

Intergovernmental Oceanographic Commission
Reports of Meetings of Experts and Equivalent Bodies

Joint IOC-JGOFS CO₂
Advisory Panel Meeting

Seventh Session
Warnemuende, Germany
2-4 June 1997

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IOC-JGOFS/CO₂-VII/3
Paris, 16 December 1998
English only

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1. WELCOMING

Chairman Andrew Watson opened the seventh session of the IOC-JGOFS Advisory Panel on Ocean CO₂ at 08:30, 2-4 June 1997, at the Baltic Sea Institute in Warnemuende, Germany. The Director of the Institute, Prof. Bodo von Bodungen, also welcomed participants and underscored the importance of obtaining an estimate of the ocean CO₂ sink with narrower error bands than we have today. The complete list of participants with addresses, telephone numbers, etc. can be found in Annex II. Watson then thanked Bernd Schneider and those who assisted in hosting the meeting at the Institute.

2. ADOPTION OF THE AGENDA

The Panel members were invited to comment on the provisional agenda. After brief discussion, the Panel adopted the agenda as given in Annex I.

3. RECENT EVENTS AND UPDATES

3.1 REVIEW OF EVENTS AND ACTIVITIES

Arthur Alexiou reviewed the events and activities in the Global Ocean Observing System (GOOS) Program. A common understanding of the GOOS concept is being promoted through three key planning documents: the GOOS Principles, the GOOS Strategic Plan and the GOOS 1998, a blueprint for developing implementation of GOOS. GOOS is restructuring somewhat to simplify relationships between the Intergovernmental Committee for GOOS (I-GOOS) and the Joint Scientific and Technical Committee for GOOS (J-GOOS). It will be directed by a GOOS Steering Committee (GSC), chaired by Worth Nowlin, that combines the current J-GOOS and the I-GOOS Strategic Subcommittee. Links with other observing systems (i.e., the Global Climate Observing System (GCOS) and the Global Terrestrial Observing System (GTOS)) are developing for jointly defining requirements for space observations and for data and information management. The Climate Module is developing plans for a Global Ocean Data Assimilation Experiment (GODAE) which has been adopted by the Committee on Earth Observing Satellites (CEOS). The Health of the Ocean Module is developing pilot projects. A new Capacity Building Panel has been established for developing capabilities in developing States. Appointments will be made shortly to Panels for the Coastal and the Living Resources Modules. To gain tangible support and commitments for GOOS from governments and National agencies, a GOOS Agreements Meeting is being planned for September of 1998 as an International Year of the Ocean event.

3.2 OOPC TIME SERIES WORKSHOP

Liliane Merlivat briefed the Panel on the Time Series Workshop held in Baltimore Maryland 18-20 March 1997 and cosponsored by GOOS, GCOS, WCRP and JGOFS. It was convened to examine the contribution that time series observations have made to ocean science and to:

- assess the viability and feasibility of maintaining the existing stations;
- weigh the options for re-occupying sites for which long records exist and for which new technology might offer more cost-effective systems; and
- identify, on the basis of research results from programs like WOCE, TOGA and JGOFS, and scientific plans for new programs, where there are sound cases for establishing new sites.

The workshop provided a forum whereby an objective assessment of the unique contribution from time series data could take place and an opportunity to formulate objective criteria and specific suggestions for time-series observations that will be critical in future monitoring. Also undertaken was an evaluation of the role of various time-series observations that will be critical in future monitoring. The JGOFS sites at Bermuda and Hawaii were prominent in the discussions. The complete Report of the workshop can be found on the web at:

3.3 STATUS OF MODELING

Fortunat Joos was unable to attend the meeting but he provided the following update on ocean CO₂ modeling issues for the report.

Modeling studies of Sarmiento and LeQuere and of Maier-Reimer and his colleagues addressed the impact of ocean circulation changes induced by global warming on the oceanic CO₂ uptake. The main conclusions of the two studies are highly controversial. Sarmiento and LeQuere found that changes in ocean circulation have the potential to dramatically affect future oceanic CO₂ uptake whereas Maier-Reimer's group concluded that changes in ocean circulation are not important for modeling future atmospheric CO₂ concentrations. (See also section 7.1)

Maier-Reimer and colleagues have implemented a prognostic carbon cycle model in which various feedback mechanisms are operating which tend to cancel each other. On the other hand, Sarmiento and LeQuere used as an assumption in the global warming scenario that export production remains at today's level except in regions where the nutrients are depleted. This assumption is not very realistic under a changed ocean circulation. Additionally, they assessed two upper-limit scenarios by assuming a fully operating marine biosphere and an abiotic ocean to explore the potential range of oceanic CO₂ uptake. There remain two open issues:

- (i) How realistic are simulated future ocean circulation changes for a prescribed radiative forcing scenario?
- (ii) How will the marine biosphere and the carbon export production be affected by global warming and ocean circulation changes?.

Oceanic radiocarbon measurements, e.g., ¹³C and ¹⁴C, have been and continue to be the standard tool to validate ocean circulation models on time scales of decades up to centuries. New data from the WOCE cruises will make it possible to assess ocean-circulation time scales on a much more detailed level than hitherto possible. The information contained in the ¹³C and ¹⁴C signals in inorganic carbon is complementary. The distribution of ¹³C in DIC, besides by physical transport, is also strongly affected by the cycling of organic carbon. The ¹³C recorded in sediments provides a link between the contemporary ocean and the paleocean. Large data sets of ¹³C measured on sediment cores exist. A full exploitation of the information contained in the DIC ¹³C signals is presently hampered by the quality and the small amount of published data. It is thus important that measured data are made available as soon as possible and that ¹³C measuring programs are continued.

Joos reported that N. Gruber has reconstructed anthropogenic DIC distribution in the Atlantic. He found, in agreement with Chen's results, an inventory of 22 ± 5 Gt C in the North Atlantic and 18 ± 4 Gt C in the South Atlantic for the year 1982. Joos also noted that Keeling and his colleagues, and Heimann and Meier Reimer have provided new estimates of the oceanic CO₂ uptake based on the observed decrease in atmospheric oxygen and on ¹³C observations.

3.4 TAKAHASHI'S GLOBAL FLUX ESTIMATES

The first comprehensive global surface CO₂ flux climatology produced by Takahashi of the Lamont-Doherty Earth Observatory and his colleagues is now in press [Takahashi et al.,1997]. Rik Wanninkhof explained that the climatology was prepared by combining data sets from several investigators with large holdings. The resulting 250,000 data points were binned into 6-hour averages, normalized to the year of 1990 and subsequently mapped on a 4° X 5° grid. Monthly global distributions of "delta pCO₂" (pCO₂ in water minus pCO₂ in air) for each grid box were determined by interpolation in time and space using a 2-dimensional lateral transport model and the advective flow field derived from the GFDL general circulation model developed by Cox and Bryan [Bryan and Lewis, 1979]. Gas exchange coefficients were derived from parameterization of global monthly mean winds (from Esbensen and Kushnir [1981]) using three frequently used relationships [Liss and Merlivat, 1986; Tans et al., 1990;

Wanninkhof, 1992] . The resulting global uptake rates range from 0.6 to 1.3 GTonnes/yr (excluding equatorial fluxes for a non-El Niño year) with an uncertainty of 75 % resulting from the numerical interpolation scheme.

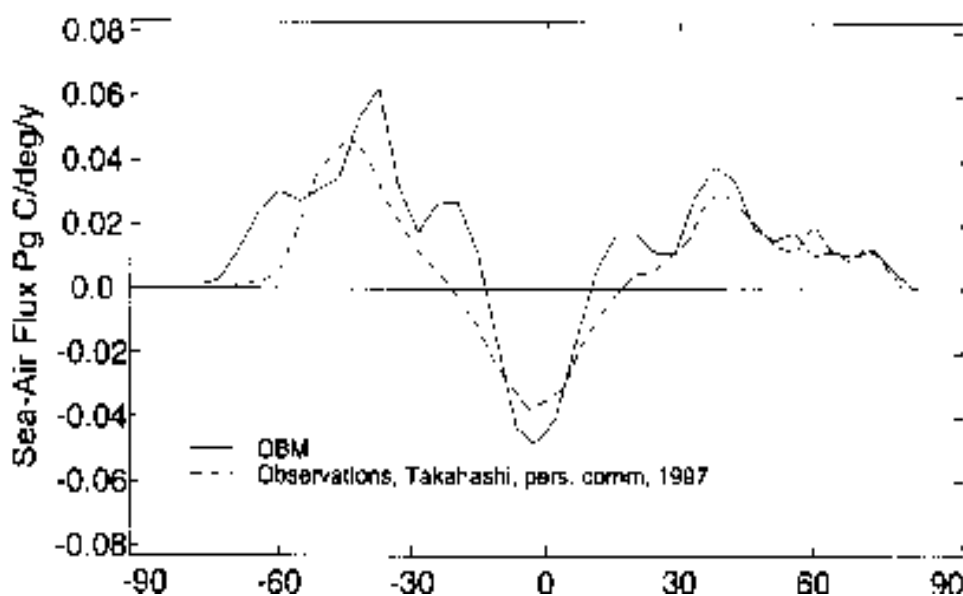
The zonal fluxes compare favorably with the fluxes derived from the Ocean Biogeochemical General Circulation Model developed by Sarmiento and co-workers at Princeton (see Figure 1). An interesting difference is the broader equatorial CO₂ source in the climatology compared to the model. Comparison of the climatology with observations in regions where the climatology is not constrained by data shows significant differences (see Figure 2). This clearly indicates that incorporating more data will improve the constraints on the global CO₂ fluxes calculated in this manner. The efforts by the IOC- JGOFS CO₂ Sub-Panel to create a data inventory and subsequently a data repository of surface pCO₂ data will be crucial in these efforts.

Wanninkhof emphasized the importance of increasing the data set. Takahashi's exercise seems to be smearing the detail in air-sea fluxes that models show. There is now more data to include from the Indian Ocean.

The discussion focussed on the extent to which Takahashi's "pCO₂ climatology" adequately represents the seasonal pattern, and to what extent interannual variability in CO₂ fluxes can be inferred from a pCO₂ climatology and "real" wind information. This approach suggests far less variability in the "ocean sink" than had been proposed by Francey et al from their analysis of ¹³C variations in the atmosphere.

One interesting feature that was noted was that the predicted net ocean flux (about -2GtC/yr estimated from the pCO₂ field is comparable with other estimates. This had not been considered likely given the high-frequency spatial and temporal variability that is observed.

C.S. Wong pointed out that his data base for the North Pacific (especially from the recent time series on the *R.V. Skaugran*) shows very high seasonal variability and also a substantial effect of severe storms. His estimate has the North Pacific as a large sink of CO₂ (about 0.7 GtC/yr) in contrast to earlier suggestions by Tans and his colleagues that it is a small source.



