Reports of Meetings of Experts and Equivalent Bodies

# Joint IOC-JGOFS Panel on Carbon Dioxide

## **Fourth Session**

Plymouth, U.K., 14-16 June 1993





### 21 MAR 1994

Intergovernmental Oceanographic Commission Reports of Meetings of Experts and Equivalent Bodies



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#### In this Series entitled

Reports of Meetings of Experts and Equivalent Bodies, which was initiated in 1984 and which is published in English only, unless otherwise specified, the reports of the following meetings have already been issued

- Third Meeting of the Central Editorial Board for the Geological/Geophysical Atlases of the Atlantic and Pacific Oceans Fourth Meeting of the Central Editorial Board for the Geological/Geophysical Atlases of the Atlantic and Pacific Oceans Fourth Session of the Joint IOC-WMO CPPS Working Group on the Investigations of 'El Niño' (Also printed in Spanish)
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This report is a continuation of the series of Carbon Dioxide Panel Meeting Reports I through III previously printed under a cover reflecting the Panel's original joint sponsorship by the Joint Global Ocean Flux Study (JGOFS) and the Committee on Climatic Changes and the Ocean (CCCO). With the decision to phase out CCCO in December 1992, agreement was reached to continue this Panel under joint sponsorship of JGOFS and IOC.

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#### 1. WELCOMING

The Fourth Session of the Joint IOC-JGCFS Panel on Carbon Dioxide was held 14-16 June 1993 at the Citadel Hill Aquarium of the Marine Biological Association in Plymouth, U.K. The meeting was hosted by the Plymouth Marine Laboratory (PML), the only laboratory in the country that continues to be active in marine  $CO_2$  measurements. Mike Whitfield, Deputy Director of PML, welcomed the participants to Plymouth and to the Aquarium. He provided a brief synopsis of the 100-year history of the lab which began studies of the CO<sub>2</sub> cycle in the 1930s.

#### 2. ADOPTION OF THE AGENDA

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Liliane Merlivat also welcomed the Panel and the invited guests, and expressed her appreciation to Andrew Watson for handling the meeting arrangements. She then addressed the provisional agenda and invited discussion on proposed changes. After brief discussion the Panel adopted the agenda in Annex I. A list of meeting participants is provided in Annex II.

## 3. RECENT IOC EVENTS REGARDING DEVELOPMENT OF GOOS, CCOS, AND OOSDP

A. Alexiou reviewed several events beginning with the Panel's changed status. He reminded the Panel that the SCOR-IOC Committee on Climatic Changes and the Ocean (CCCO), one of the Panel's parent bodies, had gone out of existence at the end of 1992 and the Panel was now operating as a joint body of the IOC and JGOFS. Both the IOC and SCOR were pleased to have this joint science and intergovernmental sponsorship continue. The IOC more than ever has need of the Panel's expertise to carry out its increasing international responsibility growing from the agreements reached at the 1992 United Nations Conference on Environment and Development - UNCED (e.g., Agenda 21). He referred particularly to the charge to IOC to advance our knowledge on the role of the oceans as a carbon sink (see section 6).

He then brought the Panel's attention to the first meeting in February 1993, of the IOC Committee for the Global Ocean Observing System (I-GOOS)<sup>1</sup> held just prior to the Seventeenth Session of the Assembly of the IOC. That Committee concluded that the Ocean Observing System Development Panel (OOSDP) approach to designing the climate module of GOOS was an excellent example for development of the other modules. Michel Glass (France) was elected Chairman; Grant Gross (USA) and B.N. Krishnamurthy (India) were elected Vice-Chairmen. Nations were invited to submit National Reports covering steps being taken with regard to GOOS. The observation was made that there was yet no organized body for the Global Climate Observing System (GCOS) equivalent to I-GOOS for co-ordinating intergovernmental implementation efforts.

I-GOOS adopted several recommendations which were subsequently accepted by the Assembly in the form of a broad resolution on GOOS (Annex III). Among other things, the resolution instructed the Secretary IOC to hasten the finalization of the Memorandum of Understanding (MOU) on co-sponsorship (initially by IOC, WMO, and ICSU) of a GOOS technical and scientific advisory body (expected to be called J-GOOS), and to establish Panels for the other GOOS modules, i.e., the Health of the Ocean, Living Marine Resources, Coastal Zone Environment, and Marine Operational Services. The resolution also accepted as an interim report, a document on the Health of the Ocean Module prepared by an IOC *ad hoc* Panel; it officially invited WMO and UNEP to become co-sponsors of I-GOOS; and it registered IOC adoption of

<sup>&</sup>lt;sup>1</sup> Since the meeting of the Panel, the WMO has agreed to co-sponsor the I-GOOS; I-GOOS is now the IOC-WMO Intergovernmental Committee for GOOS.

the "The Approach to GOOS" as the strategy document tor planning and developing GOOS. With respect to OOSDP in particular, the 17th Assembly of the IOC agreed that OOSDP should complete its given task for and within the World Climate Research Programme (WCRP), and that a new panel would have to be considered to follow on the present OOSDP after its final report is submitted in December 1994.

- 6 Alexiou reported on an *ad hoc* GOOS meeting organized by the IOC and hosted by the government of Japan at the Tokyo United Nations University 24-25 March 1993. That meeting was originally intended to be the first meeting of the GOOS Joint Scientific and Technical Committee (J-GOOS) but agreement on the MOU establishing such a group had not been concluded at that time. To avoid losing time till this was accomplished, the *ad hoc* group, representing both science and government/operations (see Annex IV). was assembled on short notice to set directions and actions for progress during the year. The group was chaired by Michel Glass on the first day and by Nic Flemming on the second.
- 7 That meeting took note of the two documents: "The Case for GOOS" and "The Approach to GOOS". A discussion of the status of the various GOOS modules and how overall co-ordination would take place led to the preparation of generic terms of reference (given in Annex V) that outlined tasks to be completed by Panels (yet to be organized, except for OOSDP) before the next I-GOOS meeting (approximately one year hence). These Panels might be expected to report to J-GOOS when it is formed. It was assumed that the current OOSDP would be replaced by a GOOS climate module panel upon completion of its work and that a new orientation to its terms of reference would be required at that time.

#### 4. PROGRESS REPORTS

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- 4.1 SUB-PANEL ON OCEANIC CO. STANDARDS, PROTOCOLS AND QUALITY ASSESSMENT
- A meeting of the Sub-Panel was held in Paris in November 1992. A. Poisson hosted the meeting, which was attended by A. Dickson, A. Poisson, and C.S. Wong (see Section 4.1.3). A report is in preparation, and the content of that report was summarized by Dickson.
- 9 A significant proportion of the Sub-Panel meeting was spent in planning a comparison study for various equilibrator systems. The proposed study is described in more detail in Section 4.3.
  - 4.1.1 Status of Analytical Techniques
  - The various analytical techniques used for the study of the oceanic CO<sub>2</sub> system were considered with regard to the following three criteria: (i) Are suitable reference materials available? (ii) Are written methods available? (iii) What laboratory performance studies (intercomparisons) have taken place?
    - 4.1.1.1 Total Dissolved Inorganic Carbon (C<sub>T</sub>)
    - (i) Certified reference materials are now available from A. Dickson at the Scripps Institution of Oceanography (SIO).
    - (ii) A written method exists in the 1<sup>st</sup> edition of the U.S. DOE "Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water" (edited by A.G. Dickson and C. Goyet).
    - (iii) Two laboratory performance studies have been carried out so far. The first was reported by Dickson (1992); preliminary results from the second study were

presented (see Figure 4.1-1) for laboratories using SOMMA systems<sup>2</sup> of varying vintages.

- 4.1.1.2 Total Alkalinity (A<sub>T</sub>)
- (i) The SIO reference material is stable with regard to measurements of  $A_T$ , however, as yet, it has not been certified for this parameter.
- (ii) A written method exists in version (1) of the U.S. DOE Handbook of Methods.
- (iii) No formal laboratory performance study has been held, although informal comparisons indicating possible discrepancies of about of  $5 \mu mol/kg$  have been made using the SIO reference materials.



Figure 4.1-1. Plot of the differences in  $C_T$  measured by various laboratories using extraction/coulometry from values measured on the same materials by Dr Keeling's laboratory at SIO using extraction/manometry. (Preliminary results from a laboratory performance study.)

<sup>&</sup>lt;sup>2</sup> An instrument for automating the extraction/coulometric determination of total dissolved inorganic carbon in sea water; developed by Mr Ken Johnson and constructed by the University of Rhode Island Development Group.

#### 4.1.1.3 p(CO<sub>2</sub>)

- (i) The reference materials that exist are for the measurement of  $CO_2$  in air. These are available from the U.S. National Institute of Standards and Technology (NIST). They are in good agreement (for the purposes of  $p(CO_2)$  measurements) with the WMO standards maintained by Keeling at SIO.
- (ii) No complete written method exists, although a number of measurement systems are described in the scientific literature. One such written method is in preparation for the DOE Handbook (2<sup>nd</sup> edition). This is scheduled to be available before the end of this year.
- (iii) The only comparisons made to date have been simple bilateral comparisons such as that reported by B. Schneider at the last meeting. A more formal exercise is planned for 1994 (see Section 4.3).

#### 4.1.1.4 pH

- (i) Although no reference materials are distributed from a central location, recipes and values for the pH of specified buffer mixtures in synthetic sea water have been published by Dickson (1993).
- (ii) At present no written method exists, however one is in preparation for the  $2^{nd}$  edition of the U.S. DOE Handbook.
- (iii) No laboratory performance studies have taken place.
- 4.1.1.5 Carbon-13
- (i) No reference materials presently exist for <sup>13</sup>C in sea water. The currently available certified reference materials are either a marble sample or a NaHCO<sub>3</sub> solution held by IAEA, or solid materials distributed by the U.S. NIST. Each of these are in short supply, although it is believed that IAEA is committed to supplying such materials.
- (ii) No formal written method exists presently.
- (iii) No laboratory performance study has been completed for measurements of <sup>13</sup>C. C.S. Wong is in the process of distributing a CO<sub>2</sub> gas sample for this purpose to a limited number of laboratories. The possibility has also been raised of using a batch of the SIO sea water reference material for this purpose.

#### 4.1.2 The Consequences of Thermodynamic Uncertainties

11 Another area that the sub-panel felt to be important was the need to understand the magnitude of and consequences of uncertainties in our present understanding of the thermodynamics of the CO<sub>2</sub> system. Particular importance was attached to two problems: the temperature coefficient of  $p(CO_2)$  - see Section 5.1 - and the internal consistency of different sets of measurements - see Section 5.3.

#### 4.1.3 Conclusions/Recommendations

(i) The Sub-Panel emphasized the importance of the proposed  $p(CO_2)$  laboratory performance study to enhancing our confidence in the extensive international data set for underway measurements being collected.

- (ii) The Sub-Panel emphasized the need to ensure the long-term availability of reference materials for  $C_T$ ,  $A_T$ , and <sup>13</sup>C. (For a proposed approach, see the next section:).
- (iii) The Sub-Panel encouraged the widesr read dissemination of the U.S. DOE Methods Handbook, and looks forward to its more complete 2<sup>nd</sup> edition. Concern was however expressed that there was a need for similar written descriptions of less sophisticated analytical methods.
- 4.2 REFERENCE MATERIALS, DISTRIBUTION, CALIBRATION

12 A. Dickson reported on the work of the SIO Reference Materials Program that had occurred since the last meeting. Thus far, four additional batches had been prepared for  $C_T$ . These batches are stable, with the measurements over a period of at least six months having a standard deviation of the order of 1  $\mu$ mol/kg. Three of these butches have already been certified and distributed for use at sea by scientists from a variety of countries. The fourth batch is still being certified, and will be available for distribution in about one to two months time.

- 13 The Reference Materials Program also prepared a batch of 100 bottles of each of 5 different levels of  $C_T$  which were distributed to 23 laboratories as blind samples for use in a laboratory performance study. At this time 14 laboratories have returned their results, and a subset of these are shown in Figure 4.1.1.
- 14 Dickson told the Panel that he had conducted discussions with Paul Ridout as to whether it would be possible for the Standard Sea Water Service (SSWS) in Wormley, United Kingdom, to take over on a commercial basis the production and distribution of reference materials at some time in the future. It was concluded that the SSWS would be able to prepare and distribute reference materials, but that they would need to contract out the certification to other laboratories. A trial batch of reference material will be prepared at Wormley within the next year so as to allow the SSWS to prepare a more detailed costing of the procedures required. Dickson also mentioned that he was initiating discussions with the U.S. NIST to ascertain if they had a possible role in the future of sea water reference materials. H. de Baar suggested approaching the European Community (EC) for support for the Wormley production.
- 15 Dickson informed the Panel about a workshop on troubleshooting the SOMMA systems at PMEL, Seattle, the first week of November 1993. It will be held in conjunction with a DOE CO<sub>2</sub> meeting. The Panel endorsed the workshop.
  - 4.3 INTERCALIBRATION OF EQUILIBRATORS
- 16 At the last meeting of the Panel, A. Watson proposed an exercise to compare equilibrator systems in a laboratory environment. A. Alexiou sent out a questionnaire to a number of scientists around the world to assess the interest in participating in such an exercise. Almost all responses received were positive, and the Sub-Panel on Oceanic CO2 Standards, Protocols and Quality Assessment was charged with designing such an exercise.
- 17 The Sub-Panel proposed the following goals for this exercise:
  - (i) To provide an intercalibration of the measurement systems that are currently used to provide values of  $p(CO_3)$  in sea water.

As used here, the term "measurement system" includes both the equilibrator and the analyzer used to measure the  $CO_2$  content of a gas phase (gas chromatograph, non-dispersive infra-red spectrometer, etc.). It does not include the uncertainty inherent in each "participant's "standard gases": a suite of standard gases will be provided for common use.

If it is desired to provide a comparison of the various standard gases used by different groups in different countries, this should be planned as a separate experiment involving the shipment of gas samples to a central laboratory for analysis and intercomparison. Ideally, this should be organized in conjunction with the  $CO_2$ -in-air network whose members have addressed this problem on a number of occasions.

- (ii) To provide a forum for the discussion of the current state of the art of the design of such instruments.
- (iii) To make recommendations for an optimal measurement procedure, with emphasis on the calculations that are used to reduce instrumental data and hence provide information which can be used to guide future developments in measurement systems for p(CO<sub>3</sub>).
- The Sub-Panel also endorsed a proposed strategy for the proposed exercise:
  - (i) The exercise should be under the control of a single organizer who will be responsible for preparing the final report.
  - (ii) Participants will bring their instruments to a central site (6-8 groups at a time).
  - (iii) Cylinders of air with different levels of  $CO_2$  will be previded by the central site. These will be used to directly compare the response of analytical systems to wet and dry gases.
  - (iv) Measurement systems will be compared directly using a uniform well-characterized source of sea water. (Appropriate ancillary measurements will be arranged by the central site.)
  - (v) An experiment will be planned to measure the time constants of the various equilibrator systems (ideally using a step change in  $p(CO_2)$ ).
- 19 The Sub-Panel proposed that a list of potential invitees be assembled for a first such exercise. These invitees should be selected to provide substantial international representation as well as to reflect a variety of equilibrator styles and variation in analytical techniques. The Panel suggested that the various other groups that could not be accommodated in the first exercise because of logistical problems, should be invited to participate as observers.
- 20 After some panel discussion, a list of 11 potential participants was approved comprising scientists from the following countries: Australia, Canada, France, Japan, Netherlands, United Kingdom, and the USA. At least four distinct equilibrator designs are represented as well as both gas chromatographic and non-dispersive infrared analysis techniques.
- 21 It was decided to hold this exercise at the Scripps Institution of Oceanography under Dickson's direction. Dickson agreed to schedule the exercise 6-10 June 1994, and to endeavor to arrange the financial support needed to put on the exercise (not to include the travel costs of the various participants).

