon with carbon stored in the atmosphere and land biosphere. The partial pressure of this gas at the sea surface directly influences the flux of CO_2 between the atmosphere and the oceans. To understand and to predict this partial pressure further requires, however, that the carbon cycle in the oceans be understood. Since this cycle involves chemical reactions of bicarbonate and carbonate salts and organic compounds which influence the CO_2 partial pressure, it is also prudent to measure these other carbon compounds. Thus our study of "oceanic CO_2" perforce includes consideration of all of the important species of oceanic carbon.

This report is a result of a meeting of Working Group 75 convened in October, 1988 to provide a review of plans for a world-wide program to measure oceanic CO_2. At previous meetings in May, 1984, and September 1985 Working Group 75 prepared reports indicating how such a program might be carried out. Those reports assessed analytical methods and recommended means of standardizing measurements. They also identified ships and oceanic expeditions which might become available to study oceanic carbon, and it proposed additional sampling efforts where more sources were yet identified.

The present report reflects our further deliberations on these topics, and our discussions of several additional chemical parameters not considered in 1985. Expressed as a revision of the 1985 report, this new report represents a complete summary of our recommendations to establish a program dedicated to determining the diurnal, seasonal, and interannual variability of the oceanic carbon cycle. We are pleased that rapid developments in ocean programs of JGOFS and WOCE have been the impetus to carry out the frame work of a global CO_2 survey proposed and further discussed in previous SCOR Working Group 75 meetings at Hamburg, Lake Arrowhead, Les Houches and finally Woods Hole.

October, 1988

C. S. Wong
Chairman of Working Group 75

Editors of SCOR Working Group 75 Reports:	C.D. Keeling, 1984 (Lake Arrowhead)
	C.D. Keeling, 1985 (Les Houches)
	C.S. Wong, 1988 (Woods Hole)

1. *Scientific Basis for Oceanic CO_2 Studies*

There is growing concern that the planet Earth is in the midst of a climatic change - a "greenhouse warming" - as a result of human perturbations on a global scale. While this global warming has not been demonstrated unequivocally, the scientific evidence from ice cores showed convincing correlation between temperature changes and levels of carbon dioxide (CO_2). CO_2 and other "greenhouse gases" have been increasing in the atmosphere at an unprecedented rate over the past century due to human activities. Continued increases in the anthropogenic emissions of these chemical constituents could, over the next century, have profound implications for the Earth's delicate radiative balance.

Predicting climatic change is difficult due to large uncertainties in the suite of variables that comprise the global environment "equation". Various model-based scenarios of the Earth's response to the anthropogenic CO_2 overburden have been produced, but these are of questionable validity in part because of uncertainties in quantitative estimates of CO_2 sources and sinks.

The world's oceans are the major buffering control on the ratio of increase of CO_2 in the atmosphere, and be absorbing about 2.5 billion metric tons of carbon per year (nearly 40% of the annual release from fossil fuels). However, this number is derived from atmospheric measurements and statistics of fossil-fuel combustion, and not from direct carbon measurements in the oceans. We presently do not know the degree to which this estimate reflects the actual value, or where the anthropogenic CO_2 is going, especially on the decadal time-scales. Nor do we know the relative roles of the terrestrial and oceanic biosphere on this same time-scale. Producing reliable estimates of future climate scenarios requires an understanding of the ocean's capacity for removing the atmospheric CO_2 burden that are anticipated for the coming decades and centuries.

Tantalizing hints of change are now emerging. The observations of the partial pressure of CO_2 gas in the Sargasso Sea made during the International Geophysical Year(1958), GEOSECS expedition (1972) and TTO expedition (1981) show a significant trend, approximately paralleling the atmospheric CO_2 increase recorded at Mauna Loa Observatory in Hawaii. Also a backward-in-time calculation to assess the uptake of CO_2 in water masses previously exposed to the atmosphere and now sinking into deep ocean shows intriguing results. Yet these signals cannot be said unequivocally to demonstrate, by observations, the changes that we believe are occurring. The carbon system contains many variables which must be constrained, and the large natural abundance and variability of carbon in the oceans can confound all but the most carefully planned experiments.

The scientific justification for an oceanic CO_2 program has been articulated in numerous reports. Quite simply, we need to document the changing CO_2 partial pressure, total inorganic carbon content, and the acidity (or alkalinity) of the ocean in order to discern the forces modulating the atmospheric CO_2 rise. Climatic change will affect oceanic circulation, perturbing not only uptake of CO_2 from fossil fuels, but also the rate of transport of carbon carried by biotic fluxes.

To define the scientific basis for observing changes of oceanic carbon with time, we must be aware of both the invasion of CO_2 from fossil fuels, and of natural, possibly climatically induced, exchanges such as appear to have occurred, for example, during the last ice age. These changes, possibly driven by changes in biologically fixed carbon, may be of similar magnitude to the fossil-fuel effect observed over the last century. We note that invasion of CO_2 from fossil fuels alone will not be accompanied by any direct perturbation of the oceanic oxygen, phosphate, or nitrate distributions, whereas a climatic change affecting the biological fixation of carbon will be accompanied by large perturbations in these variables. Hence distinguishing the changes in carbon from these two phenomena is possible by careful measurements of the chemical species of the oceanic carbon cycle.

The first problem we face is to understand the natural variability of the carbon cycle in the oceans. For atmospheric processes, the seasonal and latitudinal effects have been well studied. Oceanic processes are poorly known, however.

In general, the spring warming of the oceans raises the CO_2 partial pressure (P_{CO2}). The autumn cooling reverses this trend. These effects are moderated, and in some places overridden, however, by biological fixation of CO_2 in the spring and regeneration of CO_2 in the fall. P_{CO2}, is also influenced, indirectly, by variations in wind strength and by the depth of the oceanic mixed layer, which perturb the P_{CO2} signal because they influence the rate of exchange of CO_2 gas between the atmosphere and the oceans. Intermittent upwelling of deep water can also cause P_{CO2} to vary.

P_{CO2} as a parameter of the oceanic carbon cycle has the virtue that it is the most readily measured property. It may be directly linked to the global atmospheric CO_2 distribution; it drives the air-sea exchange. The ocean variability of P_{CO2} is large both in space and time, however. Lack of understanding of this variability is currently a limiting factor in our progress to understand the oceanic carbon cycle. We recommend careful studies together with detailed model calculations at selected oceanic sites to assess the processes controlling seasonal and interannual variability in CO_2.

Measuring CO_2 alone does not, however, provide us with enough information to document the time dependent oceanic carbon cycle which controls the variability of CO_2. Currently the most troublesome, yet the most important additional parameter in need of study is dissolved inorganic carbon, which we will refer to in this report as "DIC". The currently available imprecision in DIC measurements is 1 micromole of carbon per kilogram of sea water, a magnitude which is approximately equal to the anticipated annual increase in DIC in surface ocean water brought about by the uptake of CO_2 from fossil fuels. Unlike CO_2, DIC is not directly a function of the temperature of measurement. On this account, and because it directly indicates the amount of inorganic carbon in the oceans, observation of changes in DIC is a primary goal in assessing oceanic carbon.

Ultimately, the excess CO_2 entering the oceans will be neutralized by dissolution of carbonaceous minerals, particularly calcium carbonate derived from planktonic organisms. The time scale of such dissolution is not known, and the likelihood that this dissolution is already occurring is a contentious point. Highly accurate direct measurements of calcium and carbonate would provide a reliable means to detect dissolution related to CO_2 uptake. Calcium can be estimated from salinity but should be measured directly. Carbonate is best determined indirectly from simultaneous measurements of DIC and of alkalinity, the latter being an important parameter related to the electrical charge balance of the inorganic carbon system in sea water. By combining all three measurements, the saturation state of sea water with respect to planktonic carbonate minerals can be determined and the chemical response of ocean water to the uptake of atmospheric CO_2 properly understood.

Particulate and dissolved organic carbon are components of the detrital organic carbon pool which contribute to the carbon mass balance, yet they yield less information than the preceding variables and require less intensive study. The flux of particulate organic carbon, however, reveals important information on the temporal variability of the biological fixation of carbon.

The principal nutrient chemicals: phosphate, nitrate, silicate and the pigment chlorophyll, are, in the strictest sense, not part of the oceanic carbon cycle, but they are essential parameters to watch because of their close relationship to the biological fluxes in the oceans. The inorganic fractions which appear as products of remineralization, when organic remains of plankton decay and are oxidized, are typically in nearly constant proportion to the amount of CO_2 released. Much can be learned by observing simultaneous changes in carbon species and nutrients. In addition to the inorganic species, organic phosphate and nitrate are often in significant concentration and deserve more study than has to now been given to them. Chlorophyll in the upper oceans as a measure of the photosynthetic activity of marine plants may become a useful global scale parameter, especially if it can be detected from earth-orbiting satellites, a prospect in the 1990's.

Carbon isotopic studies of the ocean carbon system yield important information on long time scales. Most models of oceanic CO_2 uptake have been calibrated by means of radiocarbon (carbon-14). Gaining further information on oceanic ventilation times by this means is clearly important. Stable isotopic carbon (carbon-13) studies also yield important information. The oceanic carbon-13 trend from fossil fuel CO_2 uptake is too small to be observed at this time, yet we may gain insight into the oceanic carbon cycle by additional knowledge of the natural variability of oceanic carbon-13.

The acidity of sea water, expressed by the chemical activity parameter, pH, can be calculated from measurements of DIC and alkalinity, but owing to uncertainties in the thermodynamic reactions which control oceanic acidity, and because pH can be measured more readily than DIC and alkalinity, it is useful to include direct pH measurements as a check on the consistency of the other measurements recommended here.

In the space available in this report, not all of these carbon parameters could be given full consideration. We emphasize, in the sections which follow, those parameters which appear to us to be most critical and most in need of more intensive study: P_{CO2}, DIC, and alkalinity. The organic fractions, calcium, isotopes, pH, and nutrients are considered, but more briefly. Since we were asked expressly to address the general technical problems involved with setting up a global oceanographic program emphasizing CO_2, this limited approach should be adequate as a first step.

2. Technical Basis for Oceanic CO_2 Studies

2.1 Measuring Equipment and Methods

Essential to a successful study of oceanic CO_2 is the adoption of consistent procedures for measuring the principal chemical components which characterize the oceanic carbon cycle. For large-scale and long-term surveys, such as we envision and discuss below, measurements of these components should be made using the same equipment, or at least equipment with very similar performance characteristics. In this section we discuss existing instruments which measure these components, with emphasis, as needed, on devices and procedures which produce data of high precision and accuracy. We assess the prospects for improving instrumentation, and in some cases we single out for adoption, instruments and procedures which we believe, on the basis of our present experience, to be best suited to a world-wide oceanic CO_2 program. A summary of key scientific terms used in this discussion is given in Table 2.1.

2.1.1. CO_2 partial pressure (P_{CO2})

The partial pressure of CO_2 i.e. P_{CO2}, exerted by sea water is measured by determining the CO_2 concentration in a carrier gas equilibrated with sea water. For the quantitative determination of P_{CO2}, a non-dispersive infrared analyzer or a gas chromatograph can be used.

Owing to the small sample size required and a low consumption rate of calibration gases, the gas chromatographic method (using a flame ionization detector which detects methane gas converted from CO_2) has become the preferred method in recent years. An imprecision of 0.05% is achieved for routine CO_2 analyses. The average level of CO_2 in surface ocean water is approximately 340 microatmospheres (μatm), close to equilibrium with the pressure exerted by atmospheric CO_2.

For gas-seawater equilibration, two types of equilibrators are commonly used:

a) an open system equilibrator, in which a large volume of sea water is continuously sprayed into an equilibration chamber, and

b) a closed system equilibrator, in which a fixed volume of a carrier gas is recirculated in a closed loop through a fixed sea water sample of 100 ml to 10 liters.

The former is used for continuous measurements of P_{CO2} in surface water, while the latter is used for subsurface water samples of limited volume. In some cases, for surface water, the equilibrated gas is sealed in a glass flask for storage, rather than analyzed aboard ship. The flasks, 100 to 200 ml in size, are stored and shipped back to a shore-based laboratory for CO_2 analysis. This method has been successfully used for ship-of-opportunity operations, in which an adequate facility for operation of a dedicated CO_2 analyzer is not available on board the ship.

Since the fractional change of sea water P_{CO2} is about 4% per ^{o}C, the experimental error for P_{CO2} depends largely on the measurement of the temperature at which the carrier gas is equilibrated with sea water. To achieve a precision of 0.3% (or 1 μatm for a typical surface water having a CO_2 of 340 μatm), the temperature of equilibration should be measured to 0.1^{o}C or better. The degree of equilibration also affects the precision of CO_2 measurements. Therefore, we recommend that the performance of the equilibrator used for measurements be well documented, and the pressure of the carrier gas be measured or controlled.

Since a major objective for P_{CO2} measurements in surface water is to obtain the ocean-atmosphere difference in P_{CO2}, we recommend that the CO_2 analyzer, whether an infrared analyzer or a gas chromatograph, be calibrated using standard gases specified by the World Meteorological Organization (WMO, see section 2.2.1.1) and that ambient atmospheric CO_2 be measured as well as P_{CO2} in the water. Furthermore, we recommend that the CO_2 in sea water be reported in a pressure unit, preferably in atmospheres, rather than in a concentration unit.