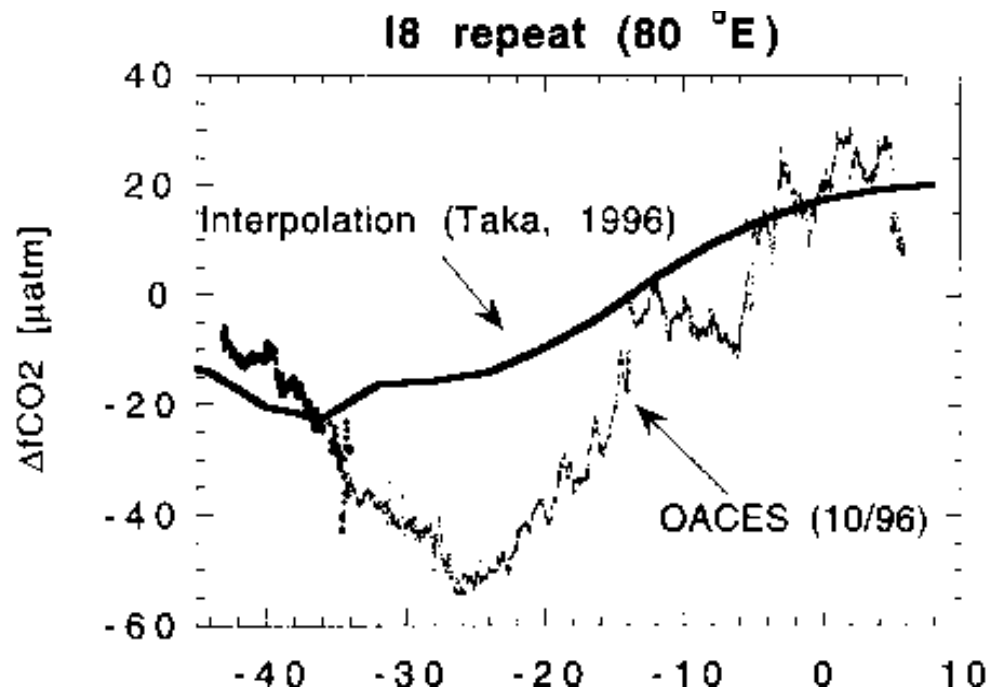


Figure 1. Comparison of air-to-sea CO₂ fluxes for the climatology derived by Takahashi et al. 1997, and from the output of the Princeton ocean biogeochemical model. The yearly fluxes are for zonal bands with negative values indicating the flux from the ocean. Figure courtesy of R. Murnane, Princeton U.

Figure 2. Comparison of sea water pCO₂ for the climatology derived by Takahashi et al., and from observations obtained during OACES cruise in October 1996 for a transect in the southern Indian Ocean along nominally 80°E.

3.5 DOE OCEAN MARGINS EXPERIMENT

Douglas Wallace commented on the experiment off the East coast of the U.S. to study the role of the continental margins in the sequestration of CO₂ in the ocean. Moorings in the area between Chesapeake Bay and Cape Hatteras included biogeochemical sensors. The control-volume array consisted of 10 moorings in a box 15 km on a side. The O₂ sensors were 90 % reliable; pCO₂ sensors were 50%. Once the data are fully assembled they will be passed on to CDIAC.

3.6 ATMOSPHERIC CO₂ ISSUES

Graeme Pearman was unable to attend the meeting but submitted a report on atmospheric issues. His comments are included in the relevant sections of this report.

Members were informed of 5th International Carbon Dioxide Conference, the next in this quadrennial series of Conferences on the carbon cycle. It will be held at Cairns (Great Barrier Reef), Australia, September 8-12, 1997. It promises to be the most comprehensive conference on the issues of the global carbon cycle ever held, with participation from all major laboratories around the world and contributions from atmospheric, oceanic (physical and biological) and terrestrial biological fields. Whilst a number of members of the Panel are expected to be in attendance, others might like to consider talking part. Further details, including a list of both the oral and poster presentations are available at the web site:

<http://www.dar.csiro.au/pub/events/co2_conf/>.

Pearman suggested it might be an excellent time for the Panel to hold an informal get-together.

4. OCEAN CO₂ MEASUREMENT ISSUES

4.1 PROGRESS WITH REFERENCE MATERIALS

Andrew Dickson briefly described the preparation of Reference Materials (RMs) for C_T and A_T measurements and presented statistical information about the distribution of bottled RMs. Approximately 16,000 bottles were provided to CO₂ groups all over the world. Dickson stated that the number of RMs delivered to non-U.S. groups is growing and at present is about 50% of the total number. Furthermore, certification procedures for C_T and in particular for A_T were addressed. A two-stage open cell titration with a coulometric HCl determination is used to determine A_T in the RM. Accuracy of this method was examined by the analysis of synthetic solutions (tris, borax, sodium carbonate). It was pointed out that the weakest point in the determination of A_T is the choice of the chemical model which is used to determine the equivalence point. Other uncertainties are due to the determination of the NaCl background alkalinity. Improvements can be achieved by recrystallization of NaCl in the presence of chlorine. F. Millero reported on a comparison between the two-stage titration and the coulometric determination. Despite the use of different chemical models, agreement within ± 2 mol/kg could be achieved. Dickson mentioned that the production of RMs for C_T and A_T will be continued and that also certification of pH is planned. However, due to a reduced budget, the distribution policy will change in the future and the users of RMs will probably be charged (about \$50/bottle) for production and certification of the RM.

C.S. Wong outlined the requirements of RM for ¹³C/¹²C measurements. For data quality control over a long period of time, it is important to ensure both the compatibility to WMO atmospheric ¹³C standards and an oceanic calibration system. These include:

- (i) Seawater DIC RM from SIO, seawater, and seawater accessible from station P, at 1000 m, 2500 m, regularly (on cost recovery basis);
- (ii) Gaseous working standards t values close to atmospheric and oceanic values, e.g., - 8‰, -1.5‰, 0‰, +2‰. The Ocean Biogeochemistry Group at IOS has facilities which produce standards by blending gases of depleted and enriched ¹³C. Cylinders of these gases are available for the oceanic community, but the costs of production have not been worked out. IAEA gaseous standards are also available for atmospheric work (-8‰) at costs of about \$ 2000 per cylinder.
- (iii) Solid limestone NBS19 is available through IAEA. An oceanic solid RM can be created at lower costs, if there is sufficient demand.

4.2 INTERCOMPARISON EXERCISES.

Dickson reported no further progress with the report on the Scripps Equilibrator Test. It has suffered due to other priorities and lack of funds.

Ludger Mintrop reported on the first international, at-sea intercomparison of underway pCO₂ systems. After the equilibrator test at the Scripps laboratory, there was general agreement in the community that a second step was necessary for a controlled at-sea exercise under realistic and identical conditions for the different measurement systems being utilized. The test was funded through the German JGOFS project and carried out in June 1996 aboard the R.V. METEOR on the first leg of cruise 36 in the North Atlantic. Ten institutions from seven countries participated. Annex III contains a more detailed description of the test.

4.3 CRUISE-TO-CRUISE DIFFERENCES

With the end of the WOCE Hydrographic Program surveys and CO₂ observations taken on these surveys, the next step of data synthesis has commenced. The utility of the total dissolved inorganic carbon (DIC) data sets obtained on individual cruises will be greatly increased if they can be combined for each ocean basin, and subsequently to global scale. Wanninkhof informed the meeting that the US DOE survey team and NOAA/OACES investigators have developed working groups to synthesize the basin data. The synthesis efforts include:

- (i) Inventory of cruises and status of data quality control
- (ii) Comparison of cruise to cruise differences at cross over points with emphasis on differences in deep water. This effort will not be limited to DIC but will include other carbon parameters, oxygen, nutrients, and hydrographic parameters as well. Some of the parameters will be handled by WOCE/WHP investigators. Wanninkhof mentioned that an initial look comparing data at some crossover points from different cruises showed differences at great depths for salinity, but with systematic trends.
- (iii) Assess the cause of differences, that is, determine if they appear to be instrumental offsets or changes in water masses.
- (iv) Recommend corrections to be applied to datasets.

Current working group chairmen and participants are:

Atlantic Ocean: Goyet (Chair) Wallace, Wanninkhof, Takahashi;
 Pacific Ocean: Feely (Chair), Winn;
 Indian Ocean: Sabine (Co-Chair), Peng co-chair, Wanninkhof;
 Southern Ocean: Takahashi (Chair), Feely.

Wanninkhof believed the CO₂ Panel should play an important role in this effort by acting as a conduit for other national programs to collaborate. Many oceanographic issues of international importance such as oceanic uptake of anthropogenic CO₂, verification of results from large-scale ocean computer models predicting future uptake, and perturbation of the oceanic carbon system by climate change can only be quantified by comprehensive oceanic coverage. The large expansion of oceanic carbon programs in several nations in the past decade has given us an unparalleled opportunity to resolve the issues if datasets are shared.

Douglas Wallace proposed that it should be brought to the attention of WOCE that the high quality CO₂ data set taken on WOCE cruises can provide a valuable constraint for the analysis of data on nutrients observations taken on WOCE cruises. It was agreed that a letter should be written to the WOCE Scientific Steering Group suggesting this application of the well calibrated CO₂ data obtained by JGOFS on these cruises. The letter sent is shown in Annex IV.

4.4 STATE OF KNOWLEDGE OF THERMODYNAMICS OF CO₂ SYSTEM

Andrew Dickson stated that the scope for studying this problem is great. Depending on which constants one uses, an error of up to 2.4 % can result in computing pCO₂. He alluded to potential problems, e.g., in using the single solubility constant (K_o), and although boron ancillary data are pretty well known, the pH that is used needs to match the K values used.. Dickson agreed to write a paper detailing how bad the situation could be.

4.5 CO₂ SYSTEM CALCULATIONS IN ANOMALOUS WATERS

Petr Makkaveev illustrated one aspect of this problem when working in Black Sea waters. There, the simplified approach employed in open ocean waters for deriving alkalinity (accounting for only the boron and carbon) can yield errors of up to 11% or more because the concentrations of other ions are much higher in the Black Sea than in the major ocean basins. A description of Makkaveev's analysis of Black Sea alkalinity is provided in Annex V.

4.6 VARIABILITY IN THE CARBON/NUTRIENTS SYSTEM

C.S. Wong showed long term changes that appear in the record obtained from Line P sections. He attributed changes in the record variously to dust from Alaska, periods of high winds, and higher fresh water input. He showed the nitrate supply was diminishing; upwelling had moved off the coast at Scripps a distance of 50 miles or more. Winter values of pCO₂ had not changed noticeably over the entire record but summer pCO₂ levels showed an increase of 150 µatm in 20 years due to the lower nitrate and consequent lesser draw-down.