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#### 5. STATE OF KNOWLEDGE REPORTS

#### 5.1 DEPENDENCE OF pCO<sub>2</sub> ON TEMPERATURE

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# The partial pressure of CO<sub>2</sub>, $pCO_2$ , of water of a given chemical composition varies strongly with temperature. A precise knowledge of the temperature dependence is important when $pCO_2$ in a seawater sample is measured at a temperature different from the *in situ* temperature and also for modelling the ocean-atmosphere CO<sub>2</sub> exchange. The temperature dependence of $pCO_2$ , described by the function:

$$f'(T,T_0) = \frac{pCO_2(T)}{pCO_2(T_0)}$$
(1)

can be determined in different ways. Takahashi and collaborators measured  $f(T,T_0)$  directly, by analyzing pCO, of various representative water samples at different temperatures and found that an exponential function,

$$f(T,T_0) = \exp(0.0423[T-T_0])$$
(2)

fitted all their results well, independent of salinity and water composition (Takahashi et al., 1991; Takahashi, pers. comm.). However, their experimental work has not been published. Copin-Montegut (1988, 1989) and other authors before her (see references therein) used a different approach. She calculated pCO, for different temperatures and salinities based on the relevant chemical equilibrium equations and constants as proposed by the UNESCO CO, subpanel of JPOTS (UNESCO, 1987), based on the evaluation of Dickson and Millero (1987). Copin-Montegut presented a formula for the effect of temperature and salinity on pCO<sub>2</sub>. Fink and Siegenthaler (unpublished) have re-determined the temperature dependence using the chemical equilibrium equations proposed by Copin-Montegut and compared the results obtained using (i) the set of equilibrium constants recommended by UNESCO (1987) (with minor exceptions), and (ii) for the first and second H<sub>2</sub>CO<sub>3</sub> dissociation constants, K<sub>1</sub><sup>+</sup> and K<sub>2</sub><sup>\*</sup>, the more recent values of Goyet and Poisson (1989). Figure 5.1 shows the difference (in µatm) of pCO<sub>2</sub> as a function of temperature between the Takahashi exponential formula (2) and the full equilibrium equation formalisms, for 3 types of seawater with prescribed pCO<sub>2</sub> at 20°C of 350, 572.5 and 750 µatm. For Figure 5.1(a), the UNESCO set of constants was used; for Figure 5.1(b), the K<sub>1</sub>\*, K<sub>2</sub>\* values of Goyet and Poisson. The main results are as follows:

- (i) There are significant deviations in the  $pCO_2$ -temperature relation f (T, 20°C) between the Takahashi formula and the relations determined using the equilibrium constants. In all cases considered, the Takahashi formula yields higher  $pCO_2$  for  $T > 20^{\circ}C$  and  $T < 7^{\circ}C$ ; at the extremes (0°C and 30°C) the deviations are in the range of 3 to 10%.
- (ii) The two sets of equilibrium constants also yield different results. At 30°C, the Goyet-Poisson constants lead to about 4% higher pCO<sub>2</sub> than the UNESCO constants; at 0°C, the Goyet-Poisson results are about 2% lower than the UNESCO results.
- (iii) The temperature dependence,  $f(T,T_0)$ , as derived from the equilibrium constants, is not the same for different pCO<sub>2</sub> (20°C) values. For a fixed pCO<sub>2</sub> (20°C) value, it depends only on salinity and alkalinity of the water.

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temperature t [°C]

#### 5.1.1 Discussion

- 23 In the calculation of pCO<sub>2</sub> from C<sub>T</sub>, alkalinity, etc., using the equilibrium equations, the most important constants are the carbonic acid dissociation constants,  $K_1^*$  and  $K_2^*$ , and the CO<sub>2</sub> solubility. Their relative errors (1 standard deviation) are indicated respectively as 1.2% and 2.3% (Goyet and Poisson, 1989) and 0.2% (Weiss, 1974); these errors affect the absolute pCO<sub>2</sub> results linearly. (The errors of the calculated temperature function,  $f(T,T_0)$ , should however be smaller.) Thus, the accuracy of the constants  $K_1^*$  and  $K_2^*$  is critical, as also suggested by the difference between the UNESCO and the Goyet-Poisson results (Figure 5.1). In comparison, the uncertainty of the solubility seems unimportant.
- 24 The procedure followed by Takahashi and collaborators, to directly determine the temperature dependence of pCO<sub>2</sub> for sea water samples, seems more direct and is probably more accurate than the determination via equilibrium constants. Publication of Takahashi *et al.*'s work is highly desirable, as are independent experimental determinations of the pCO<sub>2</sub>-temperature relation by other groups.
- 25 A group headed by C.S. Wong recently conducted similar experimental determinations of pCO, variations as a function of temperature. That work resulted in a value of .0420 for the coefficient of the exponential term in equation (2), very close to Takahashi's proposed figure. These results should be published as well.
- 26 Clearly, the varying results in the above discussion indicate that pCO<sub>2</sub> measurements should be made at a temperature as close as possible to the *in-situ* seawater temperature. Otherwise, the existing uncertainty about the temperature dependence can easily lead to errors of several ppm, which is not tolerable for many applications.
  - 5.1.2 Significance for calculating air-sea CO<sub>2</sub> fluxes
- 27 The regional fluxes of CO<sub>2</sub>, that have been published by Tans *et al.* (1990), were calculated as  $K_g \Delta pCO_2$ , where  $\Delta pCO_2 = pCO_2$  (seawater) pCO<sub>2</sub> (atmosphere). The value of pCO<sub>2</sub> (seawater) was determined by a variety of methods the majority of them using underway equilibrators of one design or another, where the equilibration temperature was close to the *in-situ* temperature. Thus errors in the temperature correction were likely to be small. If, however, such measurements had been made using discrete measurements of  $pCO_2$  thermostated at 20.0°C and the results back-calculated to the *in-situ temperature* using the exponential formula (2) above (Takahashi *et al.*, 1991), the flux results would depend significantly on this calculation. As a sensitivity study, Fink and Siegenthaler (unpublished) calculated corrections to the regional pCO<sub>2</sub> values and fluxes (Tans *et al.*, 1990), assuming that all the measurements had been made at 200°C comparing using the Goyet-Poisson constants to correct to the *in-situ* temperature with the use of equation (2). For this purpose, they selected a surface sample composition representative for each region from the GEOSECS or TTO data collections.
- 27 The difference is relevant in all regions with temperatures significantly different from 20°C, where it always leads to higher oceanic uptake using the Goyet-Poisson constants than for equation (2). The globally integrated air-to-sea flux, obtained in this way is 2 GtC/yr higher using the Goyet-Poisson constants to calculate the temperature correction (this can be compared to a 1.6 GtC/yr estimated by Tans *et al.*) Such differences could qualitatively change the whole picture for global fluxes. At this time, there is insufficient information to choose between the two approaches to making temperature corrections. These model calculations illustrate how sensitive the results are to the applied temperature correcti 1.
  - 5.2 GAS EXCHANGE COEFFICIENT  $(K_{r})$
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Recent developments in this field were summarized by L. Merlivat. Over the past two years a number of new field observations of  $K_{s}$ , as a function of wind speed, have been

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published. These were determined by the dual tracer and radon deficit methods, and all include estimates of the errors involved. The great majority of these are supportive of the Liss-Merlivat (L-M) empirical relation; that is, they lie considerably below the global mean <sup>14</sup>C determination or the regional "Red Sea" <sup>14</sup>C determination of Cember (1989). A small number of radon deficit measurements do lie at higher values, but at least some of these may have occurred at unusually heavy sea states.

Using satellite data from the years 1988 through 1990, the LODYC group have calculated global average gas exchange rates for each year. The yearly average varied by only about 5%. There seems little doubt now that there is a real discrepancy between the <sup>14</sup>C points and the inert tracer methods, such that  $K_g(^{14}C)/K_g(L-M)$  is  $1.6 \pm 0.2$ . The reasons for this discrepancy remain obscure. One possibility is that the dual tracer measurements are biased due to the formation of bubbles at higher windspeeds, but Merlivat gave an analysis which suggested that any such bias would tend to make the inferred gas exchange rates too high - exacerbating the discrepancy rather than helping to explain it. R. Wanninkhof's data reduction differs from other workers however, and his method appears to give the opposite effect. Another possibility is that of "chemical enhancement" of CO<sub>2</sub> exchange rates over those of inert gases due for example to biological effects.

#### 5.3 THERMODYNAMICS OF THE CO<sub>2</sub> SYSTEM

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F. Millero reported on recent advances in the thermodynamics of the  $CO_2$  system. Last year a symposium was held at the American Chemical Society Meeting in Washington DC to honor the contributions of the late Ricardo Pytkowicz to the field of Marine Physical Chemistry. This symposium resulted in a special issue of Marine Chemistry that contains a number of papers discussing the recent advances in the experimental techniques used to measure the components of the carbon dioxide system and the thermodynamics of the system in seawater. Some of the topics covered of particular interest to the Panel are given below.

- 5.3.1 Experimental Techniques
- (i) Continuous and batch pCO<sub>2</sub> measurements. In a paper by Wanninkhof and Thorning (1993) a full description of a batch (20°C) and continuous flow pCO<sub>2</sub> is described that used an infrared detector to measure the concentration of CO<sub>2</sub> in air equilibrated with seawater. The precision of the system is  $\pm 1 \mu$ atm in pCO<sub>2</sub>.
- (ii) The SOMMA  $C_T$  coulometry system. In a paper by Johnson *et al.* (1993) the coulometry system used to measure the  $C_T$  in seawater on all the JGOFS cruises is described. The system is fully automatic and has a precision of  $\pm 1 \mu \text{mol kg}^{-1}$  and an accuracy of  $\pm 2 \mu \text{mol kg}^{-1}$  at sea when Certified Reference Materials supplied by Dickson are used to monitor the system.
- (iii) Spectrophotometric pII measurements. In a paper by Dickson (1993) the spectrophotometric method used to measure pH and developed by Byrne and Breland (1989) is described. The use of seawater buffers to calibrate potentiometric and spectrophotometric pH systems is described by Millero *et al.* (1993a). The pH of the buffers is determined by measuring the emf of the solutions with a Pt |hydrogen |AgCl, Ag electrode system. The precision of the pH measurements by spectrophotometric methods is  $\pm$  0.0004 and the buffers can be measured to  $\pm$  0.04 mV which is equivalent to  $\pm$  0.0007 in pH.
- (iv) Measurements of  $C_r$  with an infrared analyzer. In a paper by Goyet and Stover (1993) an infrared system is described that can be used to measure the  $C_T$  in a scawater sample after the addition of acid. This system may prove useful in making on line continuous measurements of  $C_T$  on surface seawater.

- (v) Measurements of  $A_T$  by potentiometric techniques. In a paper by Millero *et al.* (1993b) the system used to measure  $A_T$  on the NOAA/JGOFS cruises is described. The calibration and standardization of the system is described. The precision of the system is  $\pm 2 \mu \text{mol kg}^{-1}$  when used at sea. Three titration systems are utilized to speed up the acquisition of data.
- (vi) Equations and measurements of the effect of temperature on pCO<sub>2</sub>. In a paper by Goyet *et al.* (1993) equations are given to calculate the effect of temperature on pCO<sub>2</sub> based on the constants of Goyet and Pcisson (1989). They also present measurements of pCO<sub>2</sub> as a function of temperature (-1 to 30°C) and the ratio of  $A_{\rm T}$  to  $C_{\rm T}$ . The results agree with the equation on the average to  $\pm 5 \,\mu$ atm.

#### 5.3.2 Thermodynamics

- (i) The standard potential for the H<sub>2</sub>,Pt |AgCl,Ag electrode in seawater. In a paper by Campbell *et al.* (1993) measurements have been made on E<sup>\*</sup> for HCl in synthetic seawater from 0 to 55°C and salinity from 5 to 45. The new measurements are in excellent agreement ( $\pm$  0.04mV) with the earlier measurements of Bates and Erickson (1986) and Dickson (1990a). These values of E<sup>\*</sup> when extrapolated to m(HCl) = 0 are used to characterize the pH of seawater when making emf measurements of buffers and acids in seawater.
- (ii) The dissociation constant of boric acid in seawater. Roy et al. (1993a) describe new measurements of the dissociation constant of boric acid in seawater (S = 35) from 0 to 55°C and boric acid (0.005 to 0.02 m). The results at m(Boric) = 0 are in excellent agreement ( $\pm$  0.0005 in lnK<sub>B</sub>) with the measurements of Dickson (1990b).
- (iii) The dissociation constants of carbonic acid in seawater. Roy *et al.* (1993b) describe new measurements of the first and second dissociation constant of carbonic acid in seawater from 0 to 45°C and S = 5 to 45. Over 2400 measurements were made using the H<sub>2</sub>,Pt |AgCl,Ag electrode system. The standard errors of the fitted results are  $\pm 0.002$  in pK<sub>1</sub> and  $\pm 0.003$  in pK<sub>2</sub>. The new measurements are in good agreement ( $\pm 0.002$  in pK<sub>1</sub> and  $\pm 0.008$  in pK<sub>2</sub>) with the measurements of Goyet and Poisson (1989).
- Field measurements of pH, A<sub>T</sub>, C<sub>T</sub> and pCO<sub>3</sub>. Millero et al. (1993b) describe the (iv) internal consistency of the carbonate system in the oceans as judged by measurements of all four parameters at sea during cruises last year supported by the National Oceanic and Atmospheric Administration (NOAA) as part of the U.S. JGOFS Equatorial Pacific Process Study (EqPac). Robert Byrne of the University of South Florida measured pH (25°C) using spectrophotometric techniques. R. Wanninkhof of NOAA's Atlantic Oceanographic and Meteorological Laboratory (AOML) and R. Feely of NOAA's Pacific Marine Environmental Laboratory (PMEL) measured the pCO<sub>2</sub> (20°C and in situ temperatures) using an infrared technique and  $C_{T}$  by coulometry. The Millero group from the University of Miami measured  $A_T$  by potentiometry. This is believed to be the first time that all four parameters of the CO<sub>2</sub> system have been independently determined at sea or in the laboratory. Millero's group have used CO<sub>2</sub> measurements made in surface waters during the spring NOAA/JGOFS cruise along 170°W from 10°N to 10°S to examine the internal consistency of the CO<sub>2</sub> system measurements in a recent publication. To do so, various inputs of pairs of parameters were used to calculate the components of the CO<sub>2</sub> system. Table 5.3.2-1 shows their estimates of the analytical precision (reproducibility) and accuracy of these measurements.

Analysis	Precision	Accuracy
pH (spectrophometric)	± 0.0004	± 0.002
A <sub>T</sub> (potentiometric)	$\pm 2 \mu mol kg^{-1}$	$\pm 4 \ \mu mol \ kg^{\cdot i}$
C <sub>T</sub> (coulometric)	$\pm 1 \ \mu mol \ kg^{\cdot 1}$	$\pm 2 \mu$ mol kg <sup>·1</sup>
pCO <sub>2</sub> (infrared)	± 0.5 µatm	± 2 µatm

Table 5.3.2-1: Estimates of the analytical precision and accuracy of measurements of pH,  $A_T$ ,  $C_T$  and pCO<sub>2</sub>

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These estimates of the precision and accuracy can be used to evaluate the probable errors in the parameters calculated from various pairs of measurements (Table 5.3.2-2). With the present estimates of accuracy, the most accurate calculations for  $A_T$  are obtained using the combination of pH and  $C_1$  or pCO<sub>2</sub> and  $C_T$ , while the most accurate calculations for  $C_T$  are obtained using either pCO<sub>2</sub> and  $C_T$  or pCO<sub>2</sub> and  $A_T$ . For pCO<sub>2</sub>, finally, the most accurate calculations are obtained using either the pH and  $A_T$  or pH and  $C_T$  pairs.

Table 5.3.2-2:	Estimated	probable	errors	in the	calculated	parameters	of the	carbonate	system
using various input measurements.									