2.1.2. Dissolved inorganic carbon (DIC)

The total inorganic carbon of sea water is operationally defined as the amount of carbon, in moles, evolved when sea water is acidified with strong acid sufficient to neutralize all of the weak bases present. A very small fraction is in particulate form and called particulate inorganic carbon or "PIC." The remaining fraction, mainly dissolved bicarbonate and carbonate ions, is called dissolved inorganic carbon or "DIC."

We recommend as the principal basis for achieving precise DIC measurements to strip sea water of the CO_2 gas produced upon acidification and to determine the amount removed relative to a measured volume or weight of sea water. At present, the most precise data claimed is that of the CO_2 program of the Scripps Institution of Oceanography which reports an analysis imprecision of the order of 0.50 μM/kg and a sampling imprecision of 0.80 μM/kg, for individual samples collected in one-liter glass bottles. The overall level of DIC is approximately 2000 μM/kg.

The method used to measure DIC precisely is to collect the water in 10- to 30-liter Niskin bottles at sea and flow the water into bottles cleaned and subsequently annealed, as further described in section 2.2.3.2. The water is overflowed to 50% of the volume of the container. The bottles are sealed with greased ground glass stoppers and returned to the laboratory for analysis. In the laboratory, aliquots of, typically, 40 ml are transferred into a gas tight connecting system to previously annealed pipettes closed with stopcocks. Each pipette is first weighed empty and then reweighed with the sample of sea water. The latter is then transferred by gravity flow into a vacuum system, the reaction vessel of which is also annealed. Phosphoric acid is flowed by gravity through the emptied pipette from above and thereby acidifies the sample and releases the CO_2. The evolved CO_2 is separated from water using dry ice refrigerant to cold trâps which freeze out the water. The dried CO_2 is measured manometrically.

Two manometric devices have been used. The first is a mercury column manometer calibrated as part of an atmospheric CO_2 program and demonstrated to produce measurements accurate to 1 part in 2000, and precise to one part in 4000. It cannot be adapted for use at sea.

The second device is a manometer in which a constant volume is confined by a stopcock and attached to a vitreous quartz (silica glass) spiral which rotates as a function of pressure. The degree of rotation is recorded. The manometer is calibrated using four or more gas standards consisting of CO_2 samples whose masses were determined with the mercury column manometer previously mentioned. The precision of the quartz spiral manometer during a single day of operation is as good as the mercury manometer. The operation is considerably simpler, however.

The above method, with a quartz spiral manometer as a detector has not yet been used at sea, although in principal most aspects of the method could be adapted for shipboard use. The principal adaptation relates to the necessity to use volumetric control of the pipettes instead of having them weighed.

An alternative method used widely at sea is to remove the CO_2 from 1 to 5 ml of acidified sea water by bubbling through the sample a stream of inert gas such as helium. The resultant sample is measured with a gas chromatograph. The lowest imprecision is reported to be approximately 2 μM/kg for an individual sample.

It appears likely that any of several methods of detecting the stripped CO_2 have sufficient precision to be satisfactory for measurements at sea. It is possible, however, that all methods which use small samples and which depend on the same chamber repeatedly filled with sea water samples without cleaning, fail to achieve the precision possible in the detection systems because of fouling the walls of the chamber by organic constituents of sea water or by corrosion from sea salts. Methods employing freshly annealed one-liter glass bottles overcome this problem but at much inconvenience in manipulating containers and a large amount of time needed for analysis. We recommend that all laboratories involved in measuring DIC seek means for reducing fouling in order to improve the precision of the gas chromatographic and other small volume methods so that they approach the precision when using annealed bottles.

Presently at the Scripps Institution of Oceanography, one apparatus and a single technician can measure 12 sea water samples for DIC per week. By automating the procedures, it would be possible to increase the rate of analysis by a factor of two or more, but the cost of development would be high so that several years of analyses would have to be performed before the cost of the new equipment would be offset by the saving in labor.

Other methods of detecting the CO_2 have been employed including coulometry and potentiometric titration. The coulometric method is now the recommended procedure. The titration method is used in conjunction with the determination of alkalinity, as discussed in section 2.1.4. Addition to sea water of strong acid (i.e., an acid which in water almost completely dissociates into ions) successively neutralizes carbonate and bicarbonate ions. The point of complete neutralization is identified with the alkalinity. The difference between this point and the equivalence point where the carbonate has been quantitatively converted to bicarbonate is a measure of DIC. The titration method for DIC has been widely used, but the results do not agree well with other methods, and are indeed not themselves entirely consistent. The presence of other alkaline species in sea water poses problems as discussed in section 2.1.4.; these are even more serious for the determination of the bicarbonate equivalence point than for the determination of the alkalinity.

In summary, we recommend the use of a coulometric method for determining DIC in sea water.

2.1.3. Particulate inorganic carbon (PIC).

We do not consider here this rarely measured minor property, which ranges in concentration from 0.01 to 1 μM/kg. In practice, PIC is usually determined by filtering sea water through a glass fiber or silver mesh filter, acidifying the collected particles, and detecting the evolved CO_2 gas by any of the typical gas analysis methods available. Thus, some or all PIC present in the sample is included in the analyses reported as DIC, unless the water is filtered. The quantity of PIC, except near shore, is so small, however, that its presence is usually ignored when measuring DIC.

2.1.4. Titration alkalinity (TA)

The alkalinity of sea water is operationally defined as the number of equivalents of strong acid required to bring one kilogram of sea water to the equivalence point of the carbonic acid - bicarbonate system. The problem is complex. Addition of strong acid to sea water protonates not only carbonate and bicarbonate ions, but fractions of the borate, sulfate, silicate, phosphate, fluoride and other trace chemical systems. As a result, the end point, where the rate of change in electric potential with added acid reaches a maximum, is not identical to the equivalence point. A complex representation of the solution chemistry is necessary to achieve results of high precision.

The present operational procedure of computer controlled potentiometric titration of about 100 ml of sea water yields an imprecision in the laboratory of about 1 μeq/kg, and at sea about 3 μeq/kg. The overall level of oceanic alkalinity is approximately 2300 μeq/kg.

In order to reduce the imprecision of alkalinity measurements to the desired level of 0.5 μeq/kg, progress in both physical control of the experiment (e.g. cell volume and temperature) would have to be made, and in chemical representation of species (e.g., dissolved organic carbon).

The problem of titration kinetics needs study. The stepwise titration requires stability at each step, and the hydration of carbon dioxide is notoriously slow. Although protocols for solution chemistry have recently been adopted, no such agreement on titration rapidity exists.

There are alternative procedures, such as the use of electrical conductivity or thermometry to sense the equivalence point. However, these procedures have not yet shown to be more accurate than potentiometric titrations.

Overall it seems possible to improve the determination of alkalinity, but it will require considerable skill and effort. We recommend a vigorous research program to improve alkalinity measurements parallel to a program to improve DIC measurements.

2.1.5. pH

The pH of sea water refers to the acidity of sea water expressed as a negative base 10 logarithm of a chemical activity relative to a prescribed standard activity. Glass electrodes are commonly used to measure pH. Some commercial electrodes show excessive drift before their electromotive force stabilizes in sea water and offer poor reproducibility. Returning them to low ionic strength pH standard buffers for calibration often leads to further instability. These problems can be partially overcome by storing the electrodes in sea water. Under the best circumstances, the absolute value of pH is only known within 0.01 pH unit. Relative changes can be detected, however, within 0.001 pH unit.

Most of the difficulties in measuring pH seem to arise from the liquid junction which separates the solution being investigated from the reference electrode compartment (calomel or Ag/AgCl electrode). Laboratory-made electrodes can be arranged to minimize the junction potential. These systems use either a flowing or static junction. In the latter case the solution of the reference electrode compartment is brought to the same concentrations in NaCl as in sea water. Such electrodes have a high stability (less than 0.5 mV drift in 150 hrs).

Standardization with tris and bis buffers is recommended by SCOR Working Group 10, as a method of calibration. The chemical system HCl-NaCl is known with great precision over a wide range of ionic strength. It can be used to calibrate electrodes on the scale of the U.S. National Bureau of Standards (NBS). The slope of the electrode from pH 3 to 8.5 can be checked by titrating a phosphate buffer of known stoichiometric composition brought to the ionic strength of sea water by addition of NaCl.

Using dust free solutions and extremely pure silver for the inner and outer reference electrodes increases long term stability of electrodes even more, and a precision of 0.0005 pH unit can be attained. The electrodes must be stored in sea water or sea water-like artificial solutions.

Symmetrical AgCl glass cells can be made to resist high pressure (up to 1000 atmospheres) and can be used for continuous recording at any depth or for profiling. Fouling hazards may give trouble and should be carefully avoided in high precision work.

Colorimetric methods have been developed to measure pH, giving results reported to be in agreement with glass electrode measurements.

Improvements in the precision and accuracy of pH measurements could come from further adjustment of the composition of the inner solutions of the electrode cells and by systematic calibration of the standards with hydrogen electrode cells.

Multiwavelength colorimetric procedures developed to measure pH can provide precisions, at sea, on the order of 0.001 to 0.0005 pH units. Results can be obtained which are compatible with measurements obtained electrometrically. Colorimetric methods do not require periodic buffer standardization. Multiwavelength colorimetric pH measurements employing sulfonephthalein indicators in natural sea water are quite weakly influenced by temperature. The salinity dependence of colorimetric measurements is small within the normal salinity range of ocean water. However, for measurements with precisions of the order of 0.001 pH units, the influence of salinity on sulfonephthalein equilibrium characteristics must be precisely defined. Since sulfonephthalein equilibria have very short relaxation times, colorimetric methods show particular promise for rapid in situ measurements. For colorimetric methods to realize their full potential as molecular pH standards, efforts must be made to assure indicator purity.

2.1.6. Redundancy of measurements of carbonic acid

In sea water, the three chemical species, CO_2, bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) together with hydrogen ion (H^+) are linked chemically through two thermodynamic equilibria so as to result in two independent chemical components. If the concentrations of any two of the above species are known, the remaining two can, in principle, be calculated from the quotients which express these thermodynamic equilibria. These quotients, however, vary with sea water temperature and salinity, which therefore must also be known. The combination of all species containing inorganic carbon is called the "carbonic acid system".

In practice, DIC and carbonate alkalinity, which are linear combinations of the concentration of carbonic species, prove to be more practicable to measure than bicarbonate and carbonate ions, because their concentrations, expressed per kilogram of sea water, do not vary with temperature and salinity. The alkalinity which can be measured by titration includes a contribution from borate salts, and from small amounts of several other species, as discussed in section 2.1.4. Therefore, that part of the alkalinity arising from bicarbonate and carbonate ions must, in practice, be computed on the basis of yet additional thermodynamic data. Owing to uncertainties in the thermodynamic equilibrium quotients, it is not yet possible to compute reliable values of the concentration of CO_2, and H^+, from DIC and titration alkalinity measurements. Instead, CO_2 and H^+ are usually determined by measuring CO_2 and pH, as discussed in sections 2.1.1. and 2.1.5., respectively.

We recommend the continuation of this practice of redundancy, in order to provide further checks on the thermodynamic constraints of the carbonic acid system, and to help in the detection of possible errors in measurements by noting any inconsistencies arising between measured and computed quantities.

The precision of pH measurements in sea water should be of the order of 0.002 pH unit to match the precision attained for DIC and titration alkalinity. Investigators should be encouraged to use the most reliable sensors for pH and to demonstrate that CO_2, DIC, titration alkalinity, and pH form a thermodynamically consistent set of data, when compared through the dissociation and solubility quotients of the carbonic acid system.

2.1.7. Dissolved calcium and calcium carbonate saturation

In recent years, concern about the progressive increase in the levels of fossil-fuel derived CO_2 in the atmosphere has prompted an examination of the potential impacts of increased levels of DIC on the degree of saturation of calcite and aragonite in the oceans, important to the question of long-term changes in buffering capacity. These studies have delineated the major physiochemical factors controlling carbonate saturation in the ocean.

The degree of saturation of calcite or aragonite in sea water is defined as the ion product of the concentrations of calcium and carbonate, at *in situ* temperature, salinity and pressure, divided by the stoichiometric solubility products of calcite or aragonite under *in situ* conditions. When the degree of saturation is greater than one, sea water is supersaturated with respect to the mineral; and conversely, when less than one, undersaturated. The stoichiometric solubility product of calcite or aragonite, the pressure effect on solubility products and the detailed review of the subject has been treated in full in an UNESCO technical paper #51 on the thermodynamics of carbon dioxide system in sea water, as the report by the CO_2 sub-panel of the joint panel on oceanographic tables and standards (1987).

Carbonate ion concentrations are calculated from DIC and TA using the dissociation constants, as recommended in the 1987 UNESCO technical paper #51.

Calcium can be estimated from salinity since the ratio in sea water does not vary by more than 1.5%. Direct measurements of dissolved calcium in sea water can be made by either volumetric or potentiometric titration.

For volumetric titration, a sea water sample is extracted with an organic solvent and subsequently titrated with EGTA (ethylene bis(oxyethylenenitrilo) tetraacetic acid). The endpoint of the titration is detected by visual observation of a color change. Currently, an imprecision of about 3 μM/kg has been achieved on samples analyzed under laboratory conditions. The average concentration of calcium in sea water is approximately 10,200 μM/kg.