4.7 VARIABILITY OF THE CO₂ SYSTEM AT DIFFERENT TIME SCALES

Makkaveev reported on work in progress at the Shirshov Institute to "rescue" and process archived data on CO₂ system parameters collected by various investigators in Russia during the period 1920s to 1990s. Old data were mostly pH and alkalinity, combined in more modern times with other data such as direct pCO₂ measurement. The data cover all the major ocean regions, typically 2000 stations in the Pacific and 1500 each in the Atlantic and Indian oceans. The data were referenced to common pH scales, converted to pCO₂, binned monthly and by latitude band, with mathematical interpolation and extrapolation used to fill space and seasonal data boxes for regions in which data were sparse. Results show the seasonal and latitudinal effects, including biologically driven seasonal cycles in the high-latitude and mid-latitude regions, and high supersaturations in the Southern Ocean (see Figure 3).

In response to questions during discussion, Makkaveev stated that different pH scales were converted to common scales using the Geishes constants. Future plans include recalculation using the Roy *et al.* constants. Watson suggested that, besides publication in a Russian language journal, the results of the study should be submitted to an English language journal to ensure wide circulation. The panel could

perhaps assist here by providing checks on the English style. Makkaveev affirmed that the data would be made available after publication.

The majority of Russian and former USSR data for carbon measurement system parameters are based on measurements of pH and A. Values of pCO₂ and C_T are then calculated from these values. These calculations are more complicated in anoxic waters such as the Black Sea where it is necessary to account for the alkalinity contribution of species such as hydrogen sulfide, phosphate and ammonia (see section 4.5). Two sets of data for the Black Sea differ significantly in these parameters; however the reasons for such discrepancies are not clear.

4.8 CONTINENTAL SHELF CO₂ SOURCES, SINKS AND FLUXES

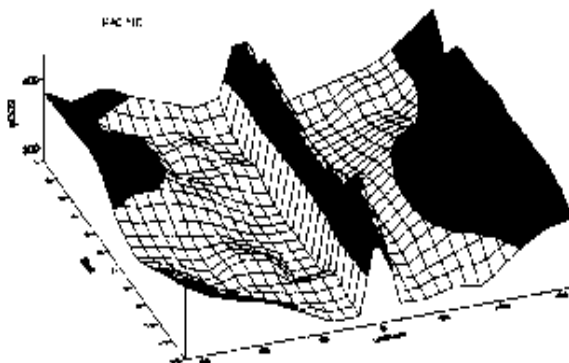
Shizuo Tsunogai discussed estimates he had made showing the possibility of as much as 1 GtC/yr being sequestered in the continental shelf areas; he referred to the process as the “continental pump”. It was suggested that the IGBP should be encouraged to consider this as an area ripe for additional study. It is not so much the missing sink problem as it is getting a measure of the total flux.

4.9 ATMOSPHERIC O₂ MEASUREMENTS TO CONSTRAIN THE CARBON CYCLE

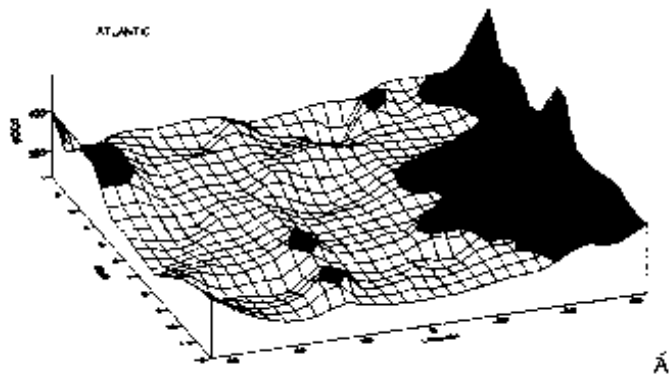
Graeme Pearman reported on using measurements of atmospheric O₂ to constrain the global atmospheric and oceanic carbon cycles. Oxygen is a key player in the global carbon cycle as it is intimately linked to CO₂ through the processes of photosynthesis, respiration and combustion. Importantly though, the air-sea exchange characteristics of O₂ and CO₂ are very different. Consequently, measurements of atmospheric O₂ provide information about the global atmospheric and oceanic carbon cycles that is not accessible through measurements of CO₂ alone. Unlike CO₂, O₂ has low solubility in sea water. This means that over time scales of years or more, uptake of anthropogenic CO₂ by the oceans

Figure 3. Seasonable variability of the surface water pCO₂ at different latitudes of the oceans.

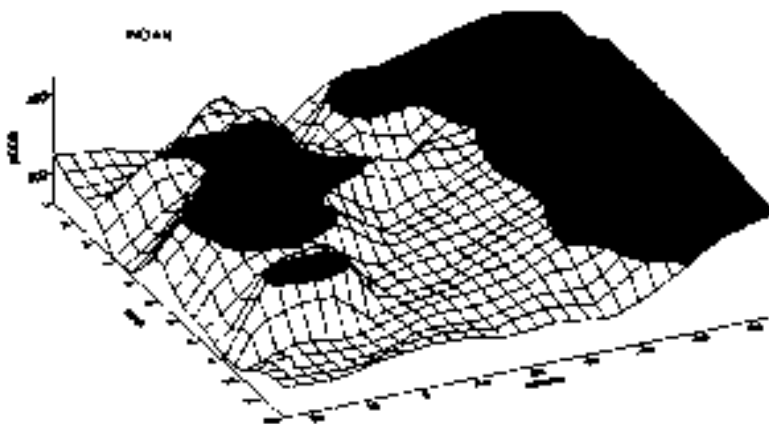
Seasonal variability of the surface water pCO₂ at different latitudes in the Pacific ocean.
Positive latitude correspond to Northern hemisphere, negative - to Southern.



Seasonal variability of the surface water pCO₂ at different latitudes in the Atlantic ocean.
Positive latitude correspond to Northern hemisphere, negative - to Southern.



Seasonal variability of the surface water pCO₂ at different latitudes in the Indian ocean.
Positive latitude correspond to Northern hemisphere, negative - to Southern.



proceeds without change to the oceanic O₂ inventory. Any difference between the observed rate of depletion of O₂ in the atmosphere and its rate of consumption predicted by fossil fuel burning may be interpreted in terms of a net change in the size of the terrestrial biosphere alone. By contrast, over shorter time scales, O₂ is rapidly exchanged between the atmosphere and oceans in response to seasonal, biological and thermal forcing. This feature makes atmospheric O₂ a useful tracer of oceanic carbon cycle processes.

Recent development of technologies capable of measuring the atmospheric O₂/N₂ ratio at the required ppm-level precision (Keeling, 1988; Bender et al., 1994) lead to the establishment of global surface monitoring programs by Scripps Institution of Oceanography (SIO) and University of Rhode Island (URI) during the early 1990's. Published records of up to 5 years duration have revealed a decreasing trend in global O₂ levels and have been used to determine the partitioning of CO₂ uptake between the oceans and the terrestrial biosphere over this period (Bender et al., 1996; Keeling et al., 1996). However, the mean long-term O₂ trend and corresponding carbon budget terms are not yet well constrained, due mainly to the early 1990's being a period of anomalous low CO₂ growth rate. Continued monitoring of atmospheric O₂ through these programs and the more recently commenced program of the Commonwealth Scientific and Industrial Research Organisation (CSIRO) is expected to deliver progressively tighter constraints on the global carbon budget as the records become longer.

Other strategies to determine the trend in atmospheric O₂ have been explored. An estimate for the period 1977-1985 has been obtained by URI from air retrieved from the South Pole firn (Battle et al., 1996), but with precision limited by uncertainties associated with the dynamics of air movement within the firn. Trends deduced from sampling of other firn sites are likely to become available in the future, with the possibility of uncertainties being further reduced by careful selection of sites and by improved characterisation of the fractionating processes occurring within the firn. Work currently in progress at CSIRO aims to determine the mean O₂ trend spanning the 19-year period 1978-1997 using the Cape Grim Air Archive, a collection of air samples collected in high-pressure tanks at the Cape Grim Baseline Observatory, Tasmania, for the purpose of being put aside as an archived record of background atmospheric composition (Langenfelds et al., 1996a).

Measurements reported by both SIO and URI (Bender et al., 1996; Keeling and Shertz, 1992, Keeling et al., 1993) show large seasonal cycles in both hemispheres which have been attributed to surface exchange processes. The southern hemisphere signal is driven primarily by seasonal air-sea fluxes and has been used to estimate rates of marine productivity, integrated over the oceans of the southern hemisphere. Inter-annual variability in marine productivity is evident. Further information relating to the spatial and temporal behaviour of the ocean carbon cycle will be provided through continued monitoring of atmospheric O₂ at the surface sampling stations as well as through sampling from other platforms such as aircraft and ships. Measurements of O₂ have already been incorporated into the CSIRO aircraft sampling program which obtains monthly vertical profiles from altitudes between 0 and 7.5 km in the troposphere above Cape Grim (Pak et al., 1996; Langenfelds et al., 1996b). First results have revealed a seasonal variation in the vertical gradient which is expected to further constrain the marine productivity estimates.

For further information see:

Battle, M, M Bender, T Sowers, P P Tans, J H Butler, J W Elkins, J T Ellis, T Conway, N Zhang, P Lang and A D Clarke (1996) Atmospheric gas concentrations over the past century measured in air from firn at the South Pole. *Nature* **383**, 231-235.

Bender, M L, P P Tans, J T Ellis, J Orchardo and K Habfast (1994) A high precision isotope ratio mass spectrometry method for measuring the O₂/N₂ ratio of air. *Geochim. et Cosmochim. Acta* **58**, 4751-4758.

Bender, M, T Ellis, P Tans, R Francey and D Lowe (1996) Variability in the O₂/N₂ ratio of southern hemisphere air, 1991-1994: Implications for the carbon cycle. *Global Biogeochem. Cycles* **10**, 9-21.

Keeling, R F (1988) Development of an interferometric oxygen analyzer for precise measurement of the atmospheric O₂ mole fraction. *Ph.D. Thesis, Harvard University*, 178pp.

Keeling, R F, R G Najjar, M Bender and P P Tans (1993) What atmospheric oxygen measurements can tell us about the global carbon cycle. *Global Biogeochem. Cycles* **7**, 37-67.

Keeling, R F and S R Shertz (1992) Seasonal and interannual variations in atmospheric oxygen and implications for the global carbon cycle. *Nature* **358**, 723-727.

Keeling, R F, S C Piper and M Heimann (1996) Global and hemispheric CO₂ sinks deduced from changes in atmospheric O₂ concentration. *Nature* **381**, 218-221.

Langenfelds, R L, P J Fraser, R J Francey, L P Steele, L W Porter and C E Allison (1996a) The Cape Grim Air Archive: the first seventeen years, 1978 - 1995, in *Baseline Atmospheric Program (Australia) 1994-95*, edited by R J Francey, A L Dick and N Derek, p.53-70, Bureau of Meteorology and CSIRO Division of Atmospheric Research, Melbourne, Australia.