Input	ΔрН	ΔA <sub>r</sub> (μmol kg <sup>-1</sup> )	ΔC <sub>T</sub> (μmol kg <sup>·i</sup> )	ΔpCO <sub>2</sub> (µatm)
pH - A <sub>T</sub>			± 3.8	± 2.1
рН - С <sub>т</sub>		± 2.7		± 1.8
pH - pCO <sub>3</sub>		± 21	± 18	
рСО <sub>2</sub> - С <sub>т</sub>	± 0.0025	± 3.4		
рСО <u>,</u> - А <sub>т</sub>	± 0.0026		± 3.2	
A <sub>T</sub> - C <sub>T</sub>	± 0.0062			± 5.7

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These results clearly show that pCO<sub>2</sub> and pH should not be calculated from measurements of  $A_T$  and  $C_T$ .  $A_T$  and  $C_T$  should not be calculated from measurements of pH and pCO<sub>2</sub>. At present, the best pairs of measurements that can be used to characterize the CO<sub>2</sub> system are pH-C<sub>T</sub> or pCO<sub>2</sub>-C<sub>T</sub>. These estimated probable errors may change in the near future as measurements of  $A_T$  improve with the use of alkalinity standards. The use of buffers calibrated with the hydrogen, silver and silver-chloride electrode system will improve measurements of pH.

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In order to analyze the internal consistency of the CO<sub>2</sub> system measurements made at sea, it is necessary to have reliable thermodynamic constants. At present, dissociation constants for carbonic acid are available from independent studies by Hansson (1973), Mehrbach *et al.* (1973), Goyet and Poisson (1989), and Roy *et al.* (1993a). In a fifth study, Dickson and Millero (1987) gave equations of the combined measurements of Hansson and Mehrbach *et al.* adjusted to the same pH scale.

The Millero group used these five sets of constants to calculate the components of the CO<sub>2</sub> system using six possible inputs: pH and A<sub>T</sub>, pH and C<sub>T</sub>, pH and pCO<sub>2</sub>, pCO<sub>2</sub> and A<sub>T</sub>, pCO<sub>2</sub> and C<sub>T</sub>, and A<sub>T</sub> and C<sub>T</sub>. The internal consistency of the measurements was determined by

examining the average (absolute) difference between the calculated and measured parameters obtained using every possible pair of input measurements. For example, the measured values of pH and  $A_T$  at each station can be combined to determine  $C_T$  and  $pCO_2$  using a given set of dissociation constants. The summary of the results given in Table 5.3.2-3 indicates that the measurements have an internal consistency of  $\pm 0.004$ -0.010 in pH,  $\pm 3$ -6  $\mu$ mol kg<sup>-1</sup> in  $A_T \pm 4$ -5  $\mu$ mol kg<sup>-1</sup> in  $C_T$  and  $\pm 2$ -7  $\mu$ atm in pCO<sub>2</sub> if reliable constants are used for the dissociation of carbonic acid in seawater.

Constants	ΔpH	ΔA <sub>r</sub> (μmol kg <sup>-1</sup> )	ΔC <sub>T</sub> (μmol kg <sup>·i</sup> )	ΔpCO <sub>3</sub> (μatm)
Roy et al.	0.009	5.1	4.3	5.5
Goyet & Poisson	0.008	4.5	4.3	4.6
Dickson & Millero	0.004	5.1	4.4	2.8
Hansson	0.005	7.4	6.2	3.7
Mehrbach <i>et ul</i> .	0.013	17.6	14.8	10.9

 Table 5.3.2-3:
 Summary of the average deviations in the calculated carbonate variables determined using thermodynamic constants.

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At present it is not possible to make a clear choice with this limited analysis of the reliability of the various thermodynamic constants. Overall, the constants given by Dickson and Millero yield the lowest average deviations (0.004 in pH, 4  $\mu$ mol kg<sup>-1</sup> in C<sub>T</sub>, 5  $\mu$ mol kg<sup>-1</sup> in A<sub>T</sub> and 2  $\mu$ atm in pCO<sub>2</sub>) for this data set. Recent laboratory measurements of the four parameters on seawater indicate that the constants of Goyet and Poisson and Roy *et al.* are more reliable. Further studies are needed to clear up this uncertainty.

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Millero was encouraged by these comparisons. They indicate that field measurements can now be made that are thermodynamically consistent with the present accuracy in measuring the various parameters of the system ( $\pm 0.002$  in pH,  $\pm 4 \mu \text{mol kg}^{-1}$  in  $A_{\text{T}} \pm 2 \mu \text{mol}$ kg<sup>-1</sup> in  $C_{\text{T}}$  and  $\pm 2 \mu \text{atm}$  in pCO<sub>2</sub>). Further calculations are needed at other temperatures especially for deep waters, to see if these findings hold for waters that have much higher levels of pCO<sub>2</sub> and  $C_{\text{T}}$ .

- 37 The Panel agreed that these comparisons were a valuable exercise and the results pointed the way toward arriving at consistency among field measurements. But they also suggested that the UNESCO JPOTS Report needs to be revisited in light of Millero's findings.
  - 5.4 DETERMINATION OF pCO<sub>2</sub> IN THE ATLANTIC OCEAN
- 38 B. Schneider reported on results of an intense field measurement programme to study the oceanic carbonate system at the Institut für Meereskunde in Kiel as part of the German contribution to WOCE and JGOFS. During six cruises in 1991-93 in the Atlantic Ocean between Spitzbergen and the Weddell Sea, the surface distribution and depth profiles of CO<sub>2</sub> partial pressure, total carbonate, and alkalinity were determined.
  - Using an equilibrator/IR underway system, the surface pCO<sub>2</sub> was recorded continuously over a total of about 15,000 nautical miles. The data of two cruises (*Polarstern*, November 1991 and *Meteor*, May 1992) were used to construct a profile for pCO<sub>2</sub> in surface water and in air between 60°S and 60°N (Figure 5.4-1). Three different regimes can be identified which give an example of how the physical and biological state of surface water acts on pCO<sub>2</sub>:



Figure 5.4-1. CO<sub>2</sub> partial pressure in surface water and in air between 60°S and 60°N in the Atlantic Ocean. The data are from a cruise with *Polarstern* in November 1991 (45°N - 60°S) and with *Meteor* in May 1992 (30°N - 60°N).

- (i) At high latitudes (>40°), surface water is highly undersaturated with respect to  $CO_2$ , the mean partial pressure difference is about 50  $\mu$ atm. Moreover, pCO<sub>2</sub> is characterized by strong small scale variability which is correlated with the variation of the chlorophyll-a contents (Figure 5.4-2a). This indicates that primary production is the main control for pCO<sub>2</sub> in these regions during spring in the southern (November) and northern (May) hemispheres.
- (ii) Between 40°S and the equator,  $pCO_2$  is less fluctuating and increases steadily from about 310  $\mu$ atm to a maximum value of almost 380  $\mu$ atm. Chlorophyll-a concentrations are low (<0.2  $\mu$ g/1) and pCO<sub>2</sub> is clearly related to temperature (Figure 5.4-2b).
- (iii) Between 40°N and the equator, the chlorophyll-a concentrations are again low, but the expected increase of pCO<sub>2</sub> with increasing temperature is masked by a salinity effect. This effect is especially important near the ITCZ (20°N -  $0^{\circ}$ ), where a strong salinity gradient (34.8% to 36.5%) is the controlling factor for pCO<sub>2</sub> (Figure 5.4-2c).



Figure 5.4-2a to c. Relationship between pCO<sub>2</sub> and chlorophyll-a at latitudes > 40° in the southern (upper line) and northern (lower line) hemisphere (a). Correlation between pCO<sub>2</sub> and temperature (b) and salinity (c) at 40°S - 0° and 20°N - 0°, respectively.

#### 6. QUANTIFYING THE ANTHROPOGENIC CO, SIGNAL IN THE OCEAN

#### 6.1 OCEAN MODELS

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In covering this topic Siegenthaler reported there has been a consolidation of ideas over the past year, but no fundamental changes new to the Panel since last year. The best estimate of the uptake of excess (anthropogenic)  $CO_2$  by the ocean is obtained by means of atmosphere-ocean carbon-cycle models. These models range in complexity from simple 1-D to 3-D general ocean circulation models (GOCMs). An essential condition for reliably calculating the oceanic  $CO_2$  uptake is that the ocean model, is calibrated (in the case of simple, parameterized models) or validated using a transient tracer, preferably bomb-<sup>14</sup>C which is a good analog for anthropogenic

 $CO_2$ . Different models, all bomb-<sup>14</sup>C calibrated, have yielded a mean uptake of 2.0 ± 0.5 GtC/yr for the decade 1980-89 (Orr, 1993; Siegenthaler and Sarmiento, 1993). This estimate depends little on the existing uncertainty of the gas exchange (see section 5.2), since the main rate-controlling process is the vertical transport of  $CO_2$ -laden water from the surface to depth.

Another approach that has been used by several groups (e.g., Tans et al., 1990) has been to constrain the surface sources and sinks using atmospheric and oceanic pCO<sub>2</sub> observations in combination with an atmospheric transport model. With the sinks adjusted such that the northsouth CO<sub>2</sub> concentration difference is correctly reproduced by the model, Tans et al.'s result for the global oceanic uptake is only 0.3 to 0.8 GtC/yr. This result, however, requires revision for several processes not taken into account. First, it is to be expected that, prior to the industrial revolution, there was a net source from the oceans to the atmosphere of order 0.6 GtC/yr. This is required to balance the flux of cerbon of atmospheric or biospheric origin coming down rivers. This must be taken into account when comparing the actual air-sea flux to estimates of the anthropogenic uptake (Sarmiento and Sundquist, 1992). Second, due to a temperature skin effect, pCO<sub>2</sub> at the very water surface is on average slightly lower than the measured bulk-water value, so that  $\Delta pCO_2$ , and therefore the air-to-sea flux, is underestimated globally by about 0.4 GtC/yr (Robertson and Watson, 1992). Finally, there is a north-south transport of carbon in the atmosphere in the form of CO, not represented in the CO, observations, which adds another about 0.2 GtC/yr. Thus, the revised Tans et al. estimate amounts to 1.5 - 2.0 GtC/yr (this range does not take into account the uncertainty of the corrections). Enting et al. (1993) used basically the same approach with a Bayesian method, including an error analysis. They obtained an oceanic uptake of excess CO<sub>2</sub> of 2.0  $\pm$  1.0 GtC/yr (of which 0.6 GtC/yr is river input).

The carbon increase in the ocean, and the inventory of excess carbon in the ocean can, in principle, be estimated based on a reconstruction of preformed (= surface)  $pCO_2$  and  $C_T$ (Brewer, 1978; Chen and Millero, 1979). This requires a correction for the addition of  $C_T$  to subsurface waters due to decomposition of biogenic particles, which has to be based on measurements of nutrients (PO<sub>4</sub> or NO<sub>4</sub>) and application of Redfield ratios (P : N : C). Uncertainties in the Redfield ratios as well as in the preformed  $pCO_2$  values and nutrientconcentrations do, however, seriously limit the application of this method.

It is perhaps prudent to point out, however, that since the publication of the Tans et al. analysis there has been a natural tendency to look for effects which would increase the global flux estimate of ocean uptake to bring it into agreement with the model-based figures. As a result, effects which might tend to decrease the air-sea flux estimate may not as yet have been fully investigated.

6.2 EVIDENCE FROM <sup>13</sup>CARBON

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C.S. Wong reported on developments in the isotopic approach for estimating net ocean uptake of anthropogenic CO<sub>2</sub>. The isotopic ratio  ${}^{13}C/{}^{12}C$  has been used extensively as a geochemical tracer in the global carbon cycle. The expression  $\delta^{13}C$  is defined as:

$$\delta^{13}C (permil) = \frac{[({}^{13}C/{}^{12}C)_x - 1]}{({}^{13}C/{}^{12}C)_x} \times 1000$$
(3)

where x is the unknown and s is the Pee Dee Belemnite Standard. Wong showed a plot illustrating illustrating the  $\delta^{13}$ C changes at 7 locations in the Pacific Ocean between 1970 and 1990 (29°N, 20°N, 0°S, 6.5°S, 16.5°S, 40°S, 50°S). These data were used to estimate the net oceanic uptake of 2.1 ± 0.8 ( $\sigma$ ) GtC/yr (Figure 6.2-1) and a net terrestrial release of a negligible 0.1 GtC/yr (Quay et al., 1992). A similar confirmation from atmospheric oxygen depletion (Keeling and Shertz, 1992) indicated the net oceanic uptake to be 3.0 ± 2.0 ( $\sigma$ ) GtC/yr, and a net terrestrial source of -0.2 ± 2.0 ( $\sigma$ ) GtC/yr.



Figure 6.2-1. Plot illustrating increase in CO, uptake based on observations of  $\delta^{13}$ C changes at 7 locations in the Pacific Ocean between 1970 and 1990 (29°N, 20°N, 0°S, 6.5°S, 16.5°S, 40°S, 50°S). From Quay *et al.* (1992).

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The  ${}^{13}C/{}^{12}C$  isotopic approach requires additional effort on (i) inter-laboratory compatibility assessment and reference standards, similar to  $C_7$ , and (ii) more extensive spatial and temporal measurements of  ${}^{13}C/{}^{12}C$  in the world ocean.

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The isotopic chemistry has been used to assess past oceanic CO<sub>2</sub> concentration and biological productivity by measuring the  $\delta^{13}$ C of plankton (Rau *et al.*, 1992). The approach will help to elucidate the marine biological effect on the global carbon cycle. Time series measurements at Ocean Station P showed that oceanic planktonic species shifts could modify the carbon cycle. In the subarctic Pacific Ocean, the chlorophyll-a in Central Pacific showed a doubling decadally (Vernick *et al.*, 1987) and the zooplankton biomass also a decadal doubling between 1960 and 1980 (Brodeur and Ware, 1992). The waters were shown by recent contaminantfree <sup>14</sup>C productivity measurements to be as productive as the equatorial Pacific, and possible enhancement by climatic events (Wong *et al.*, submitted). Episodic events are common in the subarctic waters for CaCO<sub>3</sub> flux and organic C flux with sudden explosive population blooms of forams and diatoms. Again, the very different <sup>13</sup>C/<sup>12</sup>C of calcareous shells (+2%) and particulate organic matter (-23 to -24%) could throw light on the integrated changes of CO<sub>2</sub> in the upper IOC-JGOFS/CO<sub>2</sub>-IV/3 page 18

ocean productivity. The full potential should be explored. An inverse relationship between  $C_T$  and  $\delta^{13}C$  (Figure 6.2-2) in the Northeast Pacific Ocean illustrated the possibility to infer surface  $C_T$  and pCO<sub>2</sub> from  $\delta^{13}C$  of detritus material collected in sediment traps.



Figure 6.2-2. The distribution of  $C_T$  and phytoplankton  $\delta^{13}C$  (50 - 253  $\mu$ m) collected with continuous net filtration on surface along a line from Vancouver Island to Ocean Station "P" in May 1991.

#### 6.3 ATMOSPHERIC MODELS

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G. Pearman reviewed developments in atmospheric  $CO_2$  analysis and modelling. The meridional distribution of atmospheric  $CO_2$  concentration, in conjunction with some knowledge of the transporting properties of the atmosphere, have been used to quantify the zonal sources and sinks in the global carbon cycle (e.g., Pearman *et al.*, 1983; Keeling *et al.*, 1989). Indeed, Pearman and Hyson (1986) first demonstrated that the mean concentration difference between the equatorial region and the higher latitudes of the northern hemisphere suggests that a significant part of the CO<sub>2</sub> released in the northern hemisphere from fossil fuel combustion appears to disappear at those latitudes. Using improved data and techniques, this finding was confirmed by Enting and Mansbridge (1989). Tans *et al.* (1990) carried the analysis further, by suggesting that the relatively small observed concentration difference between the surface ocean and the atmosphere must imply a northern hemisphere terrestrial sink for this carbon.