Potentiometric titrations utilize a calcium selective electrode to determine changes in potential as calcium is titrated with EGTA solution. The present operational procedure yields an imprecision of about 10 μM/kg. A computer-controlled system, similar to what is used in the alkalinity titration, could be developed which might significantly lower the imprecision.

2.1.8. Dissolved organic carbon (DOC)

The real variability of DOC in ocean water is not well known because of a lack of confidence in existing methods of analysis. We recommend that an effort be made to make DOC measurements as reliable as the most precise DIC measurements, but we offer no opinion now as to how this might be accomplished. A "Summary of Recent Developments" is in Appendix I.

2.1.9. Particulate organic carbon (POC)

Water samples, of 1 to 5 liters volume, are filtered through 0.4 to 0.8 μm silver filters. After rinsing with a strong acid, such as fuming concentrated hydrochloric, to remove inorganic carbonates, the particles collected on the filter are placed into individually marked petri dishes and frozen for shipment to a shore laboratory. In the laboratory the samples are thawed, dried, and analyzed with a carbon-hydrogen-nitrogen analyzer. In this procedure particulate carbon compounds are combusted to CO_2 at temperatures circa $1000^{o}C$ and detected with a thermal conductivity detector. Acetanilide from the U.S. National Bureau of Standards is usually used for standardization. The relative uncertainty of analysis is less than 5%.

2.1.10. Chlorophyll

Several techniques have been described for measuring this organic constituent of sea water. The techniques which are now most commonly used do not greatly differ from one another and generally agree on the following points:

a) Filtration of a sea water volume less than 1 liter on glass fiber filters, with a nominal porosity less than 1 μm (such as Whatman GF/F filters).

b) Mechanical or ultrasonic grinding of the filters in 90% acetone.

c) Measurement of the extract's red fluorescence using a blue excitation light before and after acidification of the extract with one drop of 5% HCl. Acidification allows a correction to be made for phaeopigments. The recommended optical filters are: blue 5-60 and red 2-64.

d) The chlorophyll concentration is then computed using predetermined empirical constants. The ratio of fluorescence to chlorophyll and the ratio of fluorescence before and after acidification are measured on known samples of pure chlorophyll as a means of calibration. The concentrations of these standards are determined spectrophotometrically. The blue lamp used for excitation must give an acidification ratio greater than two, otherwise the correction for phaeopigments generates large random errors.

Exposure to light of the material to be measured is to be avoided as much as possible. The glass fiber filters used to retain the chlorophyll should collect particles as small as 1 μm, since it is well established that phytoplankton cells in the range 1 to 5 μm are often dominant.

The results can be sensitively influenced by the operator. Chlorophyll is an unstable compound, and a more or less important part can be destroyed while making the measurements, thus causing dispersion of the results. It is, thus, important, when carrying out the measurements, to adhere strictly to the same procedures in order to obtain precise data.

A stable fluorescent standard at the chlorophyll wavelengths such as ethidium bromide should be used with every fluorometric analysis.

Apart from the above described technique which allows precise measurements of active chlorophyll, other techniques are available which are more rapid but which provide data less well correlated with phytoplankton biomass. In this category are continuous *in vivo* fluorescence measurements, remote sensing of the sea water color, discussed below, and sampling methods simple enough to be carried out from voluntary observing ships. These techniques are nevertheless of great value; they make it possible to describe the time variations of the boundaries of the main productive ecosystems of the oceans, and they allow us to identify large anomalies in the patterns of these ecosystems. We, therefore, recommend their use as well.

Remote sensing of the chlorophyll concentration of the upper layers of the ocean by earth-orbiting satellites is a promising method for obtaining frequent, large-scale, synoptic maps, although cloudiness partially obscures the usefulness of the method. It should be borne in mind that in some areas the chlorophyll maxima are as deep as 100 meters, but spatial variations in the vertically integrated abundance here appear to be correlated with surface variations. Furthermore, there is a need to check computational procedures with ground-based data in all regions to make this method reliable.

2.1.11. Carbon-13

Approximately 99% of natural carbon consists of the isotope, ^{12}C, of atomic mass 12, but carbon also includes approximately 1% of ^{13}C and a very much smaller fraction (approximately one part in 10^{12}) of ^{14}C. The relative proportions of these isotopes vary in natural carbon as a result of physical and chemical processes which discriminate the three masses, and for ^{14}C owing to radioactive decay. Measurements of isotopic ratios of ^{13}C and ^{14}C relative to ^{12}C are therefore useful in distinguishing processes related to the natural carbon cycle.

The principal constituents of oceanic carbon to be distinguished isotopically are the total dissolved inorganic carbon (DIC) and the total dissolved organic carbon (DOC). For both constituents, the carbon is converted to CO_2 gas which is collected quantitatively by sublimation, using a refrigerant such as liquid nitrogen. For determining ^{13}C the gas sample is purified by warming and resublimation, and then introduced into a multiple collector mass spectrometer where the mass ratios 46/44 and 45/44 are measured with respect to established standards and ^{13}C/^{12}C computed by standard procedures.

It is also possible to determine the $^{13}C/^{12}C$ ratios of particulate carbon (PIC and POC), but owing to the small amounts in sea water relative to DIC and DOC it is difficult to obtain reliable results. Some data exist, especially in connection with studies of ocean sediments, and detritus collected in sediment traps.

2.1.12. Carbon-14

The $^{14}C/^{12}C$ ratio is expressed in a manner similar to carbon-13 except that the $^{14}C/^{12}C$ is conventionally normalized to a constant standard value of the $^{13}C/^{12}C$ ratio after also determining the $^{13}C/^{12}C$ ratio on the same extracted CO_2. Carbon-14 is reported in sea water sample as ^{14}C. Since full recovery of the CO_2 from DIC and DOC is normally not accomplished; these $^{13}C/^{12}C$ ratios are not reliable except to correct the ^{14}C measurements for isotopic fractionation during processing of the water sample. It is, therefore, advantageous also to independently measure $^{13}C/^{12}C$ ratios on separate extracts to achieve complete recovery of CO_2 gas. This has seldom been done, but should be the procedure in the oceanic carbon program proposed here.

Conventionally the ^{14}C of DIC is measured on CO_2 gas samples extracted from 100-250 L of sea water on board ship. DOC, if measured, is extracted from much smaller samples and measured using acceleratory mass spectrometry (AMS). The CO_2 after purification is transferred into low-level proportional counters. With a counting time of about one week, an accuracy of ±2-4 per mil is reached routinely. Recently AMS techniques have been developed, needing only about 1 L of sea water for a DIC ^{14}C analysis. It is, however, not clear at present whether accelerator mass spectrometry will soon reach the same high precision and accuracy as conventional large volume sampling does using proportional counting.

2.2 Ocean Carbon Standards

2.2.1. Introduction

We recommend that standards be prepared and distributed to all organizations participating in the proposed oceanic carbon program. The constituents for which such standards are needed include partial pressure of CO_2 (P_{CO2}), dissolved inorganic carbon (DIC), alkalinity, phosphate, nitrate, silicate, and salinity. Salinity standards have been used routinely at sea to calibrate salinometers for many years. We need not further consider these except to note that they serve as a model for developing standards for carbon studies where none presently exist.

In the case of nutrient species, standards for inorganic phosphate, nitrate, and silicate have been available for some years, but are not widely used. We recommend that the feasibility of using such standards on all expeditions be investigated. That such standards are accurate enough, needs to be established, also that they can be stored for a sufficient time. We emphasize, however, the value in having such standards to improve compatibility of data sets from different expeditions. There is abundant evidence that the variability in measurements of nutrients in deep water from cruise to cruise is several times the variability within cruises in cases where little variability is expected. It is likely that this variability is partly or wholly instrumental and could be reduced, if the analysis equipment on board ship periodically was checked with nutrient standards.

With respect to carbon no practical standards exist at the present time. We propose that a research effort be undertaken to develop such standards, and that an organization be found to maintain the integrity of these standards and distribute them to expeditions and laboratories on a cost recovery basis. The three principal standards needed will now be discussed in turn.

2.2.2. P_{CO2} standards

2.2.2.1. Requirements for a standard

Since the difference between P_{CO2} in the atmosphere and in surface ocean water represents the thermodynamic driving force for air-sea CO_2 exchange, the P_{CO2} of standard solutions for oceanic carbon studies should be tied to atmospheric CO_2 standards as recommended below.

They should also be controlled with respect to DIC and alkalinity. The effect on P_{CO2} of changes in DIC is expressed by the Revelle (or buffer) factor, i.e. $(\Delta P_{CO2}/P_{CO2})/(\Delta DIC/DIC)$ at constant alkalinity, temperature and salinity. This factor ranges between 8 for warm, and 12 for cold, surface water, and is as large as 18 in surface waters rich in DIC. Similarly, the factor expressing the effect on P_{CO2} of changes in alkalinity (ALK), i.e. $(\Delta P_{CO2}/P_{CO2})/(\Delta ALK/ALK)$, ranges between 6 and 10 for surface water and is as large as 16 for surface waters. This means that a change of 1 μM/kg (or 0.05%) in the total inorganic CO_2 concentration or a change of 1 μeq/kg (or 0.04%) in the alkalinity will cause a change of about 2 μatm in P_{CO2}. Thus, a P_{CO2} standard based on sea water must have a high degree of stability in the DIC and alkalinity which it contains.

2.2.2.2. Specifications for a standard

Recognizing that the global mean for the CO_2 difference in the atmosphere and surface ocean water is on an order of 10 μatm, we recommend the following:

1) Standard solutions of sea water should be prepared in which the exerted partial pressures of the major dissolved gases remain stable to an imprecision of 0.05% The CO_2 partial pressure should be measured using an appropriate gas-water equilibration method in the laboratory to an imprecision of 0.05% and referred to the mole fractions of CO_2 given by atmospheric CO_2 standards measured at the same total pressure as the equilibrated sea water. The atmospheric standards should be closely compared to standards used in the global atmospheric CO_2 program of the World Meteorological Organization.

2) The DIC and alkalinity in the standard solutions be specified and individually stable to within 0.5 μM/kg and 1.0 μeq/kg, or better, respectively. The method for DIC measurements recommended in Section 2.1.2 is precise to within about 0.5 μM/kg. On the other hand, the normally obtainable imprecision for alkalinity measurements is 2 μeq/kg or greater. Thus, basic research for improving alkalinity measurements is needed.

2.2.3. DIC standards

2.2.3.1. Dry standards

Anhydrous sodium carbonate (Na_2CO_3), is a primary acidimetric standard which can be obtained commercially to a purity of 99.9%. The carbon content could be assayed to an accuracy of 99.95% for distribution. For devices which measure aliquots of sea water by removing the CO_2 and determining the amount removed, weighed samples of salt could be converted quantitatively to CO_2 gas on board ship and used directly to calibrate devices such as a gas chromatograph which measure amounts rather than concentrations. Alternatively, prepared CO_2 gas samples in breakoff tubes could be distributed. Such standards do not, however, serve to calibrate the devices which strip CO_2 from sea water. To assure performance of the entire procedure by which DIC is measured from samples of sea water, it is necessary to use aqueous standards, as discussed next.

2.2.3.2. Wet standards

Because of the serious problems which have always been associated with attempts to prepare artificial sea water, we recommend that the first approach to a wet standard be the use of an adjusted real sea water. Sea water should be collected where experience has shown that the water can be stored for long times without change in DIC. Until now no sea water appears to be constant under storage unless biological activity is stopped by an artificial agent. The Scripps Institution of Oceanography has used mercuric chloride to poison samples and found no detectable change in DIC upon storage for 1 year. Additional storage tests are needed. It seems likely, however, that if a large quantity of poisoned sea water were prepared and found to be stable when stored initially in a large container, that it could be rebottled for use at sea without any change in DIC from the time of removal from the large storage container. From a practical point of view, approximately one year's storage is the maximum needed for standards used on expeditions. Thus, within one year from now it should be possible to decide whether such samples can be prepared. A search should be made for the best possible poisoning agent.

As a first step in creating a set of sea water standards, we propose that approximately 1000 liters of deep ocean water be collected to serve as a standard containing high DIC, and that a similar amount of surface water be collected from a region of low nutrient concentrations to serve as a standard containing low DIC. Experience will later on determine what may be better sources of water. Highly productive waters show evidence of continued biological activity even when poisoned with mercuric chloride and should probably not be used to prepare standard water.

Based on the experience of the Scripps laboratory, we recommend as an initial provisional procedure that water, after being poisoned and checked for stability for six months or more, be transferred without gas exchange to one-liter bottles of silica glass (commercially called vitreous quartz) equipped with clamped ground glass standard taper stoppers. The bottles will first be cleaned with detergent or an oxidizing agent and then, after rinsing with distilled water, will be annealed at a temperature near the melting point of glass. The stoppers will be greased with a vacuum quality sealant such as Apiezon-N grease and stored in the dark.

We recommend the frequent use of such standards at least in the early stages of a carbon program. Only if it is shown that a fewer number of standardizations leads to nearly identical performance should the number be reduced. In particular, standardization should not be curtailed as a means of reducing the cost of analysis, because the cost of calibrating is a small part of the total cost. We propose that one bottle be employed at sea for each hydrographic station, or one per day for under-way work. We estimate an initial need for approximately 1000 bottles of each standard per year.