Langenfelds, R L, R J Francey, L P Steele, M P Lucarelli, D A Spencer, S A Coram and K Broadhurst (1996b). Flask sampling from Cape Grim overflights. *Baseline Atmospheric Program (Australia) 1994-95*, edited by R J Francey, A L Dick and N Derek, p.112-117, Bureau of Meteorology and CSIRO Division of Atmospheric Research, Melbourne, Australia.

Pak, B C, R L Langenfelds, R J Francey, L P Steele and I Simmonds (1996) A climatology of trace gases from the Cape Grim overflights, 1992 - 1995. *Baseline Atmospheric Program (Australia) 1994-95*, edited by R J Francey, A L Dick and N Derek, p.41-52, Bureau of Meteorology and CSIRO Division of Atmospheric Research, Melbourne, Australia.

5. GLOBAL pCO₂ DATA SET

5.1 CDIAc INVENTORY OF CO₂ DATA

Alex Kozyr provided some background on the Carbon Dioxide Information Analysis Centre (CDIAC) at Oak Ridge National Laboratory. In 1993 the US Department of Energy (DOE) Global Change Research Programme (GCRP) asked CDIAC to manage US-sponsored JGOFS CO₂ measurements taken aboard research vessels during the World Ocean Circulation Experiment (WOCE) Hydrographic Programme cruises. Although CO₂ is not an official WOCE measurement, co-ordinators of WOCE agreed to permit scientists participating in the US DOE CO₂ Ocean Survey Programme and other international ocean carbon measurement programmes, to obtain sea water samples and perform carbonate chemistry measurements on WOCE cruises. The last WOCE cruises will be completed in late 1997 and the final US sponsored CO₂ data set is expected to cover 20,000 stations. All U.S. sponsored data are destined for archival at CDIAC.

To date, CO₂ and hydrographic data from 39 WOCE cruises have been sent to CDIAC. Each data set is checked using programmes developed to assess data quality and consistency. Each data set will be fully documented, published and made available without charge in a variety of ways including via Internet. To date, CO₂ data and hydrographic measurements from seven WOCE cruises have been fully documented and are now available. The remaining WOCE CO₂ data sets are either being checked, documented, or require finalization of the hydrographic measurements. CDIAC is also beginning to pursue WOCE CO₂ measurements made by international WOCE programmes.

In addition, CDIAC has also processed and documented two data sets submitted by the NOAA Pacific Marine Environmental Laboratory (PMEL), underway pCO₂ and N₂O₂ data spanning 1977-1990 from Scripps Institution of Oceanography (SIO), final shore based CO₂ measurements from the Geochemical Ocean Section Study (GEOSECS), final carbonate and hydrographic measurements from the Transient Tracers in the Ocean (TTO) study, and carbonate and hydrographic measurements from the Weddel Sea. Other oceanic CO₂ data sets residing at CDIAC include data from the South Atlantic

Ventilation Experiment (SAVE) and earlier cruises (e.g., 1957 Downwind cruise, 1961 Monsoon cruise, and the Lusiad cruises of the 1960s) will be processed.

To obtain CO₂ data from data-sparse regions and to rescue important data that may be lost, CDIAC recently teamed with the National Oceanographic Data Centre and the World Data Centre - A for Oceanography to rescue historic data from the Arctic and other regions. This collaborative effort ensures the long-term archival of these data in a machine-readable form, assessment of their data quality, full description of these data and publication and ready access to these data.

In summary, Kozyr stated that CDIAC now has the largest collection of ocean and atmospheric CO₂-related measurements in the world. Present and planned activities coupled with an increased willingness by researchers from around the world to submit their data to CDIAC will further strengthen this collection.

Kozyr noted that CDIAC has started to work on compilation of an electronic ocean-carbon atlas with all DOE, NOAA, international, and historical carbonate chemistry measurements. The computer atlas will contain profiles of all carbon and hydrographic parameters for every cruise and will be made available by CDIAC without charge to anyone. The atlas will offer an optional selection of procedures for interpolation, averaging, smoothing and sub-sampling of data and results. The Atlas will help to locate data from a simple query, to produce plots (fields, sections, etc.), and will run different statistical and oceanographic applications.

For more information about CDIAC's data collection, check the Web page at: <http://cdiac.esd.ornl.gov/oceans/home.html>.

In discussion, the Panel expressed a desire to show its appreciation for the work undertaken by CDIAC for the international ocean CO₂ community. It was agreed that the chairman would write a letter to the US DOE that would convey this appreciation and express thanks for their efforts in establishing a database for ocean CO₂ measurements.

Alain Poisson had been expected to lead a discussion on how to get responders to the inventory exercise to submit their data to CDIAC. He was unexpectedly forced to cancel his attendance at this meeting, however, and a full discussion on the effort was hampered somewhat. It was agreed that the chairman would work with Poisson and other members to draft appropriate letters of request for data and a special cruise information form that would be sent to investigators in possession of pCO₂ data. (Note: The letters and response forms were subsequently sent in December 1997.)

6. STATUS OF ¹³C MEASUREMENTS

6.1 INVENTORY OF OCEAN ¹³C DATA

C.S. Wong, chairman of the sub-panel on ¹³C, reported on an inventory of ¹³C samples collected so far by Canadian and U.S. groups. By Canadian researchers, in the North Pacific depth profiles have been taken mainly on meridional WOCE lines, on a transect towards Australia and on a line off Kamchatka, the latter in cooperation with Russian groups. Along zonal transects from Canada to Japan surface samples were collected, average sampling distance about 2^o. Time series were sampled mainly along line P and at station P. Due to other measurement programs, so far, only a smaller part of the samples have been measured.

Apart from the Canadian samples, U.S. groups (such as Paul Quay, Charles Keeling) concentrated on WOCE lines in the Pacific collecting depth profiles and several surface transects. Atlantic samples, however, are scarce compared to the Pacific data set. Though not all samples have been measured yet, those where C_T has been measured by manometric methods in Charles Keeling's lab have been extracted and are ready for ¹³C determination.

Besides WOCE lines and some other transects, ¹³C samples are routinely taken at the time series stations HOT and BATS. Also a great number of ¹³C data have emerged from the ¹³C measurements carried out by the Woods Hole AMS lab. A total of 12000 samples have been analyzed for the Pacific and Indian Oceans, while the Atlantic is only represented by about 300 samples. Precision of the ¹³C measurements by the AMS-technique is estimated to be about 0.015‰.

S. Tsunogai reported on Japanese of ¹³C measurements along a meridional transect at 165°E where GEOSECS data are also available. He pointed out that from C_T measurements, corrected for different apparent O₂ utilization (AOU) and phosphate consumption, a northward increase of surface values could be observed. Supported by the ¹³C data, these waters obviously lose CO₂ to the atmosphere in winter, before carbon fixation in summer extracts CO₂ from the atmosphere. Because of the higher atmospheric values nowadays, the winter source term is reduced, leaving the summer sink function unaffected. The net effect makes the North Pacific a sink for CO₂ at present, in contrast to preindustrial times.

T. Johannessen added that in Norway and other Scandinavian countries a substantial ¹³C sampling program has been conducted since 1986, covering the Nordic Seas and the Arctic Ocean. Efforts are being undertaken to make these data available to the community to help fill the gap in the Atlantic ocean data. Still, very few data exist in the Atlantic, compared to other oceanic regions.

C.S. Wong pointed out the need for reference standards (i.e., gas standards and sea water reference material) to bring measurements by different groups to a common level for comparison purposes. He emphasized the need to regularly conduct intercomparison exercises on a continuing basis to ensure long-term data quality control.

6.2 ATMOSPHERIC MEASUREMENTS

Graeme Pearman was unable to attend the meeting and provided the following report to the Panel.

Measurements of δ¹³C of CO₂ assist the partitioning of fossil CO₂ into terrestrial and oceanic reservoirs. Measurements of O₂/N₂ have recently been applied to the same task (see below). The methodology for both tracers involves the measurement of temporal or spatial changes and relating the changes to net carbon fluxes between surface reservoirs and the atmosphere. However, for both tracers, atmospheric variations can be influenced by second order effects. In the case of the δ¹³C tracer the large gross turnover of CO₂ with oceanic and terrestrial reservoirs can change atmospheric δ¹³C in the absence of a net flux, if the exchanging reservoirs are out of isotopic equilibrium. Regional disequilibria, particularly in the oceans, can be appreciable and are heterogeneous, so that it is difficult as yet to determine global average values. A large number of process studies and surveys of surface carbon isotopic composition in recent years, when fully assimilated, are expected to go part way to improving estimates of global isotopic disequilibria.

A further barrier to reducing uncertainties in terrestrial fluxes derived from atmospheric δ¹³C data is the limited spatial coverage of high precision isotopic observations, stemming in no small part to calibration uncertainties which have so far generally prevented merging of data from different sampling and measurement networks. Calibration uncertainties within a network are also implied in the serious conflict between published records of inter-annual variability in global terrestrial and oceanic exchanges. In each case the uncertainties are considerably larger than quoted precisions of individual network results. (This should be seen in the context that the precision requirements for global carbon budgeting using atmospheric δ¹³C measurements are close to an order of magnitude higher than for conventional δ¹³C applications). Since 1991, an "operational inter-calibration" has been developed between NOAA and CSIRO networks which is now monitoring comparability to within around 0.01 per mil in δ¹³C in seasonal values. A number of previously unidentified systematic effects have been identified in each laboratory. Coupled with improved conventional high pressure cylinder calibrations the operational inter-calibration is on the verge of providing spatial coverage of order 100 global sites with high precision and unprecedented robust verification.

For further information concerning these and related issues, members of the Panel are invited to contact Dr Roger J Francey (rjf@dar.csiro.au).

7. GLOBAL CHANGE ISSUES

7.1 ANTHROPOGENIC CO₂

With improved accuracy of measurements and a large increase in observations of carbon system parameters and nutrients, estimates of anthropogenic CO₂ uptake in the oceans can be improved or verified. Three different approaches can be taken to quantify anthropogenic CO₂ uptake:

- (i) Use of general ocean circulation models (GCM) incorporating biogeochemical models with differing levels of sophistication (e.g., Sarmiento [1992]).
- (ii) Determine the difference in carbon uptake compared to previous cruises by multi-variate techniques [Wallace, 1995] or by comparison with preformed values along density horizons.
- (iii) By extrapolating preformed DIC values from the surface to the interior and subtracting the increase in DIC due to remineralization and calcium carbonate dissolution. This method was first proposed by Brewer, and Chen and Millero [1978; 1979] and has recently been improved by Gruber et al.[1996].