- 48 Several studies have shown why the analysis based on the observations of oceanic pCO<sub>2</sub> might lead to an underestimate of the role of oceanic uptake (see section 6.1). The reasons include, uncertainties concerning the correction of pCO<sub>2</sub> for the temperature difference below the surface and at the very surface of the ocean, transport of carbon to the ocean from the terrestrial biomass via rivers, thus bypassing the air-sea exchange mechanism, and the atmospheric transport of carbon as carbon monoxide rather than CO<sub>2</sub> (Robertson and Watson, 1992; Sabine and Mackenzie, 1991; Sarmiento and Sundquist, 1992; Enting and Mansbridge, 1989).
- 49 Improvements in the application of such atmospheric techniques for constraining the global carbon budget are currently progressing in two significant ways. In the first instance, the quality and validation of the transport models are being improved. Models are now more often three-dimensional representations of the atmospheric mixing processes. They are more adequately validated by their capacity to distribute other trace gases and, more recently, by a formal treatment of the errors associated with the process (Enting *et al.*, 1993).
- 50 The second improvement which is being developed, is a more critical evaluation of the data selection procedures placed on the monitoring data, prior to their being used in such studies. Pearman pointed out that for many of the baseline atmospheric observatories, 50% or more of the observations are rejected from the data set on the basis that they do not represent space scales of relevance to these studies. While this is probable generally true, there is a concern that there is also a danger that such rejection may bias the data, or that the selection criteria are inappropriate for the applications of the data in these models.

#### DISCUSSION OF PAPERS ON CO, OCEAN SOURCES AND SINKS

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During the intersessional period, G. Kullenberg, Secretary IOC, requested assistance of the  $CO_2$  Panel in the preparation of a paper assessing the current knowledge on ocean  $CO_2$  sources and sinks. This request related to Agenda 21, which was adopted at the United Nations Conference on Environment and Development (UNCED) in Rio de Janeiro, June 1992 which lists a specific role for IOC relating to the carbon budget. Merlivat believed that the Panel should react positively to this request. In her response, she indicated her intention to draft a preliminary document which would serve as the basis for a formal paper for the IOC that would be developed at this meeting by the Panel as a whole. Subsequently, two new papers on this topic came to her attention: Siegenthaler and Sarmiento (1993) and Sundquist (1993), that pretty much covered the subject matter she intended to address. Accordingly, these two papers were distributed to the Panel members in lieu of the one Merlivat had planned to prepare.

After discussion of the recent literature and contradicting hypotheses on the ocean's role in the global carbon budget, the Panel decided on the form the paper should take. An outline was developed and individual writing tasks were assigned as indicated in Annex VI. It was agreed that text would be delivered by 31 July to A. Alexiou who would prepare an appropriate foreword as well as assemble and edit the paper. The complete draft, estimated to be 10-20 pages, would then be distributed to the Panel for a final review before transmitting it formally to Kullenberg. Consideration was given to subsequently preparing a summary of the paper for publication in EOS.

#### 8. NEW TECHNOLOGIES

#### 8.1 OCEAN

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Brewer described progress by G. Friedrich at the Monterey Bay Aquarium Research Institute (MBARI) on development of a buoy system that could be deployed to obtain time-series data from areas such as the Southern Ocean, the tropics (e.g., TOGA-COARE) and in the region of mode water formation. In these areas, particularly in the Southern Hemisphere, Pearman advised that the atmospheric concentration of  $CO_2$  can be estimated to about 1  $\mu$ atm and IOC-JGOFS/CO<sub>2</sub>-IV/3 page 20

hence good values of atmospheric  $pCO_2$  could be obtained. Mackey noted that, in the Southern Ocean, servicing of the buoy *in situ* would be very difficult and that the power requirements may restrict the deployment of the system due to cloud cover and short daylight hours limiting the energy available from the solar cells. Brewer suggested that this could be minimized by increasing the capacity of the battery supply and adjusting the duty cycle of the instrument. More details concerning description of the apparatus and its performance are provided in Annex VII.

- 54 Brewer advised that the cost of the system had not yet been determined although the basic cost of the ATLAS buoy was about \$20K. If these systems are to be widely deployed, there should be an agreed protocol for data handling and storage, and individual components should be constructed in modular form. This would allow the buoys to be deployed, serviced and retrieved by ships of different nationalities.
- 55 The LI-COR detector measures  $CO_2$  in wet air and can correct for the presence of water vapor. Although this can be done with good precision, there was some discussion as to the accuracy. This may not be of great importance, however, if buoys are deployed in areas where there are large temporal changes in pCO<sub>2</sub>.
- 56 Merlivat reported on the status of development of the pCO<sub>2</sub> sensor based on colorimetric techniques. The recent efforts have concentrated on the design of the optical spectrometer which must have a precision of  $0.5 \times 10^{-3}$  units in optical density. This requirement has now been achieved.

#### 8.2 ATMOSPHERE

#### 8.2.1 Gas Chromatography

- 57 Pearman referred to new developments in the measurement of atmospheric composition in general and  $CO_2$  in particular. He gave a very preliminary report on recent developments in gas chromatographic techniques for  $CO_2$  measurements in the atmosphere. Currently, measurement precision has approached that of the better NDIR technologies (i.e., 0.02  $\pm$  0.03 ppmv). There is an expectation that a precision of significantly better than 0.01 ppmv will be attainable in the next few years. Given this and the special advantages of gas chromatography (i.e., linearity over a wide concentration range, specificity of the measurement), it is anticipated that gas chromatography may become increasing); used in atmospheric monitoring programmes in the second half of the 1990s. A technical report on some of this progress will be given by L.P. Steele, at the WMO Meeting of Experts. (See section 12.)
- 58 As measurement precision approaches one in 10<sup>5</sup> or greater, scientists experience significant problems of integrity of the gas composition in storage and reticulation. New approaches will be necessary at these levels of precision.

#### 8.2.2 Mass Spectrometry

59 Isotopic measurements of CO<sub>2</sub> are increasingly being used in atmospheric studies as a method of distinguishing between the effects of terrestrial and oceanic carbon exchanges. As with other areas of atmospheric chemistry measurements, there has been a significant increase in measurement precision recently. For example, measurements of the stable carbon ratio with a precision of  $0.01^{0}/m$  are now possible on samples of about 50 ml of air (10  $\mu$ g carbon). The same problems of gas handling mentioned above are experienced at this level of measurement precision.

#### 8.2.3 Oxygen Measurements

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The oceanic reservoir of carbon is significantly larger than that of the atmosphere, and, even allowing for the buffering effect of the ocean carbonate system, the oceanic reservoir available for exchange on decadal time-scales is similar to that of the atmosphere. Thus exchanges

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of  $CO_2$  with the atmosphere will have an effect on atmospheric concentrations that is strongly modulated by the exchange with the oceans. Contrastingly, Pearman showed that the atmospheric reservoir of oxygen is approximately 100 times larger than that of the oceans, and about 10,000 times larger than the reservoir of the ocean available for exchange with the atmosphere on time-scales of decades. Thus, measurement of changes of the concentration of oxygen is a far more direct way of assessing the total oxidation taking place in the atmosphere, including the combustion of fossil fuels, loss of soil organic carbon and biomass burning. Though this fact has been appreciated for many years, techniques for the measurement at the necessary precision in a background of 21% oxygen have not been available.

61 Recently, new techniques, capable of measuring to one in 10<sup>6</sup>, have become available (e.g., Keeling and Shertz, 1992). This is an exciting new development. These measurements are based on interferometric techniques or on the vastly improved precision of mass spectrometry.

#### 9. OCEAN COLOR SATELLITES

O. Brown was unable to attend this meeting of the Panel to present an update on the status of ocean color satellites. Brewer informed the Panel that plans for launching U.S., Japanese and German satellites for ocean color were on track. The U.S. Sea-Viewing Wide Fieldof-View Sensor (SeaWiFS) was scheduled for launch in the first quarter of 1994. Brewer believed that there has been an overreaction in the scientific community to a small concern voiced about the effect of clouds and boundaries on the data and that the SeaWiFS overall capabilities will definitely be a major improvement over the Coastal Zone Color Scanner (CZCS). For example, it has a sensitivity 4 times better that the CZCS. Hooker and Esaias (1993) provide a detailed description of the SeaWiFS project.

Brewer voiced a personal concern regarding the lack, in existing plans, of defined ocean experiments for the ocean satellites planned to be orbited in this decade. Large sums have been invested and much more will be needed for these satellites that are now in the pipeline before they are actually launched. Budget pressures are intense and, without a strong set of experiments to back them, these satellites could be in jeopardy.

#### 10. TIME SERIES DATA

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#### TIME SERIES DATA

S. Tsunogai reported on the large field effort by Japan to obtain long time series of ocean data. The Japan Meteorological Agency (JMA) has accumulated oceanographic data (including  $CO_2$ ,  $CH_4$ , CFCs in the atmosphere and ocean) along fixed lines in the waters around Japan every season for more than 50 years. For over 25 years it has obtained data sets from Japan to the Equator in the Western North Pacific on a semi-annual basis. Recently, the regular survey in the western North Pacific has been intensified to 3 or 4 times per year (see Figure 10-1). The National Institute for Environmental Studies (N!ES), the Meteorological Research Institute and Hokkaido University are also contributing to this growing data set. For example, the NIES in June 1991 began a high-frequency, long-term monitoring operation on a Japan-Korea ferry which makes two round trips weekly across the Korea Strait. Measurements consist of continuous sampling of T, S, pH, and fluorescence and automated bottle sampling (up to 36 sea water samples per cruise) for nutrient analyses. The *in situ* biomass data set will be valuable for calibrating/validating ocean color satellite observations.

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Tsunogai encouraged the Panel to consider giving increased priority to obtaining time series data on the vertical column both at fixed stations and along repeated cruise tracks. He believed that the global  $pCO_2$  survey may be overdominating the available resources to the detriment of the other data needed for understanding of the long-term ocean carbon cycle. He

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recommended greater emphasis be put on the total suite of chemical and isotopic observations needed to quantify the net global carbon flux, and to determine how the ocean is "tending".



Figure 10-1. Repeat lines and major currents where oceanographic observations are made in the western North Pacific by JMA. Small open circles are fixed stations for the deep water sampling.

#### 11. CO<sub>2</sub> GLOBAL MEASUREMENT CO-ORDINATION

- 66 Susan Kadar reported on her activities at Woods Hole Oceanographic Institution to compile an inventory of ocean CO<sub>2</sub> data. A standard inquiry was prepared and mailed to about 30 known researchers. Thus far about 40% have responded and she was optimistic that more would be received soon. She believed that it was likely the U.S. JGOFS Office will be the umbrella for a CO<sub>2</sub> data office to be established in 6-8 months.
- 67 Regarding the WOCE data, the situation at present is that the center in Hamburg is putting toge her the WOCE fields. If the  $CO_2$  data are reported as part of the Chief Scientist's report, they will go to the Hamburg Office. The U.S. Department of Energy data center at Oak Ridge also accepts U.S. data from the WOCE Hydrographic Programme. It will also accept data from other countries as well.  $CO_2$  data at Oak Ridge does not have ancillary data such as salinity and nutrients.
- 68 Kadar reported that though she had a growing workload, she was, in principle, willing to continue with the co-ordination task but to make better progress, some part time assistance might be needed.
- 69 The Panel voiced its appreciation and strongly encouraged the inventory initiative. There is the usual problem of individual scientists being reluctant to hand over their data before having their manuscripts published. Panel members agreed that individual scientists should be asked to contribute to the general inventory, indicating the earliest time of intended data release (according to either technical/calibration or publication policy considerations).
- 70 Merlivat pointed out that the inventory to be drawn up is especially crucial for all those datasets <u>not</u> collected under the aegis of the JGOFS or WOCE as these programmes already are following procedures for data sharing among investigators as well as with various international CO<sub>2</sub>-climate agencies.
- 71 Brewer expressed the view that it is generally desirable to strive towards not only an inventory of cruises, but also toward one coherent dataset. Pearman reflected on very similar problems some twenty years ago when arranging the co-ordination of atmospheric research activities and data handling. At some point it had been agreed that all participants would make their provisional data available to each other within one year of collection. This worked quite well for most (but not all) of the participants.
- 72 Right now, in Pearman's view, the general drive towards one centralized large database is outdated. With the current availability of electronic mail, Pearman believes that individual scientists should be able to exchange databases easily, and an agreed protocol is highly desirable.
- 73 Through the discussion it became clear that the Carbon Dioxide Information and Analysis Center (CDIAC) at Oak Ridge now has available a variety of oceanic CO<sub>2</sub> datasets such as the pCO<sub>2</sub> dataset collected by Weiss over the past several years. Encouragement of other workers to use this facility is one option to improve availability.
  - 11.1 CONCLUSIONS AND RECOMMENDATIONS
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The Panel agreed on the following:

(i) Each country would be requested to identify a liaison scientist responsible for assuring that various scientists and research groups in his/her country inform S. Kadar about the existence of their datasets. The following individuals were found willing (in some cases suggested) to serve as liaison scientists, albeit in some instances only temporarily until permanent contact persons could be identified:

D. Mackey M. Frankignoulle A. Watson C.S. Wong A. Poisson B. Schneider	Australia and New Belgium Britain Canada France Germany	Zealand	
S. Tsunogai H. de Baar T. Johannessen D. Turner A. Chen D. Wallace	Japan The Netherlands Norway Sweden Taiwan USA	(J. Rommets	JGOFS data manager)

Scientists in other countries (not identified above) are encouraged to submit information about their datasets directly to S. Kadar, and also to identify a national liaison for each country. The  $abov \cdot$  contact persons are expected to urge chief scientists for all cruises (including WOCE) to explicitly mention shipboard CO<sub>2</sub> measurements in cruise reports.

- (ii) The ongoing effort by S. Kadar to compile an inventory deserves strong support as well as further input by fellow scientists. In the near term, say within three months, a draft version of the list should be sent out for corrections and any necessary ancillary information, such as dates at which provisional as well as final data will become available. Within six months the complete inventory would be made available by S. Kadar.
- (iii) At median range the objective is to make datasets mutually available by exchanges between individual scientists and research groups. Preferably datasets will also be taken up in existing database systems (JGOFS, WOCE in various countries, U.K. BODC, U.S. NODC, etc.) while submission of datasets to CDIAC at Oak Ridge is highly recommended. Brief information on methods, blanks, accuracy, etc., should accompany the actual data so as to allow users to evaluate data quality.
- (iv) The rapid development and definition of stringent protocols for measurement, calibrations, etc., is crucial for assuring that new data to be collected will be of optimal analytical quality. Here the efforts of members of the IOC-JGOFS Panel are of utmost importance, where the ongoing activities of A. Dickson towards defining protocols and providing accurate standards are an outstanding example. Workshops like the one envisioned towards intercalibrating seawater/air equilibrators, or the coulometry workshop organized by M. Roberts (NOAA/PMEL) are just as necessary. The drive towards more accurate values of thermodynamic constants (Goyet, Poisson, Millero, Roy) obviously also contributes towards more accurate measurements and internal consistency. Proper description, including error intervals, of theoretical as well as empirical relations between  $pCO_2$  and temperature is essential for accurate corrections of seawater  $pCO_2$  values derived from shipboard equilibrators.

#### 12. NATIONAL PLANS

#### 12.1 AUSTRALIA

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- D. Mackey reported on the following:
- (i) Investigators plan to obtain surface pCO<sub>2</sub> and water column  $\delta^{13}$ C, C<sub>T</sub> and A<sub>T</sub> on nearly all WOCE cruises done by Australian ships (*Franklin* and *Aurora Australis*).
- (ii) Surface pCO<sub>2</sub> is planned on many of the Hobart-Prydz Bay voyages of Aurora Australis.

- (iii) The Franklin will be operating in the Indian Ocean from mid-1994 for 1-2 years. At present, there is insufficient manpower to collect  $pCO_2$  data. This could change with the addition of more staff or when the assistance of graduate students becomes possible.
- (iv) Plans call for collecting data along WOCE-SR3 during the Austral winter of 1995.
- 12.2 CANADA

C.S. Wong reported that, in 1993, the Marine Chemistry Division of the Bedford Institute of Oceanography (BIO) plans to conduct on the CSS Hudson one WOCE line between Greenland and Labrador from 60°N 48°W to 53°N 56°W, with measurements of  $C_T$ ,  $A_T$ , nutrients and halocarbons, and one cruise to the Ronne Ice Shelf and the Filchner Ice Shelf in the Arctic, between 70°N and 74°N and 30°W and 60°W, with similar measurements. Contact: P. Jones.