Some standards should be taken to sea and returned unused to the distributing organization for storage checking.

2 2.4. Alkalinity standards

2.2.4.1. Dry standards

Anhydrous sodium carbonate is a primary standard which can be used where it is possible to prepare wet standards on board ship to sufficient precision. In the past, sodium borate decahydrate has also been used to test the titration equipment used to determine alkalinity but is more difficult to maintain owing to water of crystallization. In addition to a dry sodium carbonate standard, we recommend the use of wet standards, as discussed next.

2.2.4.2. Wet standards

Some storage tests to determine how well alkalinity standards can be preserved in sealed ampoules have been completed at Woods Hole Oceanographic Institution; others are still in progress. We are hopeful that DIC wet standards, as discussed above, will also serve as alkalinity standards. Silica glass cannot contribute additional alkalinity to the sample by dissolution of the glass except for dissolved silica. By measuring the silica at sea any increase can be controlled and taken into account when the standard is used. We do not expect as large a rate of dissolution as has been found with soft glass, but additional testing is needed to determine this. With respect to alkalinity, gas exchange after opening the bottles is not a problem. Therefore the standard water remaining after withdrawing aliquots for DIC standardization can be handled without special gas tight equipment.

2.2.5. Calcium standards

2.2.5.1. Dry standards

Calcium carbonate ($CaCO_3$) is a primary standard which can be obtained commercially to a purity of 99.99%. In addition to a dry standard, we recommend the use of wet standards.

2.2.5.2. Wet standards

As in the case of alkalinity standards, we are hopeful that the wet standards for DIC will also serve as standards for calcium.

2.2.6. Isotopic standards

These are well established for both carbon-13 and carbon-14 and will not be discussed here.

2.2.7. Precision and accuracy of standards in general

To accomplish the goals of the carbon program, an imprecision below 1 μM/kg is needed for DIC. This is because biological processes cause changes in DIC in more or less fixed proportions to inorganic phosphorus and nitrogen such that an imprecision of 1 μM/kg produces the same order of error in carbon as in the nutrients. It has been found desirable to attain the highest precision attainable when studying nutrients. There is a similar need with respect to carbon.

The maximum secular change in DIC to be expected from the burning of fossil fuel and the sequent absorption of carbon by ocean water is 1 μM/kg per year. To study interannual changes in carbon, a precision to 1 μM/kg is again desirable. Because such studies need to be pursued for many years, and we cannot guarantee standards to be valid that long, an *accuracy* to 1 μM/kg is also needed. The direct extraction of CO_2 from sea water and its manometric determination is essentially an absolute method, and there is therefore hope that the accuracy attained by this method is developed and used as a comparator. With respect to alkalinity, an imprecision below 2.0 μeq/kg is needed to keep track of the portion of change in DIC which is owing to addition or traction of carbonate ion from sea water to the same precision as recommended for DIC. But a lower imprecision of 0.5 μeq/kg is needed to relate DIC and alkalinity to CO_2 owing to the buffer factor effect. A precision to 1 part in 2000 for alkalinity and DIC results in a precision in calculating CO_2 of only about 1 part in 200. We need to control DIC and alkalinity precisely enough to calculate CO_2 to about 1 part in 500, as discussed above. Therefore efforts to improve precision of DIC and alkalinity standards should continue until the errors are reduced well below 1 μeq and 1 μM/kg with respect to both precision and accuracy.

2.2.8. Implementation of standards

Since the final meeting of SCOR WG-75, the JPOTS sub-panel on standards for CO_2 measurements took up the responsibility to research into the availability of reference materials for oceanic CO_2 measurements. Pyrex bottles of sea water preserved by mercuric chloride and kept from contact from atmosphere by greased stoppered bottles, were distributed from the Institute of Oceanographic Sciences, UK, for an intercomparison study of DIC and TA with participation of 12 international laboratories, as described in detail in the UNESCO technical Paper in marine science #59 (1990). Scripps Institution of Oceanography produced a prototype reference sea water for DIC and TA and distributed for an international intercomparison study, as described in the UNESCO technical paper in marine science #60 (1991). The JPOTS sub-panel was replaced by a sub-panel on oceanic CO_2 standard under the Joint JGOFS/CCCO Panel on CO_2, to research and coordinate the distribution of reference sea water to international laboratories participating in the WOCE Global CO_2 Survey and other major oceanographic expeditions so as to establish data quality control for DIC, TA, pH and P_{CO2} measurements in sea water. Scripps Institution of Oceanography, the central lead group for international CO_2 standards activities, in distributing reference sea water for DIC now and expected to do so for TA soon, for WOCE and US JGOFS time-series cruises. The Centre for Ocean Climate Chemistry in Canada is also conducting research on reference sea water for DIC/TA and P_{CO2} gaseous standards. A third group may be established in Europe for European Common Market countries in future.

2.3. Intercalibration

An intercalibration for total alkalinity (TA), dissolved inorganic carbon (DIC), calcium, pH and P_{CO2} measurements was recommended to be organized, jointly with the Marine Chemistry Working Group of the International Council for the Exploration of the Sea (ICES) and SCOR Working Group 75. The Laboratoire de Physique et Chimie Marines, University of Paris, responsible for organizing the exercise, showed that one litre Pyrex bottles were adequate for alkalinity purpose. The Institute of Oceanographic Sciences at Wormley, UK prepared sea water samples at 4 salinities 10, 30, 35, 38.5, preserved by mercuric chloride for distribution to 12 international laboratories participating in the intercomparison exercise. The study was described in the UNESCO technical paper in marine sciences #59 (1990).

Another intercalibration was sponsored by SCOR, UNESCO, ICES and IAPSO for DIC and TA. Scripps Institution of Oceanography produced a prototype reference sea water, calibrated manometrically by the WMO CO_2 Central Laboratory at SIO. Ampoules of such sea water preserved by mercuric chloride and kept out of contact with the ambient atmosphere using greased ground-glass stoppers, were distributed to international laboratories to intercompare DIC and TA. The results were described in the UNESCO technical paper in marine sciences #60 (1991).

2.4. Network Design

2.4.1. Regions to study

In order to determine the natural processes affecting the variability of carbon concentrations in the oceans and to provide the necessary data required to produce a global budget for CO_2, we recommend that an integrated international program be established to study oceanic carbon variations in the five major ocean basins and the polar regions. Principal among these areas are:

a) *The equatorial belt from 10^{o}N to$10^{o}S$*, where the seasonal variations in carbon are of the same order as interannual variations. A time series station in the Pacific ocean could be occupied using Christmas Island (2^{o}N) as a port while, in the Atlantic ocean, Ascension Island (8^{o}S) could be used.

b) *The subtropical gyres*, where it is expected that the variability in carbon is low. Anthropogenic signals will not be masked by high frequency local noise due to biological activities or unstable physical conditions. A time series station in the North Pacific could be occupied using Honolulu (22^{o}N) as a port and, in the South Pacific, Tahiti (17^{o}S) could be used. In the Atlantic Bermuda (23^{o}N) could be used. We have not identified a port for the Indian Ocean.

c) *High latitude circulation systems*, where the seasonal cycle in carbon is expected to be large North Pacific ocean stations could include one in the Bering Sea and one at Ocean Station 'P' (50^{o}N, 145^{o}W). A south Pacific ocean station could be established south of Hobart, Tasmania (43^{o}S). In the north Atlantic ocean, Weather Station 'M' (66^{o}N, 2^{o}E) or a station in the vicinity of Iceland could be used.

d) *The coastal zones*, where it is anticipated that high variability in carbon will be encountered, related to upwelling and strong horizontal advection. Existing coastal stations could be used.

2.4.2. Time and space coverage

It has long been recognized that the oceanic carbon system is dynamic and complex with large spatial and temporal variations. We believe that long-term and frequent coverage of key regions of the oceans is needed in order to separate the small anthropogenic CO_2 signal from large natural variabilities in carbon concentration. Three types of sampling schemes are envisioned for such a coverage:

a) Network Stations. We define a network station as a site occupied by a research vessel continuously or visited at least six times a year over many years. Only such stations will provide truly reliable information on seasonal variabilities. Suggested locations of stations in key regions to ensure at least minimal space coverage were already noted above in section 2.4.1. The JGOFS Scientific planning includes time-series stations. The U.S. National Science Foundation supports two such stations near Hawaii (Station H) and near Burmuda (Station S) and the Canadian Department of Fisheries and Oceans at Station P in N.E. Pacific waters.

b) Special cruises. Network stations will provide important information at key points, but to establish large-scale, ocean-wide spatial variations will require, in addition, special cruises in the vicinity of these key stations. In some areas, special cruises should be more frequent than once per year in order to provide supplemental seasonal data. Less frequent special cruises reaching every key region of the world oceans are also needed to provide data to indicate ocean-wide secular changes. Some already planned special cruises are discussed in section 2.5., below.

c) Ships-of-opportunity. Given presently available resources as a guide, it is likely that an oceanic carbon program will not be able to afford and maintain a complete network of CO_2 sampling stations similar to the present atmospheric CO_2 sampling program. As a result, ships of opportunity should be used to provide cost-effective platforms for collecting additional data. More remote, yet oceanographically important regions, could be covered economically by this means.

2.5. Coordinated Observational Programs

To document large-scale spatial and temporal variability in the oceanic carbon cycle in both surface and subsurface waters requires a coordinated program of measurements in which use is made of research vessels and commercial vessels that both frequently and infrequently cross the major ocean basins along the same tracks.

The JGOFS/CCCO CO_2 Panel has been responsible for such coordinated observational program on CO_2. It is in charge of providing guidance to the global CO_2 survey as a JGOFS program on WOCE ships to be used in the once-time World Hydrographic Program 1991-1995. The latest plan on the CO_2 Panel's activities towards the acquisition of the global CO_2 data set is reproduced with permission from CCCO, from the Report of Second Session of the joint JGOFS-CCCO Panel on CO_2 met 22-26 April 1991 in Paris, France, as Appendix II.

2.6. Data Archiving and Distribution

Because the oceanic carbon program which we recommend is envisioned as an integrated international effort extending over decadal time scales, we perceive an ongoing need for a central data repository and for consistency in format, reporting and dissemination of oceanic carbon cycle measurements. A corresponding effort in the standardized reporting of atmospheric CO_2 monitoring data has already been established by the World Meteorological Organization (WMO). We recommend the creation of a parallel and equivalent staff position to coordinate the time archiving and dissemination of the oceanic carbon observations.

Since an oceanic carbon program will involve many countries and observing ships, the early adoption of a uniform format for the reporting of data is a high priority. The format adopted in the 1970's for the Geochemical Ocean Section Study (GEOSECS) program offers a possible model for archiving. Coordination of the oceanic carbon and atmospheric CO_2 data bases will require close cooperation with WMO personnel.

3. Organizational Basis for Oceanic CO_2 Studies

3.1. Planning

We recommend that a permanent international program to address the carbon cycle in the oceans be organized with the help of existing international organizations concerned with oceanic research. An international planning entity focused directly on the carbon cycle of the oceans is desirable. Under usual circumstances this would be self-evident, but in the case of oceanic carbon research, recent planning and research activities have been influenced by the possibility of far reaching consequences of man's intervention into the carbon cycle. These possible consequences have attracted attention well beyond the usual limits of interest in marine chemistry. This attention has brought unusual elements into planning of oceanic carbon cycle research.

At present a major impetus for studies of oceanic carbon relates to the presumed impact of atmospheric CO_2 on climate. It is argued that we cannot predict future levels of atmospheric CO_2 without a better understanding of the response of the ocean to increasing CO_2. Awareness of changes in CO_2 in the past, as revealed by ice cores, heighten the need, because it makes it appear likely that natural variations will occur which must be distinguished from anthropogenically caused variations, if we are to understand the CO_2 buildup in future decades.

The connection of the carbon cycle research with climate studies is largely based on concern for this buildup of CO_2 in the atmosphere and the predicted warming of the air by the greenhouse effect. But what if it should turn out that the greenhouse effect is small? It appears to us that in the present context much of the impetus for carbon cycle research would then disappear.

It is important to study the carbon cycle for its own sake both for intrinsic scientific reasons and because other important changes besides climatic changes may attend the rise in atmospheric CO_2, and the introduction of polluting chemicals to the oceans. For example, rising CO_2 will increase the acidity of ocean water and will thereby alter the carbonate chemistry of the oceans.

We, therefore, recommend the establishment within the oceanographic community of scientists of a planning entity directly concerned with the carbon cycle of the oceans.

3.2. Scientific Meetings

SCOR Working Group 75 has been organized for the purpose of preparing technical information on the methodology of oceanic CO_2 measurements. It has not been able to devote a significant part of its activities to presentations of scientific data and interpretation. We recognized, however, the great value of a symposium in the near future to address in depth the principal scientific topics of oceanic carbon studies.

Accordingly, we recommend that an international symposium on the carbon cycle in the oceans be held in future. A suitable organizing body, in our opinion, is the Marine Chemistry Commission of the International Association of Physical Sciences of the Oceans (IAPSO), perhaps co-sponsored by other international organizations such as the Committee on Climatic Changes and the Ocean (CCCO).