A comparison of approach (i) and (iii) has recently been performed for the Atlantic along nominally 25°W from 40°S to 60°N using a dataset obtained during the 1991/93 NOAA/OACES cruise. General trends are similar with large calculated uptakes in the North Atlantic and smaller uptakes in the tropical and sub tropical gyres. Specific inventories from the three methods differ by about 20 % with the GCM providing the smallest estimate (see Figure 4). The large uptakes inferred for the North Atlantic by Chen and Millero [1979] can be in part explained by the "anomalous" AOU values and air-sea pCO₂ disequilibria in this region and/or by incorrect assumptions about winter outcrop values. Given the large quantity of high-quality data, it is unlikely the limitations for the uptake estimates are attributable to the DIC data, the suspects are the assumptions about concentrations of DIC, A_T and O₂ in the outcrop regions, and estimates of photosynthetic coefficients (Redfield ratios).

8. SOUTHERN OCEAN IRON EXPERIMENTS

A. Watson reminded the Panel of the result of the Pacific ocean "Ironex" experiments which provided conclusive evidence that iron supply was important in determining CO₂ concentrations in the surface waters of the equatorial Pacific. However, our present understanding of the carbon cycle suggests that only in the Southern Ocean would such effects have a substantial influence on atmospheric pCO₂ values. It thus becomes of increasing importance to discover whether similar effects can be observed in the "high nutrient low chlorophyll" regions of the Southern Ocean.

A proposal to test Southern Ocean iron limitation, submitted to US-JGOFS in late 1995, was turned down, as was a proposal submitted to the U.K's NERC in 1996. In both cases the reasons for

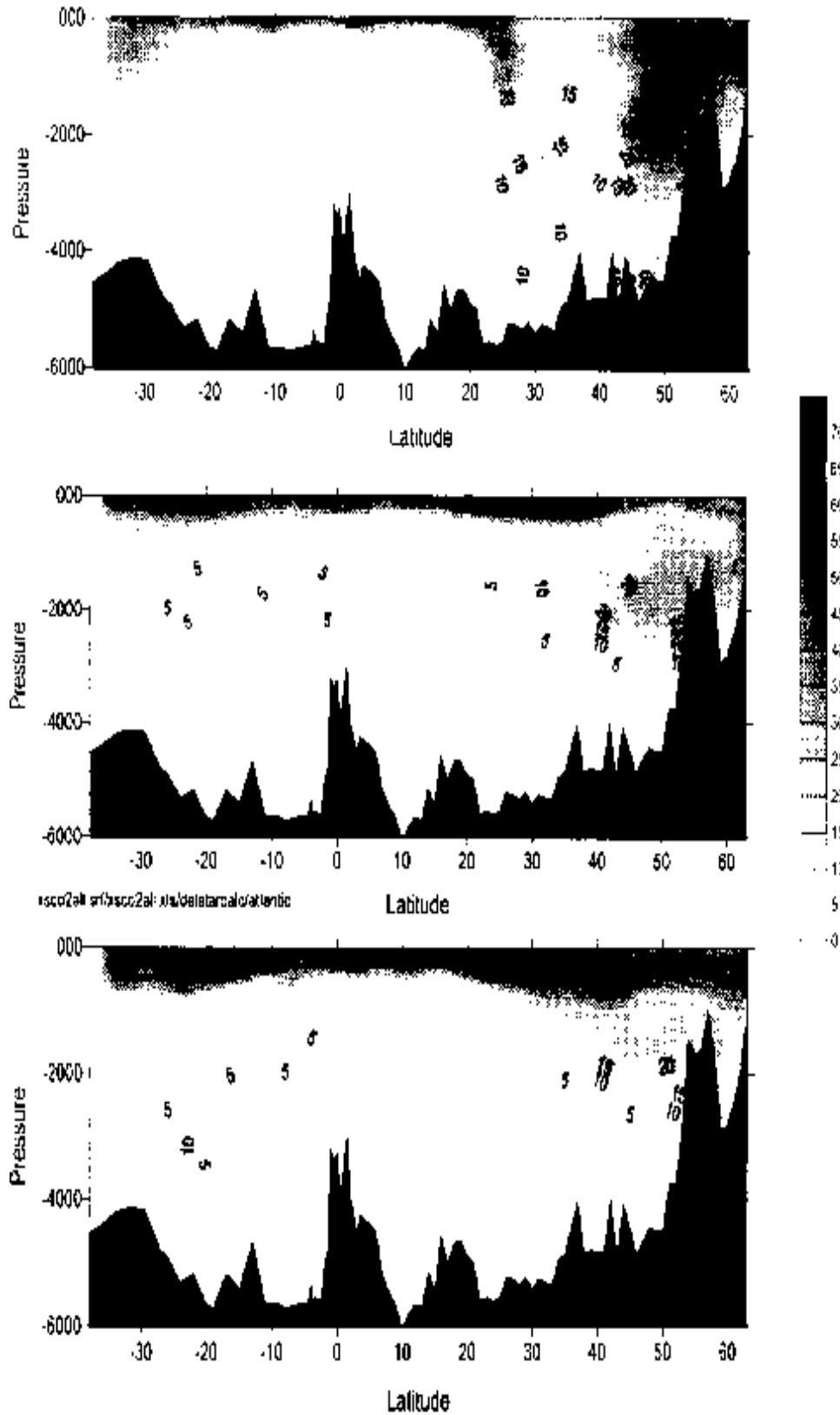


Figure 4.
Anthropogenic CO₂ input (in mol/kg) determined by using:
(a) the method proposed by Chen et al. 1979;
(b) the Princeton 3-D Ocean circulation model; and
(c) the method of Gruber et al. (1996).

declining the proposals were not related to the quality of the science, but rather to logistical and political constraints. However, proposals are now funded by a European consortium and a New Zealand-led group, and it seems very likely that "Southern Ocean Ironex" will take place before the end of the decade

C.S. Wong claimed that the North Pacific was also important for such studies. It is episodically "fertilized" by a variety of atmospheric iron sources and this will have implications for phytoplankton speciation and their genetic ability to use iron.

The Canadians are thus planning an enclosure in conjunction with the Japanese Central Reserach Institute of the Electric Power Industry (CRIEPI). This will examine the effects of iron on productivity and phytoplankto speciation, and on areas such as the production of DMS.

9. EMERGING TECHNOLOGIES

9.1 AUTONOMOUS OCEAN SYSTEMS

Liliane Merlivat updated the Panel on developments regarding the CARIOCA Buoy system. It has been deployed successfully in the Greenland Sea on a drifter and in the Mediterranean Sea on a mooring with an additional feature of a wind- speed sensor mounted on top of the ARGOS buoy.

At the DYNAMED site (JGOFS time-series mooring) during the period May 1995 to March 1996, both pCO₂ and SST were continously measured and pCO₂ at constant temperature was also computed. Effects of deepwater mixing will be to increase pCO₂.

Another test, 16 January to March 1997, The fluorometer for Chl-a detected changes due to a big spring bloom and mixing. Ten hours after the wind increased, fCO₂ also increased. It also detected a large biological change in spring with a large chl-a increase. In March-June 1997, SST and fCO₂ both increased, but when corrected to 13°C, fCO₂ at 13°C was quite constant.

The CARIOCA test in the Greenland Sea gyre was successful in -1°C waters on a drifting buoy, from 75°N 5°W to an island in the south of Norway (15°E). The major change in fCO₂ was due to mixing of deep waters, with minor changes due to gas exchange and the solubility effect. Diurnal changes in Chl-a was also recorded clearly.

A test in the equatorial Pacific was successful for three weeks, but then failed due to fouling.

Andrew Watson described two new features: (i) the addition of pH to the IMCORP buoys so that pH can be estimated along with pCO₂ since both systems use the same dye; and (ii) using a ship-of-opportunity to do pCO₂ (photometric dye), pH and DIC (LICOR IR) worked very well. For DIC the accuracy was $\pm 6 \mu\text{M}$ for a 3 minute measurement and improved to $\pm 4 \mu\text{M}$ for a 20 minute measure.

Andrew Dickson showed results of tests of an underway pH system. The pH stabilized to within 0.001 after half an hour. The reliability has improved to the point where others can use it with minimum instruction. Now the system can be kept working for three to four weeks. It has been successful in detecting changes due to upwelling and composite changes due to mixing and productivity.

Rick Wannikhof alerted the Panel to the installation on two TOGA moorings, of MBARI analyzers for f CO₂ and nutrients. The installation was made about six months ago and looks promising. He indicated there were plans for outfitting the new NOAA ship as a test bed for autonomous sensors. MBARI plans to install sensors for pCO₂, TCO₂ and Chl-a on the NOAA ship.

9.2 ATMOSPHERIC INSTRUMENTATION

Graeme Pearman's report provided descriptions of new instrumentation for atmospheric measurements as follows:

- (i) Absolute measurement standards. The University of Colorado and the Climate Monitoring and Diagnostics Laboratory, Boulder have developed a manometric system for absolute calibrations of CO₂-in-air gas mixtures. The purpose is to routinely calibrate CO₂ standards for use in the propagation of the CO₂ calibration scale world-wide. Intercalibration between sites is necessary in order to compile comparable global data sets. The system has been tested to 00.1 ppmv but is not fully operational yet. Further information is available in:

Cong Long Zhao, Pieter Tans and Kirk Thoning (1997). A high precision manometric system for absolute calibrations of CO₂ in dry air. *J.Geophys.Res.*, **102**, 5885-5894.

- (ii) *In Situ* Atmospheric Measurement. The CSIRO Division of Atmospheric Research, Melbourne is developing a fully computer controlled, remotely controlled CO₂ analyser system for performing baseline atmospheric observations of CO₂ at Cape Grim Observatory, north-west Tasmania. It uses non-dispersive technology as with most existing monitoring systems.

There are several objectives of the new instrumentation:

A. reduction by a factor of 20 in the consumption of reference and calibration gases achieved through low flow rates and reduced internal volumes and surface areas.

A reduction in the number of levels in the calibration scale hierarchy.

An increase in precision and accuracy, achieved by computer control of all instrument operating variables, namely temperature, pressure, and flow.

- Ability to perform in situ measurements, calibration standard measurements and flask measurements all on the same system.
 - A reduction in operating costs, achieved by automation of the measurement process.
 - Preliminary calibration runs indicate performance to better than 30 ppbv is possible.
- (iii) Simultaneous Measurement Of Multiple Species Including CO₂. The University of Wollongong has developed a prototype instrument capable of measuring the concentration of several species in air simultaneously, including CO₂. It uses Fourier-transform infrared technology. It is well suited to research applications involving chambers enclosing plant and soil materials. The precision is species dependent, and is affected to some degree by the ability to accurately model all the spectral components. Some field experience has been gathered. For further information see:

M B Esler, D W T Griffith, S R Wilson and L P Steele (1996) Carbon monoxide, nitrous oxide, methane and carbon dioxide- trace gas analysis by Fourier Transform Infrared (FTIR) spectroscopy. In Baseline Atmospheric Program, Australia 1994-95, p.117-119, CSIRO Atmospheric Research, Melbourne.