- The Centre for Ocean Climate Chemistry (COCC) of the Institute of Ocean Sciences (IOS) plans in 1993 to conduct one WOCE line in Okhotsk Sea from 43.5°N 138.0°W to 58.5°N to 141.8°W with three stations in the Sea of Japan and the Kurile Basin, and 30 stations along WOCE P1 in a joint Russia/Canada/USA expedition on board the *AK Nesmeyanov*. Measurements will include T, S, O<sub>2</sub>, nutrients, C<sub>T</sub>, A<sub>T</sub> and freons. Sampling for <sup>13</sup>C, <sup>18</sup>O, <sup>14</sup>C, <sup>3</sup>H and DOC will be made. On a Russian "PRILIV" cruise, sampling for C<sub>T</sub>, A<sub>T</sub> and nutrients are planned in the central Subarctic Pacific. Two cruises between the west coast of Vancouver Island and Station P (50°N, 145°W) are planned for 1993 to measure T, S, O<sub>2</sub>, C<sub>T</sub>, A<sub>T</sub>, pCO<sub>2</sub>, and freons as WOCE repeat hydrography lines. In 1994, the WOCE P15 line along 165°W from the Aleutians at 57°N, to Fuji at 10°S will be conducted with measurements of T, S, O<sub>2</sub>, nutrients, C<sub>T</sub>, A<sub>T</sub>, pCO<sub>2</sub>, freons and with sampling for <sup>13</sup>C, <sup>18</sup>O, <sup>14</sup>C, and <sup>3</sup>H. A Canada-Japan ship-of-opportunity programme on the *Skaugran* will be started in late 1993 to measure T, S, pCO<sub>2</sub>, and to obtain samples for C<sub>T</sub>, A<sub>T</sub>, nutrients and <sup>13</sup>C. Contact: C.S. Wong.
  - 12.3 FRANCE
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Merlivat reported on the plans that France has developed for field  $pCO_2$  measurements. Scheduling is shown in Figure 12-1.



Figure 12-1. Schedule of France JGOFS activities at sea for 1993-1998.

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The oceanic areas where the indicated program cruises are scheduled to take place

are:

EUMELI -- Tropical Atlantic EPOPE -- Tropical Pacific ANTARES -- Southern Indian/Antarctic FRONTAL -- Western Mediterranean Sea

For the time series:

Gulf of Lions -- Western Mediterranean Ligurian Sea -- Western Mediterranean Antarfix -- Indian Ocean South of Kerguelan

Other  $pCO_2$  measurements are made along WOCE lines in the western Indian Ocean (1993, 1995) and the tropical Atlantic (1993). Repeat sections are made in the central west Indian Ocean (Program MINERVE) and in the Atlantic and Pacific aboard a voluntary observing ship along the line from Le Havre to Panama to Noumea. (Program ECOA).

12.4 GERMANY

Three institutions are working on oceanic CO<sub>2</sub> research: the Institut für Meereskunde in Kiel (IFMK), the Institut für Biogeochemie und Meereskunde in Hamburg (IFBM), and the Institut für Polar- und Meeresforschung in Bremerhaven (AWI). In 1994 the Institut für Ostseeforschung in Warnemünde (IOW) will also start with a JGOFS project on the seawater/CO<sub>2</sub> system. This work will concentrate on the carbon cycle in marginal seas, especially the Baltic Sea, and on  $pCO_y/C_T$  measurements in the North Atlantic.

For 1994, the following cruises are planned:

- (i) Winter 1993/94, RV Meteor, North Atlantic (Hamburg-Ponta Delgada-Recife), parameters:  $C_T$ ,  $A_T$  (IFBM);
- (ii) Winter 1993/94, RV Polarstern, Southeast Pacific/Bellinghausen Sea, parameters: C<sub>T</sub>, A<sub>T</sub>, pCO<sub>2</sub> (AWI/co-operation with NIOZ);
- (iii) April/May 1994, RV Polarstern, eastern Weddell Sea, parameters:  $C_T$ ,  $A_T$ , pCO<sub>2</sub> (AWI/co-operation with NIOZ);
- (iv) October/December 1994, RV Meteor, North Atlantic (Brest-St.Johns-Hamburg), parameters:  $C_{T}$ ,  $A_{T}$ , pCO<sub>2</sub> (IFMK, IOW).
- 12.5 JAPAN
- Tsunogai reported that Japan is gearing up to undertake long-duration operational observations under GOOS. These will include observations for research as well as operational use of all the important climate variables. Japan's ongoing, long-term  $CO_2$  observation programmes described in Section 10 will continue into the foreseeable future.
  - 12.6 NORWAY

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T. Johannessen described a Norwegian programme, begun in 1993, to study the Carbon Budget and Deep Convection (CARDEEP) in the Greenland, Iceland, and Norwegian Seas (GIN-Seas). The objective is to better understand the role deep-water-forming regions in the GIN-Seas play in the global oceanic  $CO_2$  uptake. Background and the data collection plan of CARDEEP are included in Annex VIII.

Johannessen also updated the Panel with regard to weather station M which has been operating since the early 1950s. New activity has been planned in order to observe changes throughout the year with respect to carbon cycling. New equipment for the weather ship *Polar Front* is needed to start this activity. The aim is to achieve detailed timeseries throughout the year that cover the most important parameters related to studies of the carbon cycle.

#### 12.7 THE NETHERLANDS

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- 84 H. de Baar reported that the excellent relationship between the Netherlands Institute for Sea Research (NIOZ) and the Alfred Wegener Institute led to an agreement to study the Antarctic CO<sub>2</sub> system during 1993-1996 during cruises of *RV Polarstern*. The first two are scheduled November 1993 into January 1994, and April-May 1994. Underway measurements will be made of pCO<sub>2</sub>,  $C_T$  and ancillary data (nutrients, fluorescence, skin SST) in surface waters. In addition, pCO<sub>2</sub>,  $C_T$  and  $A_T$  will be measured along vertical profiles at selected stations. Together with observations during outbound and homebound cruises traversing the South Atlantic, 4 out of typically 5-6 cruises of *Polarstern* each Antarctic season will produce CO<sub>2</sub> data.
- 85 Observations taken on the *Polarstern* along 3 transects in the South Atlantic appear to validate the hypothesis that 20-40°S zone is a substantial sink of CO<sub>2</sub>. Five more transects are scheduled until early 1995 and a second phase is envisioned 1995-2000.
- 86 Planning is also well advanced for NIOZ participation in some of the French JGOFS cruises of the ANTARES programme in 1994, 1995 and 1996. Studies will be made of dissolved organic carbon (DOC), its concentration, molecular composition, isotopic composition and microbial turnover rate. In addition the 1995 cruise will have a NIOZ team studying the role of iron in the Antarctic ecosystem.
- 87 For the period 1996-1998 NIOZ will examine several options during a planning meeting 29 January 1994. The first includes field programmes to occupy stations in the Northwest Indian Ocean that will be occupied by the US, UK and Germany in 1994-1995. The second is participation in a North Atlantic field study in 1998 proposed by R. Lampitt. A third is a field study in the South Atlantic sector of the Polar Front utilizing a non-ice certified ship on an outbound of homebound trip to/from the Indian Ocean.
- 88 A summary of the NIOZ activities during 1987-1993 was given by de Baar. It is included as Annex IX.
  - 12.8 UNITED KINGDOM
  - The group at Plymouth Marine Laboratory is the only one in the U.K. making regular measurements of CO<sub>2</sub> parameters at sea for geochemical purposes. This group's plans are as follows:
    - (i) North Atlantic (1993-1995): with funding from the U.K. Department of the Environment, pCO<sub>2</sub> measurements will be made from three merchant vessels plying regular routes all year round, for a period of one or two years. The measurements will be made using a new generation of CO<sub>2</sub> underway analyser based on a LI-COR instrument, which operates in fully unattended mode and is plumbed into the engine room of the ship. The first one will be installed in July 1993 with the others to follow over the next 6 months it is hoped.
    - (ii) Southern Ocean (1992-1995):  $C_T$  and  $pCO_2$  data were collected in the Bellingshausen sea region of the Southern Ocean during Austral spring 1992, as part of an extensive U.K. BOFS programme in that region, to investigate the association of phytoplankton activity and carbon fluxes with ice-melt. Data were collected over a lengthy cruise track from Capetown to Capetown during

February/March 1993, and a similar cruise track will be run again in 1994. It is planned to cover pCO<sub>2</sub> and  $C_T$  according to WOCE protocols on WHP line A23 from the Weddell Sea to Rio, provisionally scheduled for early 1995.

- (iii) Northwest Indian Ocean (October 1994): Plans have been submitted to mount a JGOFS-style process study in this region, to include  $pCO_2$  and  $C_T$  measurements.
- (iv) Pacific Ocean (October 1993): pCO<sub>2</sub> will be collected during an iron fertilization process study to investigate the effects on the biota of addition of iron to surface waters in the tropical Pacific.
- 12.9 UNITED STATES OF AMERICA
- Brewer reported that the U.S. intends to continue occupying WOCE lines and conducting JGOFS process studies according to plans, detailed in the U.S. JGOFS Implementation Plan (due to be distributed in the summer of 1993).

#### 13. RELATED MEETINGS

- 91 The Panel was advised of two meetings concerning CO<sub>2</sub> which will be held in September this year. The first is a WMO Meeting of Experts on Carbon Dioxide Measurements to be held in Rome, September 7-10. This is a meeting of a group which is somewhat the atmospheric counterpart of the IOC-JGOFS CO<sub>2</sub> Panel. It has a 20-year history and has been the main mechanism which has co-ordinated the international comparability of atmospheric measurements, the development of measuring techniques, data reporting and archiving methods. G. Pearman is the organizer/chair of the meeting. C. Keeling and C.S. Wong will also be attending this meeting, and this should ensure excellent interaction between that group and this Panel. Copies of the written report of the meeting will be made available to Panel members later this year.
- 92 The second meeting is the Fourth WMO International Carbon Dioxide Conference to be held at Carqueiranne, September 13-17. Merlivat, co-convenor of the conference, reported that a very significant number of the papers to be presented at this meeting will deal with oceanic aspects of the carbon cycle.

#### 14. NEXT PANEL MEETING

The Panel agreed to schedule its next meeting at Scripps Institution of Oceanography in conjunction with the intercalibration exercise which was tentatively set for 6-10 June 1994 (see Section 4.3.) It was agreed the Panel meeting would best be scheduled the following week of 13-17 June. Discussion of the results of the exercise would be a main agenda item.

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#### ANNEX I

#### AGENDA

#### 1. WELCOMENG

2. ADOPTION OF AGENDA

#### 3. RECENT IOC EVENTS REGARDING DEVELOPMENT OF GOOS, GCOS, AND OOSDP

#### 4. **PROGRESS REPORTS**

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  - 4.1.2 The Consequences of Thermodynamic Uncertainties
  - 4.1.3 Conclusions/Recommendations

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  - 5.1.1 Discussion 5.1.2 Significance for Calculating Air-Sea CO<sub>2</sub> Fluxes
- 5.2 GAS EXCHANGE COEFFICIENT (K)
- 5.3 THERMODYNAMICS OF THE CO<sub>2</sub> SYSTEM
  - 5.3.1 Experimental Techniques 5.3.2 Thermodynamics
- 5.4 DETERMINATION OF pCO<sub>2</sub> IN THE ATLANTIC OCEAN

#### 6. QUANTIFYING THE ANTHROPOGENIC CO, SIGNAL IN THE OCEAN

- 6.1 OCEAN MODELS
- 6.2 EVIDENCE FROM <sup>13</sup>CARBON
- 6.3 ATMOSPHERIC MODELS

#### 7. DISCUSSION OF PAPERS ON CO, OCEAN SOURCES AND SINKS

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#### 8. **NEW TECHNOLOGIES**

- 8.1 OCEAN
- 8.2 ATMOSPHERE
  - 8.2.1 Gas Chromatography
  - 8.2.2 Mass Spectrometry
  - 8.2.3 Oxygen Measurements

#### 9. OCEAN COLOR SATELLITES

#### 10. TIME SERIES DATA

#### 11. CO, GLOBAL MEASUREMENT CO-ORDINATION

11.1 CONCLUSIONS AND RECOMMENDATIONS

#### 12. NATIONAL PLANS

- 12.1 AUSTRALIA
- 12.2 CANADA
- 12.3 FRANCE
- 12.4 GERMANY
- 12.5 JAPAN
- 12.6 NORWAY
- 12.7 THE NETHERLANDS
- 12.8 UNITED KINGDOM
- 12.9 UNITED STATES OF AMERICA
- 13. RELATED MEETINGS
- 14. NEXT PANEL MEETING
- 15. **REFERENCES**

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#### ANNEX III

#### IOC RESOLUTION ON GOOS

#### **Resolution XVII-5**

#### GLOBAL OCEAN OBSERVING SYSTEM (GOOS)

The Intergovernmental Oceanographic Commission,

#### Noting:

- (i) IOC Resolutions XV-4, XVI-8, XVI-10, EC-XXIII.5 and EC-XXV.3 on GOOS, which call for the IOC to develop GOOS and establish the necessary international co-ordination mechanisms, and to initiate jointly with UNEP and WMO coastal pilot monitoring activities,
- (ii) WMO Resolutions 11 (EC-XLI), 9 (Cg-XI) and 21 (Cg-XI) which express WMO support for GOOS development and relevant co-operation with the IOC,
- (iii) UNEP Governing Council Decisions 16/26, 16/27 and 16/41 which express UNEP support for actions which will meet the needs to be addressed by GOOS,
- (iv) the decisions made by UNCED, including the two Conventions and Chapter 17, Section E, of Agenda 21 (Section E, para 17.102), which call for:
  - (a) Member States to support IOC in co-operation with WMO, UNEP, *inter alia*, in the systematic collection and exchange of ocean data needed to apply integrated management approaches and to predict impacts of environmental change;
  - (b) the IOC to develop fully the strategy for providing training, education and technical assistance for developing countries through its Training, Education and Mutual Assistance (TEMA) programme,
- (v) the report of the meeting of the ad hoc panel for the Health of the Ocean Module of GOOS and the need for input from other panels and GOOS modules in order to resolve effectively the issues identified,

Recognizing the limited human and financial resources available for the GOOS planning and development,

Having reviewed the Executive Summary and Recommendations of the First Session of the !OC Committee for GOOS,

Takes note of the Executive Summary;

Decides to take the following action on the recommendations:

# Recommendation GOOS-I.1 Further Development of the Global Ocean Observing System (GOOS) and Co-ordination Mechanisms for Scientific Advice and Inter-Agency Co-operation

(i) Approves the Recommendation;

- (ii) Instructs the Secretary, in close consultation with the Chairmen of IOC and the IOC Committee for GOOS, to pursue and finalize the negotiations leading to the signature of a Memorandum of Understanding on the co-sponsorship of a GOOS technical and scientific advisory mechanism by concerned organization(s) and to facilitate the establishment of this body as quickly as possible;
- (iii) Calls upon ICSU/SCOR to assist the IOC and the co-sponsors in the establishment of scientific design panels for the GOOS modules, as a matter of urgency, ensuring that the best possible use is made of existing mechanisms;
- (iv) Instructs further the Secretary to make as wide a use as possible of ICSPRO to facilitate the formation of GOOS;

#### Recommendation GOOS-L2 The Approach to GOOS and National Commitments

- (i) Approves the Recommendation;
- (ii) Agrees that the document "The Approach to GOOS" (Doc.IOC-XVII/8 Annex 2) as amended by the First session of the IOC Committee for GOOS should be used as a strategy document for GOOS planning and development;
- (iii) Invites WMO and UNEP to co-sponsor, jointly with IOC, the IOC Committee for GOOS;
- (iv) Urges Member States, especially developed countries, to contribute to GOOS through an earmarked part of the IOC Trust Fund to support the costs of the planning and development phase of GOOS;
- (v) Urges Member States and co-sponsoring Organizations, together with the GOOS Support Office, to conduct public and information activities to promote GOOS;

#### Recommendation GOOS-I.3 Global Sea Level Observing System (GLOSS)

- (i) Approves the Recommendation;
- (ii) Instructs the Secretary to arrange, through appropriate means and in consultation with Member States, for the position of a Technical Secretary for GLOSS as part of the GOOS Support Office in order to promote and fully support GLOSS development;

# Recommendation GOOS-I.4 UNEP-IOC-WMO Long-Term Global Monitoring System of Coastal and Near-Shore Phenomena Related to Climate Change

- (i) Approves the Recommendation;
- (ii) Invites UNEP and WMO, as co-sponsoring agencies, to continue their support for the implementation of the pilot activities;
- (iii) Urges Member States to consider, and inform the Secretary on their participation in the pilot activities as well as on their possible support of and contribution to the implementation of the pilot activities;

#### Recommendation GOOS-1.5 GOOS Linkage With Existing Programmes/Activities

- (i) Approves the Recommendation;
- (ii) Agrees that the strengthening and accelerated development of existing ocean observational and data management activities, particularly IGOSS, GLOSS, DBCP, IODE, MARPOLMON, International Musselwatch, CPR and TEMA components of these programmes should be considered as a priority for GOOS development and that adequate staff and financial support should be provided for their implementation;
- (iii) Urges the Chairmen of the concerned scientific/technical subsidiary bodies of the Commission, as well as of its regional subsidiary bodies and of the Committee for TEMA, to work with the IOC Committee for GOOS and GOOS scientific advisory bodies with regard to the design, planning and development of GOOS;

#### Recommendation GOOS-I.6 TEMA In Relation to GOOS

- (i) Approves the Recommendation;
- (ii) Agrees that "Capacity Building" can only result from (a) long-term commitments and partnerships between developing and developed countries, and (b) identification and use of new and external sources of support;
- (iii) Stresses that provision of equipment should keep pace with education and training in developing countries;
- (iv) Decides to establish an earmarked GOOS/TEMA part of the IOC Trust Fund to support the TEMA-related activities within GOOS;
- (v) Urges developing Member States to:
  - (a) identify their needs in terms of human resource development and infrastructure in relation to GOOS;
  - (b) identify their existing training facilities and institutions for participation in the GOOS/TEMA efforts;
- (vi) **Requests** the IOC Committee for GOOS to provide guidance to the GOOS support office on actions required by IOC Member States and componenting agencies;

Accepts the interim report on developing the Health of the Ocean Module, and instructs the Secretary to ensure the timely completion of this report.