4. Summary of Recommendations

This report contains several proposed actions for furthering a world-wide study of the carbon cycle in the oceans. These recommendations represent the consensus of members of SCOR Working Group 75 and invited experts who attended the May, 1984, September, 1985 and October, 1988 (Appendix III) meetings. The principle recommendations are restated here as a summary of the discussions and deliberations of these meetings. If discussed above, the appropriate section number is noted.

1. A coordinated program should be organized and vigorously pursued to develop convenient, precise methods for measuring DIC and alkalinity at sea which can be adopted for general use by all participants of the global oceanic carbon program as soon as possible (related to 2.1).

2. Standard reference materials should be prepared and distributed to participants of the global oceanic carbon program for the calibration of CO_2, DIC, alkalinity, phosphate, nitrate, silicate, and chlorophyll (2.2).

3. A research effort should be undertaken to develop such standards in cases in which satisfactory standards do not yet exist (2.2.2, 2.2.3, 2.2.4, 2.2.5).

4. Standards should be used frequently, especially in the early stages of the global oceanic carbon program (2.2).

5. An international organization should be designated by the International Oceanographic Commission to maintain and distribute standard reference materials (2.2.8).

6. Measurements of CO_2 and pH should be encouraged, even though redundant with DIC and alkalinity measurements, because they can be obtained in greater number and provide needed checks on the thermodynamic consistency of the carbonic acid system in sea water (2.1.6).

7. Reference stations convenient to the major laboratories of the global oceanic carbon program should be occupied on a continuing basis to establish the reliability of adopted chemical methods (related to 2.2).

8. An intercalibration should be carried out for CO_2, DIC, alkalinity, calcium, and pH as a joint program of SCOR Working Group 75 and the Marine Chemistry Working Group of ICES (2.3).

9. We support the efforts of SCOR Working Group 10 to demonstrate that measurements of CO_2, DIC, alkalinity, and pH are thermodynamically consistent (related to 2.3).

10. The major constituents of the oceanic carbon cycle should be measured at fixed stations with a frequency of 6 to 12 times per year to establish the seasonal and interannual variability of carbon in representative regions of the world oceans. Where possible these observations should span the entire water column, but additional stations restricted to surface water sampling are also desirable to increase the coverage (related to 2.4).

11. A series of shuttle expeditions should be carried out over periods of 15 months as a first step toward establishing the seasonal variations of the major oceans (related to 2.4).

12. Additional similar sections of the ocean should be surveyed once to increase coverage and to provide the basis for reoccupation at intervals of approximately 10 years (related to 2.4).

13. Technically manned ships of opportunity should be employed where repeat sampling is possible (related to 2.4).

14. Voluntary observing ships should be employed for additional surface water observations (related to 2.4).

15. A permanently staffed international central data repository should be established to archive and distribute data obtained by the global oceanic carbon program. Primary observational data should be mitted as well as derived quantities. In the manner adopted by the World Meteorological Organization for the global atmospheric CO_2 program, flagging procedures should be used to mark questionable or irregular data rather than suppressing them from the archive (2.6).

16. A planning entity focused directly on the carbon cycle in the oceans should be established within the international oceanographic community (3).

17. An international conference should be held within the next two years to address the scientific results emerging from studies of the oceanic carbon cycle. Participants would be asked to present papers of original results. The conference would be designed to attract between 30 and 50 papers so that it could be held as a single session in 5 days. The Marine Chemistry Commission of IAPSO should be invited to co-sponsor the above proposed conference (3.2).

18. The next meeting of SCOR Working Group 75, if possible, should be held in conjunction with the above proposed conference.

19. The planners of the World Ocean Circulation Experiment (WOCE) are encouraged to include a component to support the research program on oceanic CO_2 proposed by SCOR Working Group 75 in this report. This component would include hydrographic casts able to accommodate chemical analyses of all important carbon cycle related species. The aliquots of water would be collected promptly to preserve the *in situ* DIC concentrations.

20. Coordination is sought with the Global Ocean Flux Study Program proposed by The U.S. National Research Council. Coordination with the program should be discussed at the next meeting of SCOR Working Group 75.

21. Coordination with other oceanographic programs is encouraged for the purpose of obtaining repetitive observations at fixed stations and along fixed oceanic tracks with the object of establishing seasonal and interannual variations in oceanic chemical properties.

22. Contacts will be sought with the following working groups of SCOR:

WG 71: Particulate Biogeochemical Processes.
WG 72: The Ocean as a Source and Sink for Atmospheric Constituents.
WG 78: Determination of Photosynthetic Pigments in Sea water.
WG 79: Geological Variations in Carbon Dioxide and the Carbon Cycle.

23. Strategies for optimizing ocean sampling, including orientation of tracks and station spacing, should be considered at the next meeting of SCOR Working Group 75.

24. The existing methodologies for observing CO_2, DIC, and alkalinity should be surveyed and summarized, and a manual of provisional observational methods should be produced, as a first step towards preparing a standardized methodology for oceanic carbon studies. (The chairman of WG-75 was asked to conduct such a survey.)

25. WG-75 will produce an "interim" CO_2 methodology to be published in the UNESCO technical manual series. WG-75 chairman was asked to pursue the task, by compiling key published papers on (a) pH, (b) alkalinity, (c) DIC, (d) P_{CO_2}, (e) isotopic ^{13}C, ^{14}C, (f) POC, (g) DOC, (h) software in thermodynamic calculations, (i) sources of contacts for reference sea water and material and (j) data. The manual should include a forward section, to be written by experts in each of these fields, commenting or updating the published methods.

26. WG-75 recommends to SCOR to consider two major areas for replacing SCOR WG-75: (a) to organize international experiments for designing chemical model of future CO_2 changes in the ocean to guide the prediction of CO_2 changes due to natural events. The best measurements, in terms of compatibility and experimental design, will be done by world experts to be gathered at selected sites, and (b) to study the rationalization of DOC for availability of technique to the scientific community. WG-75 chairman was asked to table a proposal for such a replacement WG for consideration in the next SCOR executive meeting, and this will be established by correspondence.

5. Acknowledgments

We thank Mrs. Elizabeth Tidmarsh of the SCOR secretariat for her active and helpful support of our working group throughout the past years and of this meeting in particular. We also thank Ann S. Edwards, at the U.S. JGOFS Planning Office, Woods Hole Oceanographic Institution for her assistance in arranging our stay at Woods Hole and the meeting, and Julie Henderson at the Institute of Ocean Sciences for her assitance in the preparation of this Final Report.

LIST OF PARTICIPANTS

SCOR WG 75 Members

Dr. P. G. Brewer
Woods Hole Oceanographic Institute
Woods Hole, Massachusetts 02543
U.S.A.

Dr. R. Chesselet*
15 Quai Anatole France
5700 Paris, France

Dr. C. D. Keeling*
University of California, San Diego
Scripps Institution of Oceanography
La Jolla, CA 92093
U.S.A.

Dr. G. Lambert
Centre des Faibles Radioactivites
Laboratoire mixte CNRS/CEA
Avenue de la Terrasse
91190 Gif-Sur-Yvette
France

Dr. K. O. Munnich*
Institut fur Umweltphysik
University of Heidelberg
D-6900 Heidelberg
Federal Republic of Germany

Dr. A. Poisson*
Laboratoire de Physique et Chimie Marines
Universite Pierre et Marie CURIE, Tour 24
4, Place Jussieu
75230 Paris Cedex 05
France

Dr. Y. Sugimura+
Geochemistry Laboratory
Meteorological Research Institute
Nagamine 1-1
Yatabe, Tsukuba
Ibaraki 305, Japan

Dr. C. S. Wong
Centre for Ocean Climate Chemistry
Institute of Ocean Sciences
P.O. Box 6000
Sidney, B.C., Canada

*unable to attend
+deceased in November, 1991

Invited Experts

Dr. R.H. Byrne
Department of Marine Science
University of South Florida
St. Petersburg
Florida 33701-5016
U.S.A.

Dr. E.M. Druffel
Woods Hole Oceanographic Institution
Woods Hole, Massachusetts 02543
U.S.A.

Dr. R.A. Feely
National Oceanic and Atmospheric
Administration
Pacific Marine Environmental Laboratory
7600 Sand Point Way N.E.
Seattle, Washington, 98115
U.S.A.

Dr. C. Goyet
Woods Hole Oceanographic Institution
Woods Hole, Massachusetts 02543
U.S.A.

Dr. H. Livingston
Woods Hole Oceanographic Institution
Woods Hole, Massachusetts, 02543
U.S.A.

Dr. E.T. Peltzer
Woods Hole Oceanographic Institution
Woods Hole, Massachusetts 02543
U.S.A.

Mr. J.C. Zheng
Third Institute of Oceanography
National Bureau of Oceanography
P.O. Box 70, Xiamen (Amoy)
Fujian
People's Republic of China

TABLE 2.1. DEFINITIONS OF SCIENTIFIC TERMS AND ABBREVIATIONS

TERMS	DEFINITIONS	OCEANIC RANGE	PRESENT EXPERIMENTAL IMPRECISION
pCO_2	The partial pressure of CO_2 gas exerted by seawater at a given temperature expressed as microatmospheres (μatm).	Open Ocean (surface) - 150 to 450 μatm Coastal water - 100 to 1500 μatm	1 to 5 μatm
DIC	The concentration of total inorganic dissolved in a unit mass of seawater expressed in micromoles of CO_2 per kilogram of seawater of seawater (μM/kg). Note DIC consists stoichiometrically of approx. 1% CO_2, 90% bicarbonate (HCO_3^-), and 9% carbonate (CO_3^{2-}).	Surface water - 1900 to 2100 μM/kg Deep water - 2000 to 2300 μM/kg	1 to 8 μM/kg
ALK	The alkalinity of seawater, which is a sum of ionic charges of weak acids dissolved in in seawater including carbonic, boric, silicic, and phosphorus acids. It is synonymous to the titration or total alkalinity and is expressed in microequivalents per kilogram of seawater (μeg/kg).	Surface water - 2100 to 2300 μeq/kg Deep water - 2200 to 2500 μeq/kg	2 to 4 μeq/kg
DOC	The concentration of total organic carbon dissolved in seawater. The organic species are not specified, and all the species are included. It is expressed in the same units as DIC. Note: the oceanic ranges and imprecisions quoted to the right were from data obtained by perchlorate wet oxidation. This technique is not yet proven to be correct.	Surface water - 50 to 150 μM/kg Deep water - 50 μM/kg	4 μM/kg 2 μM/kg
POC	The concentration of particulate organic carbon suspended in seawater. It includes all all the forms of organic matter, such as fragments of tissues and fecal matter, but excludes carbon in skeletal $CaCO_3$. It is expressed in the same units as DIC.	Surface water - 1 to 60 μM/kg Deep water - 0.2 to 1.0 μM/kg	Surface water 0.05 to 3 μM/kg Deep water 0.01 to 0.5 μM/kg
PIC	The concentration of particulate inorganic carbon suspended in seawater. It includes carbon in skeletal $CaCO_3$ (Foraminifera and Pteropod shells). It is expressed in the same units as DIC.	Less than 1 μM/kg	0.05 μM/kg
pH	$-\text{Log}(H^+)$ or $-\log A_{H^+}$, at a specified temperature. pH may be defined on several scales such as the NBS pH scale, or in moles of H^+ per kg of seawater. The oceanic convention is not yet firmly adopted.	Surface water - 8.0 to 8.2 Deep water - 7.8 to 8.1	0.01 pH units 0.02 pH units
Ca	The concentration of calcium dissolved in seawater, expressed in micromoles per kilogram of seawater (μM/kg).	Surface water - 9800 to 10200 μM/kg Deep water - 10100 to 10300 μM/kg	3 to 10 μM/kg
O_2	The concentration of oxygen gas dissolved in seawater expressed in micromoles of O_2 per kilogram of seawater (μM/kg).	Surface water - 200 to 350 μM/Kg Deep water - 0 to 300 μM/kg	1 μM/kg
Nutrient	The concentration of nutrient species, such as NO_3^-, PO_4^{3-} and SiO_3^{2-}, in seawater expressed in micromoles per kilogram of seawater (μM/Kg).	Surface water: NO_3 - 0 to 30 μM/kg PO_4 - 0 to 2 μM/kg SiO_3 - 0 to 60 μM/kg	NO_3: 0.2 μM/kg PO_4: 0.01 μM/kg SiO_3: 0.5 μM/kg
Chl-a	The concentration of active chlorophyll-a in seawater expressed in micrograms per kilogram (μg/Kg)	0 to 600 μg/l	

APPENDIX I

SUMMARY OF RECENT DEVELOPMENTS IN DISSOLVED ORGANIC CARBON (DOC)

DOC is derived from plankton both directly, through exudates, and indirectly, through hydrolysis and partial mineralization of dead cells. It is operationally defined as the amount of organic carbon, in moles, evolved when filtered and acidified sea water is oxidized completely.

The chemical composition of DOC is largely unknown, only less than 10% of it has been identified and found to consist of amino acids, fatty acids, carbohydrates, phenols, sterols etc. Its molecular weight ranges from less than 10^2 to larger than 10^5. The unknown nature and wide range of molecular weight distribution of DOC causes difficulty with precise determination.