D W T Griffith (1996) Synthetic calibration and qualitative analysis of gas-phase FT-IR spectra. *Applied Spectroscopy* **50**, 59-70.

- (iv) Surface Flux Measurement. The Climate Monitoring and Diagnostics Laboratory, Boulder, is currently designing and constructing a new non-dispersive infrared analyser for use in flux measurements. The major design objective for this application is to achieve the higher

frequency response needed for flux measurements. To this end the bulk of the effort is being put into the design of a tiny measurement cell of volume 1 cm³, roughly a factor of 10 smaller than that currently available commercially. In addition, the cell shape and fittings have been designed to minimize flushing times. Commercial systems generally use simple rectangular extrusions of the cells, with characteristically poor flushing characteristics. The instrument appears to be still very much in the development stage.

10. NATIONAL REPORTS

10.1 U.S.

The NOAA Ocean-Atmosphere Carbon Exchange Study (OACES) is being revised to form a more comprehensive program. Major changes which have been implemented or will likely be implemented include:

- * The formation of the Carbon Modeling Consortium (CMC)
- * A focus on hypothesis driven research
- * A de-emphasis on the long line observational work
- * An increased emphasis on automated and autonomous instruments on moorings and ships of opportunity

In 1995 the CMC was formed under leadership of Dr. J. Sarmiento of Princeton University with primary funding by NOAA/CEDEP and augmentation by NOAA/OACES. The aim of this effort is to form a coherent and comprehensive picture of the terrestrial, oceanic, and atmospheric carbon cycles by using a combination of models and field observations. The focus on the short term will be understanding interannual variability. The OACES effort to date has concentrated on an observational strategy of atmospheric CO₂ and ¹³C measurements at approximately 30 coastal stations, and comprehensive carbon system measurements (DIC, pCO₂, pH, A_T, ¹³DIC, DOC) along long lines in the ocean. This effort was leveraged on the WOCE/WHP effort. With the end of the WOCE/WHP and completion of the baseline ocean CO₂ survey, continued sponsorship of the long line effort is in doubt. The rationale to continue the effort on select nine lines covering each ocean basin has been outlined in Taft et al. [1995]. The thought in this blueprint is that a decadal reoccupation of these lines will serve as a prudent way to detect significant changes in carbon and tracer uptake between large scale surveys like those just completed under the aegis of WOCE/WHP. However, the intent of the refocused OACES is to make it a more hypothesis-driven effort with increased emphasis on atmospheric measurements and fluxes between the ocean-atmosphere-terrestrial system.

To increase our understanding of short term variability in the global carbon cycle and to increase the numbers of samples per research dollar there will be an increased emphasis on automated and autonomous instruments on moorings and ships of opportunities. In collaboration with MBARI and with augmentation of funding by NASA, OACES has outfitted two TOGA/TAO moorings in the equatorial Pacific with pCO₂ sensors. The moorings also are equipped with automated nitrate analyzers, fluorometers, and optical sensors. The NOAA buoy tender ship, Ka'imimoana, has an underway pCO₂ instrument which will give equatorial pCO₂ data of unparalleled resolution. Furthermore the NOAA ship BROWN will be outfitted with a suite of underway sensors (DIC, pCO₂, chlorophyll, O₂) and will have a dedicated operator on all cruises. Aside from increasing our surface observations over large parts of the world's oceans, the ship will serve as a test bed for autonomous sensors for moorings and ships of opportunities.

10.2 U.K.

Since the disbanding of the CO₂ group at Plymouth in late 1995, there has been relatively little activity. A. J. Watson is currently in the process of rebuilding a CO₂ research group, based at the University of East Anglia. Activities during 1996 have included:

- (i) participation in a process study called 'PRIME' in the North Atlantic. This study used tracer-labelling techniques to study the budgets of carbon, nutrients and trace species, such as DMS, in a body of water that was tracked over a period of two weeks in the North Atlantic near 60°N, 20°W;
- (ii) participation in the Chilean JGOFS programme "Sectorial Antapagusta" cruises. These are a study of the intense upwelling region off Chile taking place in January and June 1997.

10.3 JAPAN

Japanese scientists organized an international symposium related to JGOFS at Mutsu, northern Japan, in November 1996. The title of this symposium was "Biogeochemical Processes in the North Pacific".

At the JGOFS-SSC meeting in May, Japanese JGOFS announced that the North Pacific Process Study will begin in April 1998. Japanese groups are focusing on the long-term biogeochemical observations by setting up the fixed station in the western North Pacific.

During the 7th Joint IOC-JGOFS Ocean CO₂ Advisory Panel Meeting, Japan offered to host the 2nd international ocean CO₂ symposium entitled "CO₂ in the Oceans" which will be held in Tsukuba, Japan, after December 1998. (The date was subsequently set as 18-22 January 1999.)

Internationally, the Japan Oceanographic Data Centre is a member of the JGOFS-Data Management Task Team; it also acts as the Data Management Office of Japan.

The Japanese LOICZ group is planning a project, called the Western Pacific Rim Study, to investigate the connection between physical properties to biological productivity in the marginal seas along the Asian coast, using data from the Japanese satellite MIDORI (OCTS sensor).

10.4 GERMANY

In 1996 the group at the Institute for Marine Sciences at Kiel organized an international intercomparison of underway pCO₂ systems on board the METEOR. On a cruise from Bermuda to Gran Canaria 7, groups participated with their pCO₂ systems. Also a number of related parameters were measured either by underway systems or from discrete surface samples collected along the track. On a second leg, carbon data were measured on a meridional transect along 20° W from Gran Canaria up to 60° N; C_T and A_T were measured from depth profiles at hydrographic stations and surface pCO₂ was monitored by an underway system. In early 1997, a joint cruise with the Spanish partners was undertaken on METEOR in the Canary Island region under the CANIGO program.

Investigations by the Baltic Sea Research Institute, Warnemuende, on the seasonality of the CO₂ system in the Northeast Atlantic were continued during a cruise with R.V. GAUSS in June 1996. Measurements of C_T and pCO₂ were performed along the WOCE line A1E. With regard to the Baltic Sea, a balance of the CO₂ air/seafluxes was modelled on the basis of data from a summer and a winter cruise. Additionally, measurements on C_T, pCO₂, DOC and POC in the eastern Gotland Sea were initiated in order to develop a comprehensive carbon budget for this area.

Activities at the Institute for Marine Sciences in Kiel for the next 3 years will concentrate on the synthesis of JGOFS data from the North Atlantic. This will include an inventory of data collected as well as a comparison with model output from the Hamburg GCM model that was coupled with an

improved biological model. The penetration and inventory of anthropogenic CO₂ will be evaluated from the data. Another activity will be carbon measurements in the recently started Joint Research Program on the Variability of the Thermohaline Circulation. Field work is planned for 1997 and 1999 and a minor expedition in 1998, covering the Western and Eastern North Atlantic. In cooperation with Spanish groups, the carbon system in the Canary Island-Azores Region will be investigated under the European Mast III program CANIGO. Intercalibration exercises have been carried out with the Spanish groups.

The investigation in the Northeast Atlantic by the Baltic Sea Research Institute will be continued with one cruise per year. If possible, measurements will be performed along the WOCE track A1E. Also, CO₂ research in the Baltic Sea will continue with the ultimate goal to produce carbon budgets for the Baltic Sea as a whole and its sub-basins as well.

11. LOOKING AHEAD TO THE POST- JGOFS ERA

The key questions looming for the post-JGOFS era that the Panel considered were:

- (i) What program should succeed JGOFS?
- (ii) What role should the new entity take in relationship to IGBP?

Several initiatives proposed in the past as follow-on programs have fallen by the wayside. For instance, interest in the Global Ocean Euphotic Zone Study (GOEZO) has waned and appears to have been dropped by IGBP. Andrew Watson informed the Panel about a SCOR and IGBP working group which met in January 1997 to consider the future of marine-biogeochemistry climate studies. The working group proposed a new project, the "Surface Ocean - Lower Atmosphere Study" (SOLAS), with some of the elements of GOEZO embodied in it. but with a new approach. The project would include observations and modeling built around hypotheses rather than modeling efforts to fit the data. The following goals were proposed for SOLAS:

- (i) to formulate and test hypotheses for key interactions between the marine biogeochemical system, the atmosphere and climate;
- (ii) to quantify cause and effect in those interactions;
- (iii) to incorporate this new understanding into models.

Example hypotheses in need of testing given by the working group included:

- (i) Marine sulphur emissions have a substantial effect on climate by influencing cloud albedo.
- (ii) The influence of changes in marine biogeochemistry on ocean uptake of anthropogenic CO₂ in the next century will be small.
- (iii) The principal effect on the marine production in a warmer world would be a decrease in global productivity, consequent upon a slowing of the thermohaline circulation.

Further development and prioritisation of these principal hypotheses will, however, be part of the planning of the programme - it is not intended for these to be set in stone at this stage.

The next IPCC assessment was discussed. Watson gave his impressions of the state of ocean CO₂ in the IPCC scheme of things. Research on ocean CO₂ problems has become a lower priority in the large environmental science plans. This can be attributed to several factors:

- (i) The IPCC 1995 report allocates the "missing sink" to terrestrial biosphere uptake. The ocean uptake is given at 2.0 ± 0.8 GtC/yr at 95 % confidence interval. This estimate is based on models and does not have a strong observational basis. This hard number and the lack of a

clear strategy (or ability) to constrain this value further has led to the impression that the ocean CO₂ problem has been solved.

- (ii) The role of CO₂ on greenhouse forcing is well constrained compared to other greenhouse agents. The uncertainty in the global warming potential of CO₂ is significantly smaller than, for instance, the role of clouds, aerosols, or water vapor on radiative forcing.
- (iii) Particularly in the US, climate and global change issues have been binned according to time scales; seasonal to interannual, and decadal to centennial. Ocean carbon has been put in the DEC-CEN program. Since seasonal to interannual problems often are more tractable and often appear to have a greater societal relevance (by nature of our short memories!), much of the research support has been allocated to seasonal to interannual issues.

The Panel concluded that the ocean CO₂ issues should be viewed in a different framework. They believed the focus of CO₂ research should be global change rather than the greenhouse gas issue which is well constrained. Several issues with respect to CO₂ research are of global significance, in particular feedback issues and interannual variability. We have little insight on what will happen with the ocean carbon cycle in response to global change. Two end-member scenarios are: a strong positive feedback due to SST increase, causing pCO₂ increase due to SST increase (thermodynamic effect), and pCO₂ decrease due to a more efficient biological pump in warmer oceans (biological effect). Recent modeling work [Sarmiento and Le Quere, 1996] suggest that the largest decrease in oceanic uptake capacity will occur due to global warming because of decreased thermohaline overturning. Atmospheric observations of CO₂ and ¹³C during the 1980s suggest large (1-3 GtC/yr) interannual variability in oceanic and terrestrial uptake [Francey et al., 1995; Keeling et al., 1995]. The standard deviation in oceanic uptake based on the analysis of Francey [1995] is 1.5 GtC /yr. Variations in the equatorial Pacific CO₂ source regions because of El Niños can account for roughly 1/3 of the variation but we have no firm evidence of other reasons for the large apparent interannual variability. Iron fertilization by volcanic ash from mount Pinatubo has been suggested as cause for the slowdown in atmospheric CO₂ increase in the early nineties but this hypothesis has yet to be proven.