Approves the attached Statement (Annex to Resolution XVII-5) to be proposed for adoption by the Intergovernmental Meeting on the World Climate Programme and requests the Secretary to bring this Statement to the attention of the Meeting.

Financial implications (1994-1995): Required

Anticipated 27CS (Doc.IOC-XVII/8, 6.1.1 GOOS)

Recommendation 1 Meetings of 5 Panels (2) \$330K Ad hoc Meetings (4) \$110K Total: \$440K Expected net shortfall: \$290K

\$150K

IOC-JGOFS/CO2-IV/3 Annex III - page 4 **Recommendation** 2 Translation/Publication of the Document and GOOS Brochure \$30K (Doc. IOC-XVII/8, 6.1.2 GLOSS) **Recommendation 3** Preparation and publication of the GLOSS up-dated Handbook \$20K Meeting of GE/GLOSS \$30K Sea level training courses (2) \$40K Position of GLOSS Technical Secretary \$100K Staff travel \$5K \$100K Total: \$195K Expected net shortfall: \$95K (Doc.IOC-XVII/8, 6.1.3 GOOS Coastal) **Recommendation** 4 Meetings of the Task Team on Coral Reefs (2) - \$50K Meetings of the Global Task Team on Mangroves (2) - \$50K Meetings of experts on Sea Level Project in the Indian Ocean (2) - \$50K Meetings of experts on Coastal Circulation project (2) - \$50K Workshop on plankton community structure monitoring (1994) - \$40K Preparation and publication of Methodology manuals - \$30K Consultancy services to advise countries on projects implementation and related training - \$100K Staff travel- \$20K \$100K Total: \$390K Expected net shortfall: \$290K **Recommendation** 5 None **Recommendation** 6 None \$ 350K Grand Total: \$1055K Expected net shortfall: \$705K

#### Annex to Resolution XVII-5

#### Statement for the Intergovernmental Meeting on the World Climate Programme by the Seventeenth Assembly of the Intergovernmental Oceanographic Commission Paris, France, 25 February - 11 March 1993

The Assembly of the Intergovernmental Oceanographic Commission of UNESCO at its seventeenth session, deeply concerned with the need to improve understanding and prediction of the climate change and its impact on economic development, transmits to the Intergovernmental Meeting on the World Climate Programme for its consideration the statement in the conclusion to the present text.

#### Introduction

1. The ocean plays a key role in determining Earth's climate. The Global Atmosphere and the World Ocean are an interactive system. The oceans are both a source and a sink for carbon dioxide and other "greenhouse gases". The ocean also drives the global cycle of evaporation and rainfall. Any possibility of predicting climate changes beyond a few weeks demands that the ocean behaviour be taken into account. Long-term, systematic observations in the World Ocean are needed to reduce the uncertainty which now exists with regard to the ocean's role in climate variability.

2. The Intergovernmental Oceanographic Commission, consisting of 122 Member States, was established in 1960 to promote marine scientific investigations, related ocean services and capacity building with a view to learning more about the nature and resources of the oceans through concerted action of its Members.

3. The recognition by States and Organizations of the UN System of the importance of IOC for international oceanographic co-operation and capacity building has been demonstrated in the reference to IOC as a joint specialized mechanism in the ICSPRO Agreement and as a competent international organization in the UN Convention on the Law of the Sea; and by the acceptance of the IOC in its own right as a co-sponsor of the Second World Climate Conference and at the United Nations Conference on Environment and Development.

4. IOC in its 30 years of activity, has accumulated a capital of experience, both at global and regional levels, as the only UN organization fully devoted to marine research, ocean services and related training, education and mutual assistance. The Commission established formal contacts with many governmental and non-governmental international organizations including UN, FAO, WMO, UNEP, (MO, IAEA, IHO, ICES, CPPS, ICSEM, ICSU and SCOR.

5. Since the establishment of the World Climate Programme in 1979 the IOC actively supported and participated in the planning and implementing the World Climate Research Programme, presently sponsored jointly by IOC, WMO and ICSU in co-operation with SCOR, particularly TOGA and WOCE.

6. The Commission has promoted the development of the Integrated Global Ocean Services System in co-operation with WMO; the Global Sea Level Observing System; and the International Oceanographic Data and Information Exchange (IODE) system that laid down a basic international infrastructure for the development of the Global Ocean Observing System.

#### Intergovernmental Decisions

7. The Second World Climate Conference (29 October - 7 November 1990) adopted conclusions and recommendations to create a Global Climate Observing System (GCOS). The Conference statement noted the importance of developing a Global Ocean Observing System of physical, chemical and biological measurements.

8. The United Nations Conference on the Environment and Development (June 1992) in Agenda 21, Chapter 17, Section E called for States to support the role of IOC, in co-operation with WMO, UNEP and other international organizations, in the collection, analysis and distribution of data and information from the oceans and all seas, including as appropriate through the proposed Global Ocean Observing System (GOOS), giving special attention to the need for IOC to develop fully the strategy for providing training and technical assistance for developing countries through its Training, Education and Mutual Assistance (TEMA) programme. The UNCED also emphasized that the developed countries should provide the financing for the development and the implementation of the GOOS system. Two Conventions signed by 154 countries, namely the UN Framework Convention on Climate Change and the UN Convention on Biological Diversity, also calls for systematic observation of the components of the climate and bio-diversity systems.

9. The agreement on the joint sponsorship of the World Climate Research Programme by WMO, IOC and ICSU was signed in 1992.

10. The agreement on the co-operation among WMO, IOC of UNESCO, ICSU and UNEP in organizing a Global Climate Observing System was signed in 1991 and 1992. By this agreement the cooperating organizations agreed that GCOS will be based on the co-ordinating of existing or planned operational and research programmes for observing the global climate system and that it will be based inter alia on the establishment of a Global Ocean Observing System. It is further agreed that GOOS and GCOS share a common module: the climate module for GOOS is the same as the ocean component of GCOS.

#### Action Taken

11. The Intergovernmental Oceanographic Commission, by decisions of its Fifteenth and Sixteenth Assemblies and Twenty Fifth session of its Executive Council, decided to develop a Global Ocean Observing System (GOOS) and established the IOC Committee for GOOS as an intergovernmental forum for promoting GOOS, and the GOOS Support Office within the IOC Secretariat to co-ordinate GOOS development.

12. WMO, by decisions of the Eleventh World Meteorological Congress and the 43rd and 44th sessions of the Executive Council, expressed WMO support for GOOS development and relevant co-operation with IOC.

13. UNEP, by decisions of its Sixteenth Governing Council, expressed UNEP support for actions which will meet the needs to be addressed by GOOS.

14. IOC, UNEP, and WMO agreed to cooperate in developing a Long-Term Global Monitoring System of Coastal and Near-Shore Phenomena Related to Climate Change as a contribution to GOOS, particularly its Coastal module

15. The IOC Assembly, at its seventeenth session, adopted a strategy paper for GOOS planning and implementation, and invited WMO, UNEP and ICSU to co-operate in these efforts. The Assembly also emphasized that the existing ocean observational and data management activities, particularly IGOSS, GLOSS, DBCP, IODE, MARPOLMON, Musselwatch and CPR, and TEMA components of these programmes, should be considered as a priority for GOOS development and that TEMA components of these programmes be given particular consideration. The Assembly decided to earmark a part of the IOC Trust Fund for this development.

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#### Conclusion

16. Therefore, the Member States of the Intergovernmental Oceanographic Commission requests the Intergovernmental Meeting on WCP to adopt the following recommendation:

"Recognizing the key role of the oceans in the Earth's Climate System and the urgent need to develop GOOS for long-term, systematic collection, analysis and distribution of ocean data, the Meeting assigns a high priority to the planning, development and implementation of the Global Ocean Observing System as an important contribution to the World Climate Programme. The Meeting encourages the IOC to continue the development of this system in co-operation with WMO, UNEP, ICSU and other concerned international organizations on the basis of existing and planned international and national ocean observing systems. The Meeting urges countries to support this system through their national facilities and services. The Meeting also urges countries to increase their support for the training, education, mutual assistance and capacity building programme of IOC as well as the related Voluntary Co-operation Programme, in order to enable all countries to participate in GOOS and to interpret and apply the resulting data and information and encourages the concept of partnerships between developing and developed countries."

### ANNEX VI

## OUTLINE AND ASSIGNMENTS FOR AN IOC-JGOFS OCEAN CO<sub>2</sub> PANEL PAPER ON SOURCES AND SINKS OF OCEANIC CO<sub>2</sub>

Alexiou	FOREW	YORD
Merlivat	I.	INTRODUCTION (Refer to background papers)
Merlivat (all parts)	II.	GOALS OF OCEAN CARBON CYCLE RESEARCH
(an parts)	А.	Understanding the processes relevant to global carbon cycle
	В.	Assessment of ocean uptake of anthropogenic CO <sub>2</sub> by:
		<ul> <li>determining fluxes</li> <li>determining oceanic changes of C<sub>r</sub></li> <li>developing carbon cycle models and methods to validate them</li> </ul>
	C.	Estimate possible feedbacks of future climate change on oceanic and atmospheric $CO_2$
	D.	Understanding of natural CO <sub>2</sub> variations
Watson (Main Author)	III.	AIR-SEA GAS EXCHANGE, $F = kg \Delta p CO_2$
Siegenthaler	regions	Observed fluxes = sum of natural and anthropogenic fluxes; source/sink do not indicate where anthropogenic $CO_2$ is mainly taken up! Cannot measure flux of excess $CO_2$ (directly).
Millero	Α.	Analytical methods for $CO_2$ system satisfactory (mention temperature correction for $pCO_2$ )
Millero	В.	Thermodynamic constants - consistent
Millero	C.	$pCO_2$ data: good geographical global coverage for a single "snapshot" in next 5 years but not yet different time snapshots
	Problem	ns (open questions):
Watson	Α.	What spatial and temporal $\Delta pCO2$ coverage needed?
		<ul> <li>depends on goal</li> <li>NB: Global flux cannot be determined as ∫ Kg·pCO<sub>2</sub>·dA (error too large)</li> </ul>

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Kg discrepancy field measurements - <sup>14</sup>C method (factor 1.6  $\pm$  0.3) Merlivat В. .... what kg values to be used? .... satellite obs: ocean color, sea state Pearman IV. CRITICAL REVIEW OF TANS ET AL. APPROACH (all parts) (see Siegenthaler plus Sarmiento paper) Α. Temperature skin effect Riverine carbon input B. C. Meridional carbon transport by CO in atmosphere natural interhemispheric CO2 difference: present evidence • D. Oceanic transport: Northern Hemisphere to Southern? Cross-correlation of seasonality of concentration and atmospheric E. transport? Atmospheric Transport Models • MEASURING THE CHANGE OF OCEAN C INVENTORY v. Problems: Variability of  $C_T$  (+DOC) Brewer Brewer Influence of biological and solubility pumps: preformed C<sub>D</sub> Total Α. Alkalinity, nutrients Constancy of Redfield rations (Recent paper in Nature, ٠ Sambrotto/Fanning, JGR 1992) δ<sup>13</sup>C budget (Quay *et al.*): Siegenthaler B. High-precision  $\delta^{13}$ C data needed (ocean) • Models of terrestrial biota needed . **CARBON CYCLE MODELS** VI. Development of dynamic ocean models, including C cycle, sensitivity Siegenthaler Α. studies Observations of <sup>14</sup>C and CFCs for model validation Siegenthaler Β. Siegenthaler C. Consistent intercomparison of ocean models needed Siegenthaler D. Modelling of marine biology in relation to CO<sub>2</sub> chemistry: in early stage

#### ANNEX V

#### DRAFT GENERIC TERMS OF REFERENCE FOR GOOS MODULE PANELS

[For each module: an introductory paragraph giving the present scope of the module, time-limited to permit completion of the tasks before the next IOC Committee for GO/DS meeting, in approximately April 1994. Each GOOS Module Panel will report to the J-GOOS when it is formed and should present an interim report to the first meeting of J-GOOS.]

#### TASKS

- 1. Specify the "deliverables" anticipated from the module (including from applicable existing bodies) both on the short-term (1-3 years) and long-term (10 years and longer). [Note: "Deliverables" are the data and/or interpretive products that are needed by end-users and that will be provided by the module or existing body.]
- 2. Specify how these deliverables could be provided to the users, in the sense of who would do it and what the distribution system or mechanism will be.
- 3. Specify the conceptual design for an observing system that will provide those deliverables, and elaborate on the scientific basis for the specification, indicating where the design is strong and where it is weak, and what additional scientific basis is needed.
- 4. Develop a plan for the technological needs (including existing technologies and future needed technology) in relation to this basis.
- 5. Develop TEMA and capacity-building plans to meet the conceptual design specification and technological development plan and to provide the deliverables.
- δ. Suggest methods of proceeding further with this module and any membership changes needed.

In addressing the tasks above, in so far as possible in the time allowed:

- (a) take into account, and/or make use of, existing systems and on-going programmes as far as possible, and provide cross-references to those systems or programmes;
- (b) relate the specifications and development plans to perceived or specified user needs; and
- (c) define the sampling requirements of the variables in the specifications and the related development plans, and those needed for the existing scientific and technical bodies.

**Priorities:** In the limited time available, address all the tasks to some extent, with primary emphasis on Tasks 1 and 3.