The temporal and spatial variability of DOC in ocean water is not well known because of a lack of confidence in existing methods of analysis. The High Temperature Catalytic Oxidation (HTCO) technique (Sugimura and Suzuki, 1988) developed at the Japanese Meteorological Research Institute (MRI) yielded higher DOC values than other methods in use, such as persulfate oxidation. The recent JGOFS North Atlantic Bloom Experiment of March-October, 1989, showed an encouraging agreement between MRI and WHOI, which utilized a pure platinum catalyst in a similar HTCO method (JGOFS Report #4, 1990). However, there is no universal concensus yet with other laboratories. We recommend that an effort be made to make DOC measurements as reliable as the most precise DIC measurements.

We recommend as the principal basis for achieving precise DOC measurements the determination by NDIR analysis, the CO_2 gas produced by high temperature catalytic oxidation of directly injected sea water, after removal of the DIC from the sample (Sugimura and Suzuki, 1988).

The HTCO method is currently undergoing a period of rapid evolution. In the summer of 1991, experts from around the world met in Seattle under the sponsorship of NSF/NOAA/DOE to discuss the problems and methods of measuring DOC and to outline the future directions for research. While universal agreement between the experts was not achieved, they did identify several areas which need urgent attention. These are in no particular order:

- What standard do we use: glucose, potassium hydrogen phthalate (KHP), or something more similar to natural DOM?

- Can the standard solutions be prepared in distilled water or must filtered seawater be used?

- Is there a substance which can be used to critically evaluate the performance of the catalyst?

- What is the best procedure to go about evaluating the instrument blank?

- Can samples be stored for later analysis or must they be analyzed immediately aboard ship?

- Is it possible to develop a suitable reference method, perhaps using sealed-tube combustion at high temperature?

The method used to measure DOC at present is as follows: Immediately after collection using 10 to 30 liter Niskin bottles at sea, sea water was filtered through a membrane filter (Nuclepore, 0.4 μm) without any contact with ambient air, by using a closed circuit pressurized filtration system.

The first 1 liter aliquot of the filtrate was discarded and a 20 ml aliquot of the remaining filtrate was transferred to a glass cylinder. It was acidified by adding 1 ml of 10% phosphoric acid. The CO_2 from DIC was expelled by an oxygen stream for 5 min at a flow rate of 100 ml min^{-1}.

A 200 μl sample of the degassed sea water was injected by means of a microsyringe into the oxidation column (a 18 mm dia. and 33 cm in length, quartz tube packed with 16 g of Pt-impregnated Al_2O_3 catalyst) at 680° C under an oxygen atmosphere (flow rate, 100 ml min^{-1}). The non-volatile fraction of DOC in seawater was quantitatively oxidized on the surface of the catalyst to CO_2 gas. Before introduction of the CO_2 thus generated into IR gas analyzer, it was dried by means of magnesium perchlorate. Determination of CO_2 was carried out using NDIR gas analyzer. The reaction time of the complete procedure was 4 min per sample. The electric signal from the gas analyzer was introduced into a computing integrator, the area under the recorded curve was measured and the amount of carbon was calculated.

Through the method, 100% of recovery and reproducibility were obtained with a standard deviation of less than $\pm 2\%$. The range of concentration of DOC in sea water ranged from about 300 μmoles l^{-1} in surface waters to several 10 μmoles l^{-1} in the oxygen minimum layer.

Sugimura, Y. and Y. Suzuki, 1988. A high-temperature catalytic oxidation method for the determination of non-volatile dissolved organic carbon in sea water by direct injection of a liquid sample. *Marine Chemistry 24* , 105-131.

APPENDIX II

REPORT OF SECOND SESSION OF THE JOINT JGOFS-CCCO PANEL ON CARBON DIOXIDE
22-26 APRIL 1991, PARIS, FRANCE

3. Acquisition of the CO_2 Data Set

3.1 WOCE Issues

Peter Koltermann, Director of the WOCE International Project Office, led the discussion on CO_2 data sets from WOCE, JGOFS and other activities. At one level there is the WHP data and at another is a collection of national data sets which do not look like WOCE or JGOFS. Emphasis has to be placed on seeing that the national efforts have more international coherence and that they are done with a common set of standards, e.g., the *Vivaldi* programme should do CO_2 work with CCCO-JGOFS CO_2 standards. Koltermann cautioned that if WOCE facilities are used for handling CO_2 data, care must be taken to be sure the system is not overloaded. The question of how to get non-WOCE, non-JGOFS data into the WOCE system also has to be examined.

L. Merlivat noted the CO_2 Panel was not where it would like to be with data management and cruise assignments. It was clear, however, that a central authority is needed for tracking participation of WOCE cruises. It was agreed the country in charge of a particular cruise should have first responsibility for doing the CO_2 work and, if that country cannot do it, someone else has to be approached. This central authority must have data on ships, programmes, ports of call, names of participants, dates, planned measurements, etc.

H. Livingston at the WHP Office has been tracking national commitments to the WHP lines and has kept track of national plans for WOCE CO_2 lines as well. As of 20 March 1991, the information that was available to him is in the following Tables A and B. For reference, the WOCE lines are illustrated in Figure 3.1.

Fig. 3.1 Distribution of WOCE One-Time Survey Lines 15/2/91

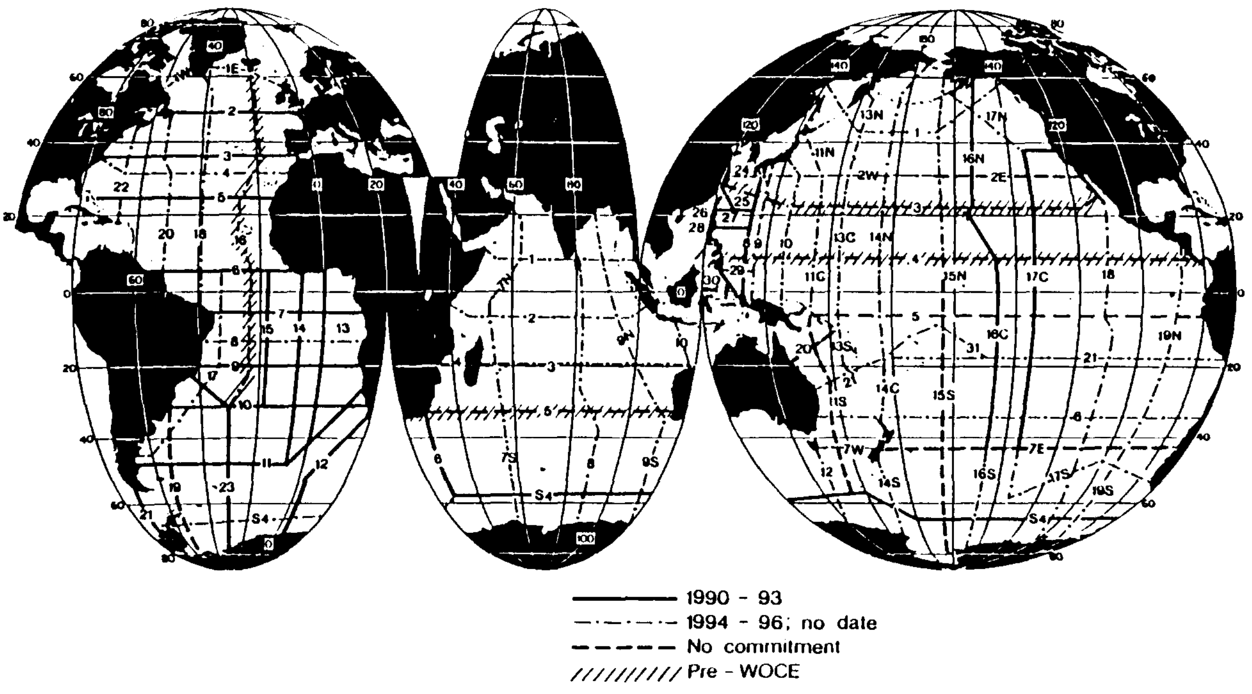

TABLE A

OCEAN CO_2 SYSTEM - THE WHP SURVEY

SUMMARY OF LINES COMPLETED OR PRESENTLY SCHEDULED

PACIFIC	ATLANTIC	ATLANTIC
PR6	A1	I4
P12	A2	I6
P13C	A4C	I7S
PR15	A6	I9S
P15	A7	I10
P16	AR7C	
P17	A9	
P19S	A11	
SR3	A12	
SR4	A18N	
	A20N	
	A21	
	A23	
	S3	
	S4	

TABLE B
NATIONAL PLANS FOR WOCE CO_2
(as of 2 May 1991)

ATLANTIC

WOCE LINE	1990	1991	1992	1993	1994	1995	1996
A1W		CAN BIO					
A1E			GER IFM/BNL/WHOI				
A2		CAN (WHEN?) BIO					
AR7E(A1)		NETH NIOS					
AR7E(A1)		GER IFM					
A4C		CAN BIO					
A6			FRA ORSTOM				
A7			FRA ORSTOM				
A9		GER IFM/BNL/WHOI					
A11			UK ?				
A12	GER LDGO*						
A1SN		CAN BIO					
A20N		CAN BIO					
A21	GER LDGO*						
A23			UK ?				
S4	GER LDGO*						

Notes: * C14 measured

PACIFIC

WOCE LINE	1990	1991	1992	1993	1994	1995	1996
P1			CAN/USSR IOS				
PR6			CAN	IOS			
SR3(#?)				AUS HOBART			
P13C		JAP		JAP			
PR15		HOKK		HOKK			
P15W					CAN IOS		
P15#			CAN/USSR IOS				
P16/17C+S		LDGO/SIO/WHOI	USA				
P16N	USA PMEL*						
P19S+			UK UCNW				
S4P		USSR/USA LDGO					
S4WP (#?)						AUS HOBART	

NOTES: *C14 PLANNED
NO WOCE STATION/DEPTH

INDIAN

WOCE LINE	1990	1991	1992	1993	1994	1995	1996
I4		FRA LPCN					
I6				FRA LPCN			
I7S					FRA LPCN		
I7S							
I9S	(#?)			AUS			
I10	FRA(89) LPCN*			FRA LPCN			

3.2 National Plans for CO_2 Studies

As alluded to earlier in this report, there are several categories of CO_2 studies being conducted. In section 3.1, the WOCE-coupled JGOFS effort is summarized. In the following paragraphs the WOCE anticipated CO_2 effort as well as the non-WOCE field work is summarized for the eight nations represented at the meeting.

3.2.1 Australia

The Australian plans for obtaining CO_2-related measurements focuses on the western South Pacific and the southeastern Indian Ocean.

WOCE

- 1991-1995, WOCE line P-12 will be occupied four times during this period. The part of WOCE line S-4 west of line P-14S will be completed at least once. WOCE line I-9S will probably be undertaken as well. A_T, C_T, pH and P_{CO2} will be obtained.

JGOFS

- 1992 and probably again in 1993, two lines will be occupied in the western tropical Pacific: one along 147°E and 1°S and 15°N; the other along 155°E between 10°S and 10°N, the latter being WOCE line P-11N. The same suite of CO_2 measurements is contemplated.

3.2.2. Canada

The Canadian national plan for CO_2 surveys resides with the Physical and Chemical Sciences Branch of the federal Department of Fisheries and Oceans (DFO). The Bedford Institute of Oceanography (BIO) at Dartmouth, N.S. on the east coast is carrying out CO_2 studies in the N. Atlantic and eastern Arctic Oceans, with Peter Jones of the Marine Chemistry Division as chief scientist. The IOS at Sidney, B.C. on the ester coast, is responsible for CO_2 programmes in the Pacific and western Arctic Oceans, with C.S. Wong as the Head of the Centre for Ocean Climate Chemistry (COCC) serving as the DFO focus for CO_2 and greenhouse gases.

WOCE Atlantic

BIO will be conducting WOCE work in the North Atlantic, with a CO_2 programme to measure concentrations of C_T, A_T, CFCs and CCl_4, and other standard oceanographic constituents such as O_2, T, and S:

- E-W sections A-1 and A-2. The extent of Canadian work depends on the German WOCE plan, which also includes part of these lines.
- One annual repeat section, Greenland to Labrador (WOCE Line AR-7W).
- The first BIO N. Atlantic cruise sailed on April 24, 1991 for 43 days along a track from 42°N 50°W, south to 32°N, then east to 40°W, then north along WOCE A-18.
- One N-S section from 60°N to 40°N along 37°W in spring in 1991.
- Controlled volume experiment will be done in the region south of Cape Farewell in Greenland.

WOCE Pacific

- 1994, WOCE Line P-15 along 170°W from 10°S to 55°N will be occupied by the C.S.S. *Hudson* in late 1994 for CO_2 and chemical tracers at depth intervals and station frequency specified for WOCE. The chemical parameters to be measured are:

T, S, O_2, CFCs
Dissolved nutrients P, N, Si
$^{18}O/^{16}O$, $^{13}C/^{12}C$
DOC
C_T, A_T, P_{CO2} (discrete samples) and P_{CO_2} (continuous), pH

Other cruises

- 1991, BIO will participate on Arctic Ocean cruise aboard Swedish icebreaker *Oden*. Measurements are planned for C_T, A_T, CFCs, as well as nutrients, O_2, T, S and other transient tracers.

- 1994, oceanographic sections in the North Pacific to be occupied at depth intervals and station frequency, not to WOCE specifications, are also planned. These include oceanographic work to be done en route from Panama to JGOFS equatorial stations at 125°W to Victoria, in 1994.