The Panel concluded that future oceanic carbon cycle research should focus on these issues of climate and global change feedbacks and interannual change. Some of the issues can be best approached by hypothesis-driven studies involving deliberate perturbations.

12. REFERENCES

Francey, R.J., P.P. Tans, C.E. Allison, I.G. Enting, J.W.C. White, and M. Trolier, Changes in oceanic and terrestrial carbon uptake since 1982, *Nature*, 373, 326-330, 1995.

Keeling, C.D., T.P. Whorf, M. Wahlen, and J. van der Plicht, Interannual extremes in the rate of rise of atmospheric carbon dioxide since 1980, *Nature*, 375, 666-670, 1995.

Keeling, R.F., S.C. Piper, and M. Heimann, Global and hemispheric CO₂ sinks deduced from changes in atmospheric O₂ concentration., *Nature*, 381, 218, 1996.

Sarmiento, J.L., and C. Le Quere, Oceanic Carbon Dioxide Uptake in a Model of Century-Scale Global Warming., *Science*, 274, 1346-1350, 1996.

Taft, B., J. Bullister, R. Feely, J. Johnson, and R. Wanninkhof, NOAA Carbon dioxide tracer program: an integrated approach to decadal ocean climate change, Unpublished, 1995.

Brewer, P.G., Direct observation of the oceanic CO₂ increase, *Geophys. Res. Lett.*, 5, 997-1000, 1978.

Bryan, K., and L.J. Lewis, A water mass model of the world ocean, *J.Geophys. Res.*, 84, 2503-2517, 1979.

Chen, G.-T., and F.J. Millero, Gradual increase of oceanic CO₂, *Nature*, 277, 205-206, 1979.

Esbensen, S.K., and Y. Kushnir, The heat budget of the global ocean: An atlas based on estimates from surface marine observations, Oregon State University, Corvallis OR, 1981.

Gruber, N., J.L. Sarmiento, and T.F. Stocker, An improved method for detecting anthropogenic CO₂ in the oceans, *Global Biogeochem. Cycles*, 10, 809-837, 1996.

Liss, P.S., and L. Merlivat, Air-sea gas exchange rates: Introduction and synthesis, in *The Role of Air-Sea Exchange in Geochemical Cycling*, edited by P. Buat-Menard, pp. 113-129, Reidel, Boston, 1986.

Sarmiento, J.L., J.C. Orr, and U. Siegenthaler, A perturbation simulation of CO₂ uptake in an ocean general circulation model, *J. Geophys. Res.*, 97, 3621-3645, 1992.

Takahashi, T., R.A. Feely, R. Weiss, R. Wanninkhof, D.W. Chipman, S.C. Sutherland, and T.T. Takahashi, Global air-sea flux of CO₂: An estimate based on measurements of sea-air pCO₂ difference, in *NAS Colloquium volume on Carbon Dioxide and Climate Change*, edited by C.D. Keeling, NAS, Washington, 1997.

Tans, P.P., I.Y. Fung, and T. Takahashi, Observational constraints on the global atmospheric CO₂ budget, *Science*, 247, 1431-1438, 1990.

Wallace, D.W.R., Monitoring Global Ocean Carbon Inventories, Ocean Observing System Development Panel, 1995.

Wanninkhof, R., Relationship between gas exchange and wind speed over the ocean., *J. Geophys. Res.*, 97, 7373-7381, 1992.

ANNEX I

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ANNEX III

AT-SEA INTERCOMPARISON EXERCISE

Technical Aspects

The intercomparison exercise consisted almost entirely of continuous underway sampling of surface seawater. Only four CTD stations were included in the programme. In order to encounter the widest possible range of surface seawater temperatures and salinities a cruise track via the Flemish Cap off Newfoundland was chosen. All participating groups operated their underway pCO₂ systems simultaneously on a separate seawater pumping system and a consistent suite of calibration gases, all of which were provided by the organizer.

As with most up-to-date research vessels, the R/V METEOR provides a special seawater pumping system for scientific purposes. From experience it is known that the use of this kind of pumping systems for measurements of dissolved gases is hampered by a number of problems. Pump action may cause cavitation when underpressure is applied to the water flow, thus making undisturbed gas measurements nearly impossible. Due to the location of the seawater intake (i.e. bow intake on R/V METEOR) air bubbles are also introduced into the water lines in rough seas. This again possibly biases the concentration of dissolved gases, at times, or even makes seawater sampling technically impossible. Furthermore the unavoidable warming of seawater during its travel from the seawater intake to the user is significant. In the case of pCO₂ measurements it is desirable to have the temperature change as little as possible.

Due to the sluggish equilibration of CO₂ between gas and water phase, sampling for CO₂ measurements (e.g., pCO₂, pH, C_T, A_T) is less susceptible to artefacts caused by imperfect pumping techniques as compared to non-reactive gases like oxygen. Nevertheless a careful sampling technique was an important aspect of the exercise. For this reason a simple and reliable underway pumping system (see also; KORTZINGER et al, 1996) was designed for use in the "moon pool" of R/V METEOR. The system consisted of a small conductivity-temperature-depth probe (CTD probe "ECO", ME Meerestechnik-Elektronik GrnbH, Trappenkamp, Germany) for measuring seawater temperature and salinity at the intake as well as a submersible pump, both of which were installed in the bottom plate of the "moon pool". To make the system as flexible as possible a separate GPS receiver (GPS 120, Garmin/Europe Ltd., Romsey, Hampshire UK) was included, CTD and navigational data from the GPS were continuously logged on a computer.

All seven underway pCO₂ systems were operated simultaneously for most of the time between June 7 and June 17. Technical problems which occurred in some of the systems only caused short interruptions. Only one system suffered heavy damage in the infrared gas analyzer and had to quit measurements on June 16. The two underway spectrophotometric pH systems were operated throughout the cruise. The newly modified coulometric SOMMA system for underway determination of C_T was tested successfully at sea and contributed 452 high-quality underway measurements along the cruise track. This new application of the well-known SOMMA system demonstrated its potential for high-quality, high-resolution surface measurements of C_T. Synchronized with the XBT survey, a total of 57 discrete samples were taken from the seawater supply and were analyzed for C_T and A_T. The discrete pCO₂ measurements could not be carried out on the same schedule; on only about 25 XBT stations were samples taken for this parameter.

In addition to the various surface measurements - whether continuous or discrete - four full depth CTD stations were carried out. Samples were drawn for measurements of all four CO₂ system parameters (pH, pCO₂, C_T, A_T) thus yielding the highest possible overdetermination of the marine CO₂ system.

Participants had all their raw data delivered to the organizer by the end of the cruise. However, final data were not available in most cases in time for the writing of this summary. These final data sets were to be submitted to the organizer by September 19, 1996. After that, much thought would be needed to go into teasing out the information contained in the data collected and into preparation of the final exercise report. The ultimate aim was to provide information on the comparability of data sets, which is

a crucial point in the current international effort to bring together all available $p\text{CO}_2$ data, and to develop recommendations for future field measurements of $p\text{CO}_2$.

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REFERENCES

Johnson, K.M., A. Kortzinger, L. Mintrop and J.C. Duinker. Coulometric total carbon dioxide analysis for marine studies: The feasibility of continuous unattended measurements aboard stationary or underway platforms, in prep., to be submitted to Mar. Chem.

Kortzinger, A., H. Thomas, B. Schneider, N. Gronau, L. Mintrop and J.C. Duinker, 1996. At-sea intercomparison of two newly designed underway $p\text{CO}_2$ systems - Encouraging results. Mar. Chem., 52: 133-145.

ABBREVIATIONS

A_T	Total alkalinity	$p\text{CO}_2$	Partial pressure of CO_2
CTD	Conductivity-Temperature-Depth probe	XBT	Expendable BathyThermograph
C_T	Total dissolved inorganic carbon	GPS	Global Positioning System

ANNEX IV

Letter sent to John Church and Breck Owens (co-chairs of the WOCE SSG), copy to John Gould, Director of the WOCE IPO, Roger Hansen, Chair of JGOFS, John Field, President of SCOR, Hartmut Grassl, Andrew Watson and Douglas Wallace.

Dear John and Breck,

On the agenda of the recent meeting (2-4 June 97) of the IOC-JGOFS CO₂ Panel was a presentation and discussion concerning an intercomparison of inorganic carbon data collected on different intersecting WOCE cruises as part of the JGOFS Global Survey of CO₂ in the oceans. This work, which has just begun with an analysis of US data collected in the Pacific Ocean, is a very important aspect of the earliest stages of data synthesis. The purpose is to ensure that the global CO₂ data set is internally consistent with respect to accuracy of measurements taken by different groups. It is intended to extend this analysis to all ocean basins sampled during the survey. This is essential because, despite the best efforts of section-by-section quality control efforts, there is a potential for systematic biases of varying signs and amplitudes to exist between individual cruise data sets. While the Panel is focussing on CO₂, Panel members believe this is true of all biogeochemical parameters. This includes WOCE parameters such as dissolved nutrients and oxygen for which, unlike CO₂, no universally accepted Certified Reference Materials exist. Biases can exist because calibrations, and therefore absolute accuracy of these parameter measurements is dependent on the in-house ability of individual measurement groups to prepare and analyse their own primary standards.

With this in mind, the Panel instructed me to draw the attention of the WOCE scientific community to the fact that the inorganic carbon data collected during the WOCE Hydrographic Programme benefited from a very extensive, internationally co-ordinated quality control programme. Notably, for almost every cruise on which inorganic carbon data were collected, there were corresponding measurements of Certified Reference Materials. The results of these analyses form the basis for an assessment of the absolute accuracy and internal consistency of the global CO₂ data set and it is becoming apparent that the data sets, in general, exhibit remarkable consistency.

The relevance of this for WOCE is, that despite the significant variability in the concentrations of individual parameters in the deep ocean (which complicate simple direct comparisons of data collected on different cruises), the stoichiometric relations between inorganic carbon and the concentrations of nutrients and oxygen are relatively robust and invariant. Analyses of results from individual cruises and high-quality historical data show that such multivariate relations hold over extensive spatial and temporal scales. Therefore a multivariate approach to the analysis of cruise data allows astigmatic biases to be identified more reliably than via direct comparisons.