#### ANNEX VI

## OUTLINE AND ASSIGNMENTS FOR AN IOC-JGOFS OCEAN CO<sub>2</sub> PANEL PAPER ON SOURCES AND SINKS OF OCEANIC CO<sub>2</sub>

Alexiou	FORE	WORD
Merlivat	I.	INTRODUCTION (Refer to background papers)
Merlivat	II.	GOALS OF OCEAN CARBON CYCLE RESEARCH
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	В.	Assessment of ocean uptake of anthropogenic $CO_2$ by:
		<ul> <li>determining fluxes</li> <li>determining oceanic changes of C<sub>T</sub></li> <li>developing carbon cycle models and methods to validate them</li> </ul>
	C.	Estimate possible feedbacks of future climate change on oceanic and atmospheric $CO_2$
	D.	Understanding of natural CO <sub>2</sub> variations
Watson (Main Author)	m.	AIR-SEA GAS EXCHANGE, $F = kg\Delta pCO_2$
Siegenthaler	regions	Observed fluxes = sum of natural and anthropogenic fluxes; source/sink do not indicate where anthropogenic $CO_2$ is mainly taken up! Cannot measure flux of excess $CO_2$ (directly).
Millero	А.	Analytical methods for $CO_2$ system satisfactory (mention temperature correction for $pCO_2$ )
Millero	B.	Thermodynamic constants - consistent
Millero	C.	$pCO_2$ data: good geographical global coverage for a single "snapshot" in next 5 years but not yet different time snapshots
	Probler	ns (open questions):
Watson	Α.	What spatial and temporal $\Delta pCO2$ coverage needed?
		<ul> <li>depends on goal</li> <li>NB: Global flux cannot be determined as ∫ Kg·pCO<sub>2</sub>·dA (error too large)</li> </ul>

.

Merlivat	B.	Kg discrepancy field measurements - $^{14}$ C method (factor 1.6 ± 0.3) what kg values to be used? satellite obs: ocean color, sea state
Pearman (all parts)	IV.	CRITICAL REVIEW OF TANS ET AL. APPROACH (see Siegenthaler plus Sarmiento paper)
	Α.	Temperature skin effect
	В.	Riverine carbon input
	C.	Meridional carbon transport by CO in atmosphere
		• natural interhemispheric CO <sub>2</sub> difference: present evidence
	D.	Oceanic transport: Northern Hemisphere to Southern?
	E.	Cross-correlation of seasonality of concentration and atmospheric transport?
		• Atmospheric Transport Models
	v.	MEASURING THE CHANGE OF OCEAN C INVENTORY
Brewer	Proble	ems: Variability of C <sub>r</sub> (+DCC)
Brewer Brewer	Proble A.	rms: Variability of C <sub>T</sub> (+DOC) Influence of biological and solubility pumps: preformed C <sub>T</sub> , Total Alkalinity, nutrients
		Influence of biological and solubility pumps: preformed $C_{p}$ Total
		<ul> <li>Influence of biological and solubility pumps: preformed C<sub>T</sub>, Total Alkalinity, nutrients</li> <li>Constancy of Redfield rations (Recent paper in Nature,</li> </ul>
Brewer	Α.	<ul> <li>Influence of biological and solubility pumps: preformed C<sub>T</sub>, Total Alkalinity, nutrients</li> <li>Constancy of Redfield rations (Recent paper in Nature, Sambrotto/Fanning, JGR 1992)</li> </ul>
Brewer	Α.	<ul> <li>Influence of biological and solubility pumps: preformed C<sub>T</sub>, Total Alkalinity, nutrients</li> <li>Constancy of Redfield rations (Recent paper in Nature, Sambrotto/Fanning, JGR 1992)</li> <li>δ<sup>13</sup>C budget (Quay et al.):</li> <li>High-precision δ<sup>13</sup>C data needed (ocean)</li> </ul>
Brewer	A. B.	<ul> <li>Influence of biological and solubility pumps: preformed C<sub>T</sub>, Total Alkalinity, nutrients</li> <li>Constancy of Redfield rations (Recent paper in Nature, Sambrotto/Fanning, JGR 1992)</li> <li>δ<sup>13</sup>C budget (Quay et al.):</li> <li>High-precision δ<sup>13</sup>C data needed (ocean)</li> <li>Models of terrestrial biota needed</li> </ul>
Brewer Siegenthaler	А. В. <b>VI.</b>	<ul> <li>Influence of biological and solubility pumps: preformed C<sub>T</sub>, Total Alkalinity, nutrients</li> <li>Constancy of Redfield rations (Recent paper in Nature, Sambrotto/Fanning, JGR 1992)</li> <li>δ<sup>13</sup>C budget (Quay et al.):</li> <li>High-precision δ<sup>13</sup>C data needed (ocean)</li> <li>Models of terrestrial biota needed</li> </ul> CARBON CYCLE MODELS Development of dynamic ocean models, including C cycle, sensitivity
Brewer Siegenthaler Siegenthaler	А. В. <b>VI.</b> А.	<ul> <li>Influence of biological and solubility pumps: preformed C<sub>T</sub>, Total Alkalinity, nutrients</li> <li>Constancy of Redfield rations (Recent paper in Nature, Sambrotto/Fanning, JGR 1992)</li> <li>δ<sup>13</sup>C budget (Quay et al.):</li> <li>High-precision δ<sup>13</sup>C data needed (ocean)</li> <li>Models of terrestrial biota needed</li> </ul> CARBON CYCLE MODELS Development of dynamic ocean models, including C cycle, sensitivity studies

## VII. NATURAL VARIABILITY, FEEDBACKS, BIOLOGY

Siegenthaler	Α.	Changes of ocean circulation
Siegenthaler	Ъ.	ENSO effects on $CO_2$ in ocean and atmosphere ( $\delta^{13}C$ in atmosphere needed; consider land biota)
Siegenthaler	C.	Rate limitation of plankton growth by CO <sub>2</sub> (Riebesell et al., Nature, 1992)
Siegenthaler	D.	Redfield ratios; see above
Siegenthaler	E.	Micronutrients (Fe)
Brewer	F.	Effect of temperature on production and remineralization
Siegenthaler	G.	Interaction with carbonate sediments, biological pump does not sequester excess $CO_2$ (long time scales)

**REFERENCES** : JGR style

#### ANNEX VII

### DESCRIPTION AND FIELD PERFORMANCE OF THE MBARI BUOY-MOUNTED pCO, MEASUREMENT SYSTEM'

#### 1. INTRODUCTION

The cost of conducting shipboard measurements and the need to find ways of monitoring chemical and biological variables on a continuous basis have encouraged the development of oceangoing sensors that can be mounted on buoys. Early in 1992, the Monterey Bay Aquarium Research Institute (MBARI) launched an investigation of the feasibility of measuring the sea-surface partial pressure of  $CO_2$  (pCO<sub>2</sub>) on one of the Institute's moorings. Rather than pursuing a new measurement technology, we decided to adapt to our use a commercially available, non-dispersive, infrared analyzer built by LI-COR, Inc. The apparatus was designed to measure the difference between sea-surface and atmospheric pCO<sub>2</sub> ( $\Delta pCO_2$ ), using ambient air as the reference gas. This approach would ensure the highest data quality relevant to air-sea exchange of CO<sub>2</sub> and also simplified the first version of this instrumentation.

#### 2. OASIS MOORING

The OASIS (Ocean Acquisition System of Interdisciplinary Science) moorings, developed under the leadership of MBARI scientist Francisco Chavez, provide ideal platforms for testing new developmental efforts (see Figure 1). Instruments mounted on the moorings collect a complete suite of physical and meteorological data every 10 minutes, and these data are relayed via radio to our laboratory every other hour. Data acquisition parameters can also be controlled from shore. The  $pCO_2$  system was mounted on the mooring that is located at the mouth of Monterey Bay on the central California coast, approximately 18 kilometers offshore in about 1,000 meters of water.



Figure 1. OASIS Mooring

Adapted from material submitted to the Marine Technology Society Journal for the fall 1993 meeting.

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#### 3. INFRARED ANALYZER

We chose a model LI-6252  $CO_2$  analyzer for this project since it has modest power consumption, a short "warm up" time and good stability. Additional factors that eased integration of this instrument into the overall package are built in data communication (RS232) and the ability to operate from a 12VDC solar panel power supply.

The analyzer is powered up hourly for 3 minutes. During a sample cycle a small diaphragm pump draws air into the instrument from an inlet located at a height of about 1.5 m. Complete flushing occurs within the first minute of each cycle. Gas from the air-sea equilibrator is continuously forced in and out of the analyzer by the effect of buoy and wave motion on the head space of the equilibrator. To eliminate pressure changes in the sample cell, the gas stream has been equipped with a Tedlar bladder. Long term pressure changes are accommodated through a small vent.

Every four hours there is a cell to cell comparison cycle and air is pumped through both cells of the instrument. All valves are latching and require power for about 10 milliseconds to switch between modes. During the comparison cycle the equilibrator continues to communicate with the remainder of the system and only about 10 ml of air are introduced into the equilibrator when the system is switched back into sampling mode. One hour of equilibration time elapses before the equilibrator gases are measured again. There has not been any long-term drift in the cell to cell offset and while early results indicated average difference between comparisons of about 2.5 ppmv, this value has decreased to about 1 ppmv in recent weeks.

#### 4. EQUILIBRATOR

The design of the equilibrator that supplies the analyzer with an atmosphere that is in equilibrium with surface seawater had to meet at least the following criteria:

- · No significant power consumption
- · Not subject to bio-fouling
- · Time constant less than one hour
- · Robust and compact.

We constructed an all-copper equilibrator 5 centimeters in diameter that used wave motion to facilitate equilibration and circulation of the equilibrated gases (see Figure 2). Tests had shown that copper resisted all bio-fouling at the mooring site, but also that the interaction between copper and seawater could alter the carbonate equilibrium. If the seawater residence time min the equilibrator could be kept short, the effect on the carbonate equilibrium could be ignored.

In the fall of 1992 we were receiving data reliably; intercalibrations, however, showed an offset between shipboard measurements and those made on the buoy. Buoy and wave motion did not appear to provide sufficient flushing of the equilibrator, and the offset was generated by interaction between the copper and the seawater. We designed an equilibrator with improved flushing characteristics, but winter weather conditions kept up from installing it until the latter part of January 1993.

The new equilibrator uses a combination of wave motion and an air pump to achieve flushing and equilibration. The air pump is pulsed on several times per hour and does not increase system power consumption significantly. No significant offsets have been observed since this modification.



#### 5. INTERCALIBRATION

Before deployment the  $CO_2$  analyzer was calibrated with a NIST  $CO_3$  ar gas mixture. This initial calibration has been used for all subsequent calculations. Intercalibration data (see Figure 3) was obtained with a similar  $CO_2$  analyzer and a shower head equilibrator connected to the seawater systems of the R/V Point Lobos and the R/V Point Sur. Due to the heterogeneity of the data, only those shipboard measurements that were obtained within a 0.5 km radius of the buoy and within about 15 minutes of a buoy sample could be used to verify the buoy data. No significant offsets have been found and we plan to collect intercalibration data every two to four weeks.



Figure 3. Intercalibration Data

#### 5. DATA

The raw data that is received from the mooring is processed daily and examined for trends and irregularities. Most of this initial data set indicates sea-surface  $pCO_2$  to be undersaturated relative to the atmosphere. Towards the end of March when some of the first upwelling events of the season occurred, a rapid rise of sea-surface  $pCO_2$  was observed (see Figure 4).



Figure 4. OASIS pCO<sub>2</sub> Data

Throughout this record there is considerable short-term variability that can be linked to one or more of the following causes:

- · Variation in atmospheric  $pCO_2$
- · Spatial variability of sea-surface pCO<sub>2</sub>
- · Tidal excursions
- · Sea-surface temperature fluctuations

Air pCO<sub>2</sub> measurements made in the early part of 1993 indicate that atmospheric values were frequently elevated by as much as 40 ppmv during periods of offshore winds. Daily wind reversals were common throughout February and March and appear to be responsible for the majority of the short-term variability in the  $\Delta pCO_2$  record.

A survey conducted on 23-24 March 1993 demonstrates the length scale of variability of sea-surface  $pCO_2$  during a moderate upwelling event. Other data sets also indicate that  $pCO_2$  gradients of 10 ppmv per kilometer are not uncommon in the vicinity of this mooring. These gradients combined with mooring and tidal excursions is probably responsible for additional variability on the one day time scale.

On relatively calm days surface temperatures can increase by 0.5 to  $1^{\circ}$ C. A temperature rise of this magnitude should elevate pCO<sub>2</sub> noticeably, but in the present data record this effect has been overshadowed by the atmospheric variability.

#### ANNEX VIII

#### CARDEEP Carbon Budget and Deep Convection in the Greenland, Iceland, Norwegian Seas (GIN-Seas)

By Truls Johannessen University of Bergen, Norway

#### 1. INTRODUCTION

CARDEEP is a Norwegian programme co-ordinated by the marine science community in Bergen, Center for Environment and Resource Studies, aimed at understanding the role deep-water forming regions of the GIN-Seas plays in the global oceanic  $CO_2$ -uptake. The locations of the study areas and transects are shown in Figure 1.

CARDEEP is attached to the EC's MAST 2 (Marine Science and Technology) Programme, under the subprogramme (hele navnet) ESOP, and we will also seek ties to JGOFS. The programme started in 1993, with main activities in the following 3 years. Funding is provided by the Norwegian Science Foundation (NAVF), EC-MAST II, and The Nordic Council of Ministers (Nordisk Ministerråd).

Below we describe some of the background and activities of CARDEEP.

#### 2. SCIENTIFIC RATIONALE

The atmospheric  $CO_2$ -content increases yearly by about 1.5ppm, which may lead to significant global warming in the next century. It is generally believed that the ocean absorbs 30-50% of the anthropogenic emissions of carbon dioxide. It is, however, far from clear where this uptake takes place and at what rates it happens, thus the large uncertainty. It is also not known how it will be affected by changes in climate and ocean circulation. Without a better knowledge of the oceanic uptake, we are faced with major deficiencies in our abilities to predict future climate change.

Since communication between the atmosphere and the deep sea occurs through deep water formation at high latitudes, these areas are particularly significant as transit-ways for the transfer of atmospheric CO<sub>2</sub> which is dissolved in the surface mixed layer and transported away from the atmosphere into the deep water realm. One potential important site where this process takes place is the Greenland Sea where convection processes form deep waters which function as a transport path for CO<sub>2</sub> drawn into the surface ocean from the atmosphere through extensive dissolution of CO<sub>2</sub> in the cold waters, and by biological pumping. Presently there is no firm knowledge base for assessing the importance of this region for the oceanic CO<sub>2</sub>-uptake. Only ccattered data exist which indicate at least potential strong seasonal sinks (Peng *et al.*, 1987; Takahashi, 1989; plus unpublished data).

Such an assessment can only be made through detailed studies of both the processes that govern  $CO_2$ -uptake in this area and the general  $CO_2$ -budget of the water masses. These must be studies done on a seasonal basis, covering both the season of winter cooling and convection, the spring bloom with enhanced biological activity and the summer/fall period of biological remineralization. We plan studies which are aimed at understanding the carbon budget in the

Greenland Sea and how the  $CO_2$  uptake and transfer interacts with wintertime cooling and convection as well as biological production.

#### 3. SCIENTIFIC OBJECTIVES

- (i) How much and at what rate can the Greenland Sea absorb carbon dioxide?
- (ii) What significance does the carbon budget in the Greenland Sea have for the global  $CO_2$  balance between the sea and the atmosphere?
- (iii) What processes (physical, biological, geochemical) are the most important for CO<sub>2</sub> uptake in the GIN-Seas?
- (iv) How will future changes in climate and ocean circulation affect CO<sub>2</sub>-uptake.

We will include both observational studies of  $CO_2$ -uptake and transport, and numerical modelling of the carbon cycle in the GIN-Seas. The field work includes linked chemical, physical, biological oceanographic studies aimed at understanding wintertime convection, the GIN-Seas carbon budget and biological carbon fixation and sedimentation.

#### 4. IMPLEMENTATION AND LOGISTICS

The main experiment, which will be interfaced with the activities of the French, German, Danish groups, will take place in 1994 and 1995. A pilot cruise to study convection and to sample water in the Greenland Sea for carbon chemistry work on-shore was conducted in February 1993. This provided the first data set of its kind of winter conditions. Four cruises per year are planned each year, covering:

- · Winter convection and cooling
- · Spring bloom
- · Summer conditions
- · Fall conditions

One aim of the 1994 and 1995 cruise planning was to combine ship-schedules so as to cover the critical seasons for as long as possible. Hence we will ensure a continuous measuring programme covering both the convective season and the main spring bloom with its high biological carbon fixation.