- 1991-1995, CO_2 surveys are being conducted under the INPOC (International North Pacific Ocean Climate) programme between USSR and Canada. A cruise is underway in the western Pacific Ocean in the *RV Vinogradov*. Another proposed cruise will be repeated twice a year for 1991-95. The chemical parameters listed above for P-15 will be measured, at least in part.

CO_2 Time Series

- Line between Victoria, B.C. and Station P (50°N 145°W) will be a designated WOCE time series section at repeat frequency of 4 times a year. CO_2, nutrients, DOC and oceanographic measurements will be done. Other lines for surface samplings only will include ships-of-opportunity between Valdez and Hawaii, Vancouver and New Zealand, as well as Tokyo and Vancouver.

Carbon Flux Time Series

- JGOFS time-series stations for C, N, Si particle fluxes are being occupied in N. Pacific Ocean. Moored sediment traps are at Ocean Station P (since 1982), station L near west coast of Vancouver Island, Station C and D in N.E. Pacific Ocean, in Bering Sea, N.W. Pacific (in cooperation with PMEL). Two stations in the subtropical gyres are being planned. These particle flux stations are for long-term seasonal and interannual variabilities of fluxes of productivity, organic carbon, calcium carbonate, nitrate and opal. as well as selected trace metals, such as cadmium. Free-floating traps (0-1000 m) will also be launched to obtain fluxes in the upper ocean.

3.2.3 France

Measurements of CO_2 in the ocean by French scientists are made under the WOCE and JGOFS programmes and aboard ships of opportunity. Plans for the coming period through 1994 are as follows:

WOCE

- 1992 (Dec) to Feb 1993, Tropical Atlantic: WHP lines A-6 and A-7 aboard *Atalante*; contact is C. Oudot.
- 1992-1994, Indian Ocean: WHP lines I-4, I-6, I-7, I-10 aboard *Marion Dufresne*; contact is A. Poison.
- 1991-continuing, Kerfix time series (*Marion Dufresne* and A. Poisson).

JGOFS

- 1991-1993, North Tropical Atlantic: French programme *Eumeli* aboard *Atalante*; contact is A. Morel.
- 1994, *Antares*: South Indian and Antarctic Ocean; contact is G. Jacques.

Ships of Opportunity

- 1989-continuing, *Minerve* in the Indian Ocean (A. Poisson).
- 1991-continuing, *Ecoa* in the Atlantic and Pacific (Y. Dandonneau).

3.2.4. Germany

The first field experiment will take place in 10-28 June 1991 in the North Atlantic ($47^oN/20^oW$ - $60^oN/20^oW$) with *F.S. Poseidon*. Methods to be used are: C_T - coulometry; A_T - titration; P_{CO2} - IR (surface, continuously), GC (discrete samples); pH - glass electrode. A pump system will be used to sample surface water, continuously for P_{CO2} and pH, and at intervals of 30 nm for C_T. In addition, seven stations are planned for the determination of vertical profiles for C_T and pH. First experiments will also be done with the alkalinity titration procedure.

In September 1991 the IFM-CO_2 group will participate in a WOCE cruise on section A1E with *F.S. Meteor* (M18). The full set of parameters of the carbonate system will be determined and as many as possible of the 65 stations will be investigated.

A transect through the Atlantic from Bremerhaven (FRG) to the Weddell Sea is scheduled for 14 November 1991 to 2 January 1992 on the *Polarstern*. A group from NIOZ (H. de Baar) will participate. Again, surface water will be sampled continuously for P_{CO2} and pH, and at distances of 30 nm for C_T and alkalinity. At about 10 stations, which are partly identical with former GEOSECS stations, vertical profiles for the four parameters of carbonate system will be investigated.

The determination of the CO_2 system during the different cruises will be complemented by measurements of nutrients, oxygen and chlorophyll. Bernd Schneider is the contact person for the CO_2 cruises at IFM-Kiel.

For 1992 planning is not yet finalized. There will be at least one cruise with *F.S. Meteor* (M21/3) from 11 May to 2 June, in the North Atlantic between Madeira and Reykjavik. This cruise is part of a JGOFS contribution of IFM Kiel. Cooperation with BNL (K. Johnson) is planned for this and the September 1991 *Meteor* cruise.

3.2.5. Japan

Tsunogai explained that the Japanese approach to studying the ocean carbon cycle has a somewhat different emphasis compared to western countries. For example, Japanese scientists put more stress on the preservation and fate of biologically produced particles and this results in more sediment trap experiments. Experiment design is based upon contrasting pairs. For marine biological activities, the pairs are the coastal and hemipelagic zones vs. the pelagic zone, the high latitudes vs. the low latitudes, and particulate organic carbon vs. dissolved organic carbon. For the gas exchange at the surface, the pairs are the extreme ocean vs. the usual ocean, the high latitudes in winter vs. the low latitudes, the intermediate water as a sink of atmosphere carbon vs. the deep water, and surface roughness (not only as a function of wind velocity) vs. wind velocity.

Five groups in Japan are planning cruises during which CO_2-related measurements will be made. Depending on the cruise, certain of the following groups of variables are planned to be observed:

(1) Total carbonate, P_{CO2}, alkalinity, pH
(2) Calcium
(3) Particulate carbon, including its vertical flux
(4) Dissolved organic carbon.

(i) The Hokkaido University Group will make measurements of group (1), (2), and (3) as follows.

JGOFS
May-Jun 1991, cruise KH-91-3 in the North Pacific, 45-25^{O}N along 165^{O}E.

WOCE
Aug-Oct 1991, cruise KH-91-5 in western Pacific, 40^{O}N-5^{O}S along 165$_0$E.
May-Jun 1993, cruise KH-93-2 in the North Pacific, 40-50^{O}N along 165^{O}E.

Other Cruises
Jun-Aug 1992, HO-92-2 and HO-92-3 in the western North Pacific, 35-44^{O}N along 155^{O}E; 39-47^{O}N along 170^{O}E; and 39-47^{O}N along 175^{O}E.

(ii) The Meteorological Agency Group will measure group (1) on the following cruise (non WOCE, non JGOFS).

1991, and each year into the foreseeable future in the NW Pacific:
- 2 cruises in a year in the area, 35-5^{O}N along 137^{O}E.
- 1 cruise in a year in the area, 30-0^{O}N along 155^{O}E.
- 4 cruises in a year in some areas around Japan.

(iii) The Meteorological Research Institute Group will measure group (1) (except for alkalinity) and (4) once or twice per year:

1991 through 1995, in the North Pacific, e.g., 43-20^{O}N along 155^{O}E;
1995 through 2000, in the South Pacific (unspecified area).

(iv) The Polar Research Institute and Tohoku University Group will measure P_{CO2} on the following cruises:

1991 and every year in the foreseeable future in the Southern Ocean during the Japanese Antarctic Expeditions on the way to and from the Japanese Showa Base.

(v) The National Research Institute for Pollution and Resources Group will continue studies on groups (1) and (3) on the following cruises:

1990 and into the foreseeable future in the western Pacific, 48°N-15°S along 175°E; this group will extend the observation network to cover all the western North Pacific.

3.2.6. Netherlands

H. de Baar provided the following information on CO_2 work done and planned by Dutch scientists:

(i) **JGOFS**

- 1989, 1990 North Atlantic Pilot Study, A_T, C_T, $^{14}C/^{12}C$, $^{13}C/^{12}C$;
- 1992, Southern Ocean (Oct-Nov), *Polarstern*, Capetown-Punta Arenas;
- 1994, Indian Ocean (with Germany, on *Meteor)*
- optional: N.E. Atlantic (47°N, 20°W time series)
- joint proposal to EEC (Lampitt-IOS)

(ii) **WOCE**

- 1990, WOCE line AR-7, Iceland Basin, coulometry for C_T (Michel Stoll);
- 1991, WOCE line AR-7, Iceland Basic (Stoll, Mario Hoppema), coulometry for C_T, titration for Alkalinity.
- 1993-1994, WOCE line AR-7

(iii) **North Sea**

- Review of greenhouse gases (Hoppema, de Baar); C-cycle (eutroph), DOC), CO_2, CH_4, N_2O, DMS;
- 1990 November: CO_2 air/sea exchange experiment; eddy diffusion vs. gradient method; Smith, Jones (BIO), Jahne (Heidelberg), Kohsiek, Oost (KNMI = Royal Neth Meteo Inst);
- 1992 Spring: CO_2 air/sea exchange experiment; repeat.

3.2.7. United Kingdom

A. Watson provided the following information on planned CO_2-related measurements by UK groups 1991-95:

(i) **UK JGOFS** (funded):

- 1991-92: Seasonal coverage of P_{CO2} in NE Atlantic on ship-of-opportunity route between Keykjavik, Iceland and Aveiro, Portugal.
- June 1991: Process study of coccolithophore bloom, NE Atlantic. A_T, C_T, and P_{CO2}.
- Spring 1992: Marginal ice zone study in the Greenland Sea (C_T, P_{CO2}).
- Austral Spring 1992: Transect from Chile to Antarctica in the Southwest Pacific sector of the Southern Ocean. Study of ice edge bloom in the Bellingshausen Sea, Antarctica.

(ii) **Others** (seeking funds):

- WOCE WHP lines A-11 (1992) and A-23 (1994).
- Ship-of-opportunity determination of P_{CO2} and C_T from British Antarctic Survey supply ship, sailing from UK to Antarctic every year (from 1992 or 1993).

3.2.8. USA

The U.S. is planning (in some cases completed) CO_2 measurements in the following areas:

Atlantic Ocean

- WOCE lines A-16, A-9, S-1, S-2 and S-4 (between S-1 and S-2).

Indian Ocean

- WOCE lines I-7N (between Oman and 8^oS).
- 1994, JGOFS Process Study in the Arabian Sea.

Pacific Ocean

- WOCE lines P-19N, P-19S, P-17 (from 35^oN to 28^oS), and P-16 (from Alaska to 28^oS).
- JGOFS lines at 95^oW, 110^oW, 125^oW, 140^oW, and 170^oW between 10^oN and 8^oS.

APPENDIX III

REPORT OF THE FINAL MEETING OF THE SCOR WG-75 ON OCEANIC CO_2 METHODOLOGY

The final meeting of SCOR Working Group 75 was held at Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, October 11-14, 1988, hosted by Peter Brewer and chaired by C.S. Wong. Participants included 4 members (P. Brewer, G. Lambert, Y. Sugimura and C.S. Wong) and 7 invited experts from U.S.A. (R.H. Byrne, E. Druffel, R.A. Feely, E.T. Peltzer), France (C. Goyet), P.R. China (J. Zheng) and U.S.S.R. (M. Stashchuk-with written submission).

The major tasks were (1) to re-examine the documents from the last meetings at Lake Arrowhead and Les Houches to identify accomplishment, unfinished tasks and new issues, (2) review of national and international activities related to WG-75 objectives, e.g. CCCO/JGOFS CO_2 Panel and preliminary results of recent JPOTS/SCOR/ICES international intercalibration on CO_2/alkalinity and (3) recommendations, including the role of a replacement working group following the termination of SCOR WG-75.

Since the first meeting at the 1983 IUGG in Hamburg, SCOR Working Group 75 has done pioneering work in focussing the global strategy and technical problems of oceanic CO_2 measurements. The WG-75 framework has been incorporated into the designs of global CO_2 measurements. The WG-75 framework has been incorporated into the designs of global CO_2 surveys under international programs of WOCE and JGOFS. The reports of the Lake Arrowhead and Les Houches meetings, edited by Keeling, reviewed the advances and technological gaps in CO_2 methodology, and provided a collective and focussed view of the oceanic CO_2-measuring community. The coordinating role of WG-75 has resulted in working with JPOTS and ICES to conduct an international intercalibration exercise on DIC and alkalinity in 1987 coordinated by A. Poisson. The urgent need for a reference sea water for future global CO_2 surveys was recognized, and WG-75 members, such as Poisson, Keeling and Wong have been working within their own national resources towards the availability of reference sea water essential to the CO_2 surveys of WOCE/JGOFS in the coming decade.

A review of the state-of-the-art in the methodology for oceanic CO_2 and carbon measurements was made. The group was impressed by recent advances in coulometry for DIC, colorimetric measurements of pH, fibre-optic sensors for *in situ* pH/alkalinity, accelerator mass spectrometry for small sample of ^{14}C in seawater, shipboard data handling capability by PC-computers and high temperature combustion method for dissolved organic carbon in seawater. The final report will be updated to incorporate these advances. A major issue was dissolved organic carbon in sea water. Sugimura's group developed this new technique which gave 50-400% more DOC than other existing methods as confirmed by a recent intercalibration at WHOI. WG-75 discussed the need for further DOC intercalibration, which could be the task of a new of replacement WG. Another idea for a replacement WG was initiated by Brewer for discussion on a scheme to gather world experts on various CO_2 parameters at the same oceanic site, such as Bermuda, to make the best possible measurements on the present-day oceanic chemical system so as to formulate a projection of future CO_2 changes in the ocean. Any deviations from this derived CO_2 chemical relationship in future global CO_2 observations would alert the scientific community on unexpected behaviour of the natural CO_2 system being titrated by fossil-fuel CO_2.

The following resolutions were made:

(1) WG-75 recommended strongly that in the very near future, global oceanic carbon programs should pursue actively accelerated activities on intercalibration and the development of reference sea water and material for quality control in creating a global oceanic carbon data set.

(2) WG-75 recommended to the SCOR Executive Committee to request IOC of UNESCO to continue support of the JPOTS sub-Panel on CO_2 standards to revisit the thermodynamics and the closure problems of the oceanic CO_2 system, till the availability of an acceptable standard reference sea water is assured. At present, the spread in DIC and total alkalinity measurements in the 1987 JPOTS/SCOR/ICES intercalibration between laboratories was as large as the fossil-fuel CO_2 signal and an all-out effort is needed to narrow down the "noise" of the interlaboratory measurement programs.

(3) WG-75 will produce an "interim" CO_2 methodology manual to be published in the UNESCO technical manual series. WG-75 Chairman was asked to pursue the task, by compiling key published papers on (a) pH, (b) alkalinity, (c) DIC, (d) P_{CO2}, (e) isotopic ^{13}C, ^{14}C, (f) POC, (g) DOC, (h) software in thermodynamics calculations, (i) sources of contacts for reference sea water and material and (j) data. The manual will include a forward section, to be written by experts in each of these fields, commenting or updating the published methods.

(4) WG-75 recommended that an international oceanic CO_2 symposium be organized in 1990 or 1991 and encouraged Professor Sugimura to host the symposium in Japan. The proceedings will be published to summarize the tasks and achievements of the working group.

(5) WG-75 recommended that SCOR should request IOS during its coming General Assembly, to encourage the world's nations to participate actively in the world CO_2 survey programs with attention to both data quality and data visibility. WG-75 expressed concerns that not enough laboratories in Third World countries be given sufficient resources to bring their capabilities to world-class levels necessary for a successful CO_2 survey program. SCOR should urge its members to increase the levels of scientific support and international agencies to devote resources to assist such endeavour.

(6) WG-75 recommended to SCOR to consider two major areas for SCOR WGs as replacement of WG-75: (a) To organize international experiments for designing chemical model of future CO_2 changes in the ocean to guide the prediction of CO_2 signals or to detect sudden deviations of CO_2 changes due to natural events. The best measurements, in terms of compatibility and experimental design, will be done by world experts to be gathered at selected sites, and (b) To study the rationalization of DOC for availability of technique to the scientific community. WG-75 Chairman was asked to table a proposal for such a replacement WG for consideration in the next SCOR executive meeting, and this will be established by correspondence.

(7) The final report and the manual should be completed before the next SCOR executive meeting.

(8) WG-75 recommended SCOR to encourage national standards laboratories with long-term CO_2 program to seek support from their respective governments of SCOR countries to accept the responsibility of ensuring the development, production and distribution of reference sea water for use in the global CO_2 program. These laboratories would also ensure long-term quality control of the global CO_2 data set through a continuing international calibrating network.

UNESCO TECHNICAL PAPERS IN MARINE SCIENCE

Issues 1-30, 32, 37 and 50 are out of stock. For availability in microfiche form please write to the UNESCO Press, Sales Division (UPP/V). 7, place de Fontenoy, 75352 Paris 07 SP, France. Out of stock titles are listed on the back cover.

No.		Year	SCOR WG
31	Coastal lagoon survey (1976-1978)	1980	–
33	Coastal lagoon research, present and future. Proceedings of a seminar, Duke University. August 1978 (UNESCO, IABO)	1981	–
34	The carbon budget of the oceans. Report of a meeting, Paris, 12-13 November 1979	1980	WG 62
35	Determination of chlorophyll in seawater. Report of intercalibration tests sponsored by SCOR and carried out by C.J. Lorenzen and S.W. Jeffrey, CSIRO Cronulla, N.S.W., Australia, September-October 1978	1980	–
36	The practical salinity scale 1978 and the international equation of state of seawater 1980. Tenth report of the Joint Panel on Oceanographic Tables and standards, (JPOTS). Sidney, B.C., Canada, 1-5 September 1980. Sponsored by UNESCO, ICES, SCOR, IAPSO. Available in Ar, Ch, F, R, S (*Примечание:* Этот доклад (текст идентичен) был первоначально издан только на английском языке под заголовком *Tenth report of the Joint Panel on Oceanographic Tables and Standards* (Десятый доклад Объединенной группы по океанографическим таблицам и стандартам)). Имеется на арабском, испанском, китайском, русском и французском языках.	1981	WG 10
38	Background papers and supporting data on the International Equation of State of Seawater 1980	1981	WG 10
39	International Oceanographic Tables, Vol. 3	1981	WG 10
40	International Oceanographic Tables, Vol. 4	1982	WG 10
41	Ocean-Atmosphere Materials Exchange (OAMEX). Report of SCOR Working Group 44, UNESCO, Paris, 14-16 November 1979	1982	WG 44
42	Carbon dioxide sub-group of the joint panel on oceanographic tables and standards. Report of a meeting Miami, Florida, 21-23 September 1981 sponsored by UNESCO, ICES, SCOR, IAPSO	1983	–
43	International symposium on coastal lagoons, Bordeaux, France, 8-14 September 1981. Available in F and S	1982	–
44	Algorithms for computation of fundamental properties of seawater. Endorsed by UNESCO/SCOR/ICES/IAPSO Joint Panel on Oceanographic Tables and Standards and SCOR Working Group 51	1983	–
45	The International System of Units (SI) in Oceanography Report of IAPSO Working Group on Symbols, Units and Nomenclature in Physical Oceanography. (SUN)	1985	–
46	Opportunities and problems in satellite measurements of the sea. Report of SCOR Working Group 70. Available in Ar, Ch, F, R, and S	1986	WG 70
47	Research on coastal marine systems. Report of the third meeting of the UNESCO/SCOR/IABO consultative panel on coastal systems, October 1984	1986	–
48	Coastal off-shore ecosystems relationships. Final Report of SCOR/IABO/UNESCO Working Group 65, Texel, Netherlands, September 1983	1986	WG 65
49	Pelagic biogeography. Proceedings of an international conference, The Netherlands, 29 May-5 June 1985	1986	–
51	Thermodynamics of the carbon dioxide system in seawater. Report by the carbon dioxide subpanel of the joint panel on oceanographic tables and standards	1987	–
52	Research on coastal marine systems. Review and Recommendations for UNESCO Programme 1987-1989. Report of the fourth meeting of the UNESCO/SCOR/IABO consultative panel on coastal systems, Dakar, 15-17 December 1986	1987	–
53	Code of practice for scientific diving: Principles for the safe practice of scientific diving in different environments. Compiled and edited by the Scientific Committee of the Confédération mondiale des activités subaquatiques (CMSA)	1988	–
54	The acquisition, calibration and analysis of CTD data. A report of SCOR Working Group 51	1988	WG 51
55	River inputs to ocean systems: Status and recommendations for research. Final Report of SCOR Working Group 46	1988	WG 46
56	The ocean as a source and sink for atmospheric trace constituents. Final Report of SCOR Working Group 72	1989	WG 72
57	Coastal marine systems: Review and research recommendations, 1988-1990 UNESCO/SCOR/IABO consultative panel on coastal systems, 15-20 December 1988. São Luis, Maranhao, Brazil	1989	–
58	Directory of source materials for the history of oceanography	1990	–
59	Inter-comparison of total alkalinity and total inorganic carbon determinations in seawater. Recommended by ICES Marine Chemistry Working Group and SCOR Working Group 75 and endorsed by SCOR/UNESCO/ICES/IAPSO Joint Panel on Oceanographic Tables and Standards	1991	–
60	Reference materials for oceanic carbon dioxide measurements. Report of the subpanel on standards for CO^2 measurements of the Joint Panel on Oceanographic Tables and Standards	1991	–
61	Manual on marine experimental ecosystems. Prepared by SCOR Working Group 85	1991	WG 85
62	Salinity and density of seawater: Tables for high salinities (42 to 50)	1991	WG 10
63	Coastal systems studies and sustainable development. Report of the COMAR Interregional Scientific Conference, UNESCO, Paris, 21-25 May 1991. Co-sponsored by UNESCO, UNEP, SCOR, IABO	1991	–
64	Coastal systems studies and sustainable development. Proceedings of the COMAR Interregional Scientific Conference, UNESCO, Paris, 21-25 May 1991. Co-sponsored by UNESCO, UNEP, SCOR, IABO.	1992	–

UNESCO TECHNICAL PAPERS IN MARINE SCIENCE

Titles of numbers which are out of stock

No.		Year	SCOR WG
1	Incorporated with Nos. 4, 8 and 14 in No. 27	1965	WG 10
2	Report of the first meeting of the joint group of experts on photosynthetic radiant energy held at Moscow, 5-9 October 1964. Sponsored by UNESCO, SCOR and IAPO	1965	WG 15
3	Report on the intercalibration measurements in Copenhagen, 9-13 June 1965. Organized by ICES	1966	–
4	Incorporated with Nos. 1, 8 and 14 in No. 27	1966	WG 10
5	Report of the second meeting of the joint group of experts on photosynthetic radiant energy held at Kauizawa, 15-19 August 1966. Sponsored by UNESCO, SCOR, IAPO	1966	WG 15
6	Report of a meeting of the joint group of experts on radiocarbon estimation of primary production held at Copenhagen, 24-26 October 1966. Sponsored by UNESCO, SCOR, ICES	1967	WG 20
7	Report of the second meeting of the Committee for the Check-List of the Fishes of the North Eastern Atlantic and on the Mediterranean, London, 20-22 April 1967	1968	–
8	Incorporated with Nos. 1, 4 and 14 in No. 27	1968	WG 10
9	Report on intercalibration measurements, Leningrad, 24-28 May 1966 and Copenhagen, September 1966, organized by ICES	1969	–
10	Guide to the Indian Ocean Biological Centre (IOBC), Cochin (India), by the UNESCO Curator 1967-1969 (Dr J. Tranter)	1969	–
11	An intercomparison of some current meters. Report on an experiment at WHOI Mooring Site 'D', 16-24 July 1967 by the Working Group on Continuous Current Velocity Measurements. Sponsored by SCOR, LIAPSO and UNESCO	1969	WG 21
12	Check-List of the Fishes of the North-Eastern Atlantic and of the Mediterranean (report of the third meeting of the Committee, Hamburg, April 1969)	1969	–
13	Technical report of sea trials conducted by the working group on photosynthetic radiant energy, Gulf of California, May 1968. Sponsored by SCOR, IAPSO, UNESCO	1969	WG 15
14	Incorporated with Nos. 1, 4 and 8 in No. 27	1970	WG 10
15	Monitoring life in the ocean. Sponsored by SCOR, ACMRR, UNESCO, IBP/PM	1973	WG 29
16	Sixth report of the joint panel on oceanographic tables and standards, Kiel, 24-26 January 1973. Sponsored by UNESCO, ICES, SCOR, IAPSO	1974	WG 10
17	An intercomparison of some current meters. Report on an experiment of Research Vessel Akademic Kurchatov, March-April 1970, by the Working Group on Current Velocity Measurements. Sponsored by SCOR, IAPSO, UNESCO	1974	WG 21
18	A review of methods used for quantitative phytoplankton studies. Sponsored by SCOR, UNESCO	1974	WG 33
19	Marine Science Teaching at the University Level. Report of the UNESCO Workshop on University Curricula. *Available in Spanish and Arabic*	1974	–
20	Ichthyoplankton. Report of the CICAR Ichthyoplankton Workshop. *Also published in Spanish*	1975	–
21	An intercomparison of open sea tidal pressure sensors. Report of SCOR Working Group 27: 'Tides of the open sea'	1975	WG 27
22	European sub-regional co-operation in oceanography. Report of Working Group sponsored by the UNESCO Scientific Co-operation Bureau for Europe and the Division of Marine Sciences	1975	–
23	An intercomparison of some currents meters, III. Report on an experiment carried out from the Research Vessel Atlantis II. August-September 1972, by the Working Group on Continuous Velocity Measurements: sponsored by SCOR, IAPSO and UNESCO	1975	WG 21
24	Seventh report of the joint panel on oceanographic tables and standards, Grenoble, 2-5 September 1975. Sponsored by UNESCO, ICES, SCOR, IAPSO	1976	WG 10
25	Marine science programme for the Red Sea: Recommendation of the workshop held in Bremerhaven, FRG, 22-23 October 1974. Sponsored by the Deutsche Forschungsgemeinschaft and UNESCO	1976	–
26	Marine science in the Gulf area. Report of a consultative meeting, Paris, 11-14 November 1975	1976	–
27	Collected reports of the joint panel on oceanographic tables and standards. 1964-1969	1976	WG 10
28	Eighth report of the joint panel on oceanographic tables and standards, Woods hole, USA. Sponsored by UNESCO, ICES, SCOR, IAPSO	1978	WG 10
29	Committee for the preparation of CLOFETA. Report of the first meeting, Paris, 16-18 January 1978	1979	–
30	Ninth report of the joint panel on oceanographic tables and standards. UNESCO, Paris, 11-13 September 1978	1979	–
32	Coastal lagoon research, present and future. Report and guidelines of a seminar. Duke University Marine Laboratory, Beaufort, NC, USA, August 1978 (UNESCO, IABO)	1981	–
37	Background papers and supporting data on the Practical Salinity Scale 1978	1981	WG 10
50	Progress on oceanographic tables and standards 1983-1986: Work and recommendations of the UNESCO/SCOR/ICES/IAPSO Joint Panel	1987	–