A smaller measurement programme is planned in connection with late summer cruises to the Greenland Sea and in areas of the GIN-Seas outside of the Greenland Sea. This will be done both as routine sections on transits in-out of the main experiments in the Greenland Seas, and on specific summer cruises planned within the Greenland Sea Programme.

#### 5. DATA COLLECTION PLAN

#### 5.1 PHYSICAL OCEANOGRAPHY

MeasurementPeriodResponsibleADCP1 month winterNERSCSEASOAR1 month winterNERSCCTD (500mi)All cruises+MNERSC/HI/GFICurrent meters1994-GFI

#### 5.2 CHEMICAL OCEANOGRAPHY

Measurement	Period	Responsible
$pCQ_2$ atm	4x yearly	SMR,UiB
$pCQ_2$ sea water (500ml)	4x yearly	SiMR, UiB
Total carbonate (Tc)(100ml)	4x yearly*	SMR,UiB/LRD
Alkalinity (250ml)	4x yearly	SMR,UiB
рН	4x yearly	SMR, UiB
Ca, Cd, Fe (250ml?)	1x yearly	SMR,UiB/UCSC†
Nutrient (P,N,Si,NO <sub>2</sub> , NH <sub>4</sub> +)(100ml)	4x yearly	HI/SMR,UiB
<sup>14</sup> C (500ml)	4x yearly*	LRD
δ <sup>13</sup> C (100ml)	4x yearly*	SMR,UiB/LRD
O <sub>2</sub> (300ml)	4x yearly	HI/SMR,UiB

\* = Measurements planned to be included on station M, 66°N and 2°E. † = Marine Sciences, Univ. of California Sta. Cruz (Dr. Ravelo)

#### BIOLOGICAL OCEANOGRAPHY 5.3

(ST = Sediment trap material)

#### **Measurement**

#### Period

## **Responsible**

•

Dissolved Organic Carbon (DOC) (50ml)	Extended station, spring	Biot.,NTH
Total organic carbon (TOC) (DOC)	Extended station, spring	Biot.,NTH
Particulate organic Carbon (POC)	1x/day spring-summer+ST	HI
Particulate organic nitrogen (PON)	1x/day spring-summer+ST	HI
Particulate organic silica	1x/day spring-summer+ST	HI
C/N-ratio	1x/day spring-summer+ST	HI/Geol.UiB
Tot.part.matter	1x/day spring-summer+ST	HI
Zooplankton biomass	1x/day spring-summer+ST	HI
Foraminifer, coccoliths	Not decided + ST	Geol., UIB
Plankton assemblages	Not decided + ST	TBS,UNIT
δ <sup>13</sup> C (org.)	Not decided + ST	Geol. UiB
8 <sup>15</sup> N (org.)	Not decided + ST	Geol. UiB
Chlorophyll-a	All st. spring and summer	HI/TBS,UNIT
Fluorescence	All st. spring and summer	HI/TBS,UNIT
Pigments	1x/day spring-summer+ST	HI
Photobiology-bio-optical rig	1x/day spring-summer	TBS,UNIT
New production	• • •	HI/TBS,UNIT
New nutrients		HI/TBS,UNIT
Production of bacteria		Biot./NTH
Rate of photosynthesis		HI
Depth of the photic zone	All st. spring-summer	HI
Remote sensing of ocean productivity	• •	
using SeaWiFS Satellite	from mid-1994 ?	NERSC/TBS,UNIT
-		

#### 5.4 TRACER

There is co-operation between HI (Blindheim) and groups in USA (LDEO and Brookhaven) on radiometric tracers in the GIN-Seas. CARDEEP need for such data will be covered through this co-operation:

- · Tritium
- · Helium-isotopes
- · Krypton
- · CFC's: F-11, F-12, F-113

#### 6. DESCRIPTION OF PLANNED ACTIVITY ON WEATHER STATION M

The weather station M has been operating since the early 50s. New activity has been planned in order to observe changes throughout the year with respect to carbon cycling. New equipment for the weather ship *Polar Front* is needed to start this activity. The aim is to achieve detailed times series throughout the year that cover the most important parameters related to studies of the carbon cycle.



Figure 1. CARDEEP study areas and transects

#### ANNEX IX

#### NETHERLANDS JGOFS ACTIVITIES AND CO, STUDIES DURING 1992-1993

From the 1987 initiation of JGOFS the Netherlands has contributed to the JGOFS core project of SCOR and IGBP. Results of the 1989-1990 Tyro cruises in the Northeast Atlantic Ocean have been published from 1990 onwards with more manuscripts and Ph.D. theses being produced. The corresponding databases are available both on disk and in a printed report and have been exchanged with JGOFS data centers of other countries (e.g., UK-BODC, US-JGOFS at Woods Hole).

#### 1. JGOFS SOUTHERN OCEAN 1992

The Antarctic Ocean JGOFS programme started with cruises of *RV Polarstern* (Germany) near the 6°W meridian, and *Discovery* (UK) and *James Clarke Ross* (UK) in the Bellingshausen Sea, to be followed by French expeditions aboard *RV Marion Dufresne* from 1993 onwards in the Indian Ocean sector of the Antarctic Ocean. Upon several years planning and preparation *RV Polarstern* left the port of Punta Arenas (Chile) at 29 September 1992 with a party of 51 scientists from six European countries as well as 44 officers and crew. From The Netherlands fifteen scientists participated and provided some pivotal investigations and activities.

The overall objective was to quantify the spring plankton bloom also with respect to the budget of carbon dioxide, with special attention to productivity along the receding ice-edge and in frontal systems. The Antarctic continent being ice-covered, it is this marine plankton photosynthesis which supports the whole Antarctic ecosystem. Most of what is known thus far about the biology and chemistry of the Antarctic Ocean relies on observations in nearshore waters, i.e., around the Antarctic Peninsula and in the Weddell and Ross Seas. However, these relatively minor regions likely are not representative for the large, eastward flowing, Antarctic Circumpolar Current, abounded northwards by the Subantarctic Front. Within the Antarctic Circumpolar Current there is a jet-stream, the Polar Front, where the eastward transport is faster, and somehow the plankton more abundant. The openwater is bounded at the south by the ice edge.

The focus of the two-month expedition was six weeks of repeated north-south transects of 600 nautical miles each at the 6°W meridian. In this period, it was spring in the Antarctic, the sea-ice was retreating. Satellite observations showed a lacey patterned ice-edge with eddy structures, their shapes apparently driven by the underlying sharp front between the ACC and the Weddell Sea gyre. The research programme consisted of the 20 recommended JGOFS core topics, along with 5 additional Southern Ocean JGOFS topics (ice- cover, -physics, -biology, silica cycle, iron/plankton interactions) as well as several other topics. Within this context NIOZ physicists studied the light and mixing regimes and also operated all CTD/Rocette-sampling, providing seawater for all other investigators. The CO<sub>2</sub> system in seawater and marine air was assessed by another NIOZ team, also studying the sea-surface skin temperature by infrared sensor for properly calculating air/sea fluxes of CO<sub>2</sub>. Dissolved oxygen and nutrients were measured by NIOZ staff both for hydrographic studies as well as supporting several biological experiments. Two NIOZ biologists took responsibility for assessment of mesozooplankton stocks, egg production and grazing. Finally a larger team studied both the abundance of various trace metals in these hitherto uncharted waters as well as the effect of one metal, iron, on the productivity of the ecosystem. Within the Polar Front, preliminary results from addition of Fe show significant enhancement of the rates of cell division judging from chlorophyll synthesis and nitrate assimilation.

All data gathered by 51 scientists have been assembled into one database organized by Joop Rommets (NIOZ) and given out to the partcipating institutes at the end of the cruise. Through 1993, more data has been added to the database held at NIOZ. This dataset served for supporting several workshops where considerable progress was made towards synthesizing the vast variety of information into a coherent description of the processes occuring in the ecosystem during spring evolution. Early 1994 the then available data, with methods descriptions, will be assembled in a final database (on disk) and a hard copy report will be made available to the international community (i.e., UK-BODC, US JGOFS etc.).

Briefly, the major finding was that Marginal Ice Zone blooms as described for neritic waters (MIZ of Weddell Sea, Ross Sea) does not occur in the the truly open ocean Antarctic Circumpolar Current. Curiously enough the British programme in the Bellingshausen Sea also witnessed the absence of spring MIZ blooms. Reasons are multifold. In our region (6°W meridian) firstly the sea-ice was found to collapse and retreat in spring, but this does not necessarily imply *in situ* melting. Freshening of MIZ surface waters was not observed. Possibly the ice flows southwestward along with the Weddell gyre and actual melting takes place elsewhere. Also the very strong winds maintained a deep mixed layer (80-100m), as opposed to the stratified regime deemed necessary to assure adequate light conditions for photosynthesis. Any *in situ* melting of the 1-2 m thick sea-ice and snow would be obscured by dilution into the 80-100m mixed layer. Seeding of the seawater by the in-ice community of algae as well as the higher amounts of Fe in the ice (30-60 nM as compared to 1-3 nM in seawater) would also be diluted 50-100 fold and thus hardly stimulate blooms.

Within the ACC proper, the biological activity was always very low, except in the Polar Front where a spring bloom evolved during the two-month period. The physical forcing of such a bloom is currently being resolved from the very complex and dynamic eddy structures and interleaving surface waters in the Polar Front (~48-50°S) zone. Otherwise the ongoing spring season and increasing chlorophyll were accompanied by a strong decrease of surface water  $pCO_2$  to lowest values of about 300  $\mu$ atm coinciding nicely with the blooms. This, in combination with the general downward transport of water at the Polar Front (formation of Antarctic Intermediate Water, AAIW), hints at the Polar Front serving as a net sink for atmospheric CO<sub>2</sub>. However, this needs confirmation by additional data at other latitudes and/or seasons, currently being pursued in a three-year CO<sub>2</sub> programme (1993-1996) set up between AWI (operator of *RV Polarstern*) and NIOZ.

The national Global Change programme has awarded a three-year postdoctoral fellowship (1994-1996) towards modelling the Antarctic ecosystem where the above dataset will serve for validation. Objective is an assessment of the evolution of the spring bloom, in analogy to the model (Lancelot *et al.*, 1993, *Polar.Biol.*, August issue) for the EPOS 1988 Weddell/Scotia Seas marginal ice zone.

#### 2. JGOFS INDIAN OCEAN 1992-1993

For almost one year the RV Tyro worked a suite of cruises constituting the Netherlands Indian Ocean Programme (NIOP). During the outbound cruise in spring 1992 from Spain to Egypt a meeting was held of the SCOR-JGOFS Indian Ocean working group, with Dr Martien A. Baars representing The Netherlands. Two NIOP legs in the Somali basin were adopted by the Indian Ocean working group as JGOFS cruises. Both cruises were focusing on 'Monsoons and Pelagic Systems' with Dr Baars and Dr Peter H. Schalk jointly serving as chief-scientists.

The first NIOP-JGOFS leg from Mombassa to Djibouti, 11 July - 11 August 1992 was run by 22 scientists of which 5 were forcign colleagues from Belgium, Germany and the USA collaborating with the staff from 3 Dutch institutes. The team surely hit the peak of the Southwest Monsoon upwelling season, with very strong winds often exceeding Bft. 8 and averaging at about Bft. 6. Among the activities were JGOFS core measurements of total CO2, POC, DOC, phytoplankton, primary production, bacterioplankton, microzooplankton, zooplankton, grazing rates, sedimentation. Additional work was done on nitrous oxide, methane, and micronekton. Blooms with high primary production were observed in upwelling waters of 20-21°C, surrounded by waters with somewhat lower temperatures (18-19°C) where the copepod *Calanoides carinatus* as well as high nutrient values also confirmed the existence of upwelling.

The second leg from Victoria to Djibouti, 11 January - 6 February 1993 was run by 21 scientists (6 foreign colleagues from Belgium, Canada, Germany and USA) during the Northeast Monsoon in the same Somali basin. The JGOFS activities were the same as outlined above. The vertical abundance of *Calanoides carinatus* as observed from Multinet tows showed the max abundance now more at depth, i.e., little upwelling taking place. The thin but intense acoustic scattering layer at the beginning of the thermocline was by RMT tows assigned to a new species of swimming crab, where guest investigator Dr Sharon Smith was pleased to get acquainted with this newcomer which had been named *Charybdis smithii*.

Results of the NIOP-JGOFS cruises and related NIOP projects will be discussed in an International JGOFS Arabian Sea workshop, planned at NIOZ, The Netherlands, in Spring 1994.

#### 3. 1992 WEDDELL SEA CO, PROJECT

In collaboration with the Alfred Wegener Institut (AWI) the CO<sub>2</sub> system was studied in a winter cruise (May-August 1992, *Polarstern* ANT X/4) and a summer cruise (December 1992, *Polarstern* ANT X/7) in the Weddell Sea. Objective was to quantify the role of the Weddell Sea, a site of deep water formation, as a sink of atmospheric CO<sub>2</sub>. Upon preparations at NIOZ the principal investigator Dr J.M.J Hoppema (Mario) is now at the staff of AWI from where the actual field work was done using NIOZ equipment. Currently the results are worked out in collaboration with Dr Fahrbach (AWI) and Prof De Baar (NIOZ).

### ANNEX X

#### GLOSSÁRY OF ACRONYMS AND SPECIAL TERMS

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AOML       Attantic Oceanographic and Meteorological Laboratory (NOAA)         AWI       Institut für Polar- und Mecresforschung-Bremerhaven         BODC       British Ocean Fluxes Study         CARDEEP       Carbon Budget and Deep Convection         CCCO       SCOR-IOC Committee on Climatic Changes and the Ocean         CDIAC       Carbon Dioxide Information and Analysis Center (USA)         CFC       Chlorofluorocarbon         COARE       (TOGA) Coupled Ocean Atmosphere Response Experiment         COCC       Centre for Ocean Climate Chemistry (Canada)         CRM       Certified Reference Material         CZCS       Coastal Zone Color Scanner         DIC       Dissolved Organic Carbon         DOE       Department of Energy (USA)         EC       European Community         EOS       Global Climate Observing System         EqPac       US JGOFS Equatorial Pacific Process Study         GCOS       Global Climate Observing System         EGOSE       Georenerical Ocean Sections Study         GIN-Seas       Greenland, Iceland and Norwegian Seas         GOCM       General Ocean Observing System         I-GOOS       IOC-WMO Intergovernmental Committee for GOOS         IAEA       International Cocanic I of Scientific Unions         IF		
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PMEL Pacific Marine Environmental Laboratory (NOAA)		
	rmel	Pacific Marine Environmental Laboratory (NUAA)

IOC-JGOFS/CO<sub>2</sub>-IV/3 Annex X - page 2

SSalinitySCORScientific Committee on Oceanic Research (ICSU)SeaWiFSUS Sea-Viewing Wide Field-of-View Sensor
SeaWiFS US Sea Viewing Wide Field of View Sensor
SIO Scripps Institution of Oceanography (USA)
SST Sea Surface Temperature
SSWS Standard Sea Water Service
T Temperature
TTO Transient Tracers in the Ocean
UNCED 1992 United Nations Conference on Environment and Development
UNEP United Nations Environment Programme
UNESCO United Nations Educational, Scientific and Cultural Organization
WCRP World Climate Research Programme
WHP WOCE Hydrographic Programme
WMO World Meteorological Organization
WOCE World Ocean Circulation Experiment

- Second Meeting of the UNEP-IOC-ASPEI Global Task Team on the Implications of Climate Change on Coral Reefs
   Seventh Session of the JSC Ocean Observing System Development Panel
   Fourth Session of the IODE Group of Experts on Marine Information Management
   Sixth Session of the IOC Editorial Board for the International Bathymetric Chart of the Mediterranean and its Geological/Geophysical Series
   Fourth Session of the Joint IOC-JGOFS Panel on Carbon Dioxide

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