The Panel therefore would like to suggest that globally-consistent inorganic carbon data collected during the JGOFS Global CO₂ Survey on WOCE Hydrographic Programme cruises could be used for an assessment of the internal consistency of WOCE nutrient and oxygen data. The CO₂ data set, because it benefited from the availability of a universally accepted Certified Reference Material, can form the basis for a multivariate analysis of the nutrient and oxygen data collected during WOCE as part of the WOCE synthesis process.

The best person with whom to discuss this further would be Panel member Douglas Wallace, Technical Director of US DOE's Global CO₂ Survey, He stands ready to help if need be and can be contacted as follows:

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Sincerely,

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ANNEX V

THE TOTAL ALKALINITY (A_T) IN ANOXIC WATERS OF THE BLACK SEA AND IN SEA-RIVER MIXTURE ZONES

It is well known that the majority of the methods for the determination of the carbon system are adapted for the average ocean conditions. When we begin to calculate components of the carbon system of the waters with anomalous salinity and hydrochemical composition that differs from the world-ocean average, certain difficulties appear. Though not important when we deal with direct measurements, it becomes critical when calculating the components. One aspect of this question - the calculation of A_T is discussed below using the example of the anoxic waters of the Black Sea and of the sea-river mixture zones.

The peculiarities of the hydrological and hydrochemical regimes of the Black Sea (the heavy continental in-flow and the stable layering between the upper and deep sea waters) create the conditions for the accumulation for dissolved inorganic carbon and other nutrients in the water column to a greater degree than in the other ocean basins. One of the complicated methodological problems that appears in the connection with this fact is the determination of A_T in deep waters and the interpretation of the results. The results of the A_T in the Black Sea waters cannot be determined as the sum of the carbon and borate alkalinity as it is for the main open ocean waters of the world (Modern Methods ..., 1992). The chemical composition of the waters of the anoxic zone of the Black Sea does not allow such a simplification.

The question of the composition of the total alkalinity of the Black Sea waters has its principal significance when using alkalinity in relation to studying the carbon equilibrium. The use of the simplified A_T calculation model may lead to large errors in the results. The calculation of all the parts of the A_T is very complicated and most likely even impossible. It is necessary to determine when the error band in calculations will be in the acceptable range and, at the same time, when the calculations will be possible and when measurements can be provided for, practically speaking.

For this purpose the main component parts of the A_T in the anoxic waters of the Black Sea were examined. The work was carried out based on the results of the scientific expeditions on board ships of the Russian Academy of Sciences (Makkaveev, 1995; Makkaveev, Bubnov, 1993) and the American expedition on the ship **KNOR** (Goyet *et al.*, 1991) and averages of the vertical distribution of the pH, A_T and the main nutrients (Zhorov *et al* 1980); Skopincev, 1975). The quantities contributing to the A_T were examined in the following way:

$$A_T = A_c + A_b + A_p + A_{si} + A_s + A_n$$

with A_c - the carbon part of the A_T , A_b - borate alkalinity, A_p - phosphate alkalinity, A_{si} - silicate alkalinity, A_s - alkalinity associated with hydrogen sulphide, A_n - alkalinity associated with nitrogen formation.

Borate Alkalinity

In the deep waters, the A_b part of the A_T falls to 0.3% and becomes less significant than the other components.

Sulphide and Hydrosulphide Alkalinity

The greater part of A_T in deep waters of the Black Sea after the carbon part is due to sulphide and hydrosulphide alkalinity which is related to the products of ionization of the hydrogen sulphide in waters: $[HS^-] + [S^{2-}]$.

The As influence on the A_T can be neutralized by precipitation of the hydrogen sulphide with $HgCl_2$: $HgCl_2 + H_2S = HgS + 2H^+ + 2Cl^-$, adding it to the sample before test (Goyet, 1991). The other way is by calculation based on the measurements of A and H_2S , using thermodynamic constants of dissociation of hydrogen sulphide (Volkov, 1984).

Nitrogen Alkalinity

Nitrate- and nitrite-nitrogen in the waters of the Black Sea deeper than 200m very quickly decreases to 0 (Skopincev, 1975). The main part of inorganic nitrogen is contained in the form of ammonium. Ammonia that is formed inside the anoxic zone does not oxidize to nitrate but is stored in these waters. The concentrations of ammonium-nitrogen in the Black Sea is very high and may reach more than 1g N/l in the near-bottom layer. But we cannot say for sure how it can influence the quantity of alkalinity. To define more precisely the contribution of ammonium on the A_T , the experimental work was done (Makkaveev, 1995) which showed that if ammonia exists in water in the form of the free ammonium it is necessary to take it into consideration. Volkov believes that the influence of this ion is 10 times less than according to my data.

Silicate Alkalinity

The concentration of dissolved inorganic silicate in the anoxic Black Sea waters rises considerably in comparison with the corresponding deep waters of the world ocean. Its concentration increases from 3 - 4 mg Si/l in the upper boundary of the anoxic zone up to 8 (and more) mg Si/l at 2000m depth (Skopincev, 1975). The dissolved inorganic silicate is presented in the main in form of the monomer of the orthosilicate acid (H_4SiO_4) and its ions (Gusarova, 1977). The contribution of the metasilicic acid (H_2SiO_3) to the total amount of the dissolved silicate is minor, only about 2% (Popov *et al.*, 1979). The concentration of the other forms of the dissolved inorganic silicate in waters is still less and their influence on the A_T value is negligible. The concentration of the Si increases with depth but the degree of dissociation of the H_4SiO_4 and H_2SiO_3 decreases with the depth (it is linked to the decreases of the pH value). These processes are balancing and for this reason the change with depth of the silicate alkalinity is small compared to the other components of the A_T .

Phosphate Alkalinity

The dissolved inorganic phosphorus is basically in the form of orthophosphoric acid (H_3PO_4) and its ions. The concentration of the phosphate rise in comparison with the world ocean is the same as that of the other nutrients. In the natural pH range (7 - 8), the $[HPO_4^{2-}]$ ion predominates (Popov *et al.*, 1979). According to Skopincev, (1975), the relative value of the $[HPO_4^{2-}]$ in deep waters is about 95% (from the total H_3PO_4), the value $[H_2PO_4^-]$ is about 4%. The contribution of the other form of phosphate to the A_T value can be neglected. It compares well with the calculations of the concentration of the orthophosphoric acid ions (Gusev *et al.*, 1989).

The results of the calculations are shown in Table 1.

TABLE 1

The average value of the parts of the total Alkalinity calculated with the use of data (Zhorov *et al* 1980); Makkaveev, Bubnov, 1993; Makkaveev, 1995; Skopincev, 1975).

Depth (m)	Ac	Ab	Ap	Asi	As	An
	mg-eqv/l					
50	3.240	0.031	0.001	0.015	0.000	0.003
75	3.247	0.023	0.002	0.014	0.000	0.004
100	3.214	0.020	0.003	0.014	0.000	0.005
150	3.272	0.020	0.006	0.016	0.005	0.012
200	3.335	0.020	0.009	0.020	0.020	0.018
300	3.380	0.020	0.011	0.022	0.057	0.026
400	3.443	0.020	0.012	0.025	0.090	0.040
500	3.574	0.019	0.013	0.024	0.096	0.055
750	3.778	0.020	0.015	0.028	0.175	0.068
1000	3.887	0.021	0.015	0.029	0.200	0.076
1250	3.878	0.020	0.016	0.032	0.215	0.078
1500	3.916	0.018	0.016	0.027	0.222	0.080
1750	3.958	0.019	0.016	0.034	0.222	0.086
2000	3.967	0.018	0.016	0.029	0.241	0.089

As may be seen from Table 1, at the 200 metre depth level the hydrosulphide, silicate and ammonium alkalinities approach equality with the boron alkalinity and, when deeper, considerably surpass it. The relative value of the boron alkalinity in the deep waters is so little (about 0.3% of the total alkalinity) that it need not be taken into consideration. If the other components are not taken into consideration, however, (i.e., the ions of the hydrogen sulfide, ammonium, orthosilicate and orthophosphoric acid) the error when calculating the components of the carbon system in the anoxic Black Sea waters can reach 11%. The analysis of the vertical distribution of the dissolved inorganic carbon and comparison of it with the distribution of hydrogen sulphide and ammonium show that its increase with depth is greater than can be explained by only the microbial transformation of sulphur and the formation of the ammonium.

Sea-River Zones

For the waters of the sea-river mixture zones the decrease of the salinity and entrance of the nutrient elements also lead to redistribution of the A_T components. In Table 2, their contribution to the A_T for the Ob river and the Enisey river are shown.

TABLE 2

Values of Alkalinity components to the A_T as a function of salinity in the Ob and Enisey rivers

S	A_T	Ab	Asi	Ap	An
0 - 5	1.141	<0.001	0.022	<0.001	0.002
5 - 10	1.293	0.005	0.006	0.002	0.007
10 -15	1.371	0.010	0.008	<0.001	0.002
15 - 20	1.708	0.017	0.004	0.001	0.003

One can see that with the decrease of the salinity the silicate part of the A_T increases. The phosphate and ammonium parts can reach high values in the near-bottom layer, where a great quantity of the organic matter is present.

One must approach each case individually taking into consideration the given task and whether the effect on the A_T of the various components is significant.

References

Goyet C., Bradshaw A.L., Brewer P.G. The Carbonate System in the Black Sea. *Deep-Sea Research*, v.38, N 2A, 1991, p.S1049 -S1068.

Gusarova A.N. The Silicate in the Ocean's Waters. Ph.D. Thesis, Moscow, Academy of Sciences of the USSR, Institute of Oceanology, 1977, p153.

Gusev V.V., et al. Phosphorous system. *Chemistry of the Ocean's Waters*. Moscow, Nauka, 1989, p.204-253

Makkaveev P.N. Dissolved Inorganic Carbon and the Total Alkalinity in Anoxic Waters of the Black Sea. *Oceanology*, 1995, v.35, N 4, c.537-543.

Makkaveev P., N. Bubnov P.V. The Peculiarities of the Vertical Distribution of the Carbon System Components in the Aerobic Zone of the Black Sea. *Oceanology*, 1993, v.33, N 3, c.354-359.

Modern Methods of Ocean Hydrochemical Investigations. Moscow, Academy of Sciences of the USSR, Institute of Oceanology, 1992, p200 .

Popov N.I., Fedorov K.N., Orlov V.V. *Ocean's Waters*. Moscow, Nauka, 1978, p327.

Skopinets B.A. The Shape of the Modern Chemical Composition of the Black Sea Waters. Moscow, Nauka, 1975, p336 .

Volkov I.I. The Geochemistry of the Sulphur in Sediments. Moscow, Nauka, 1984, p272.

Zhorov V.A., et al. The Peculiarities of the Hydrochemical Regime of the Black Sea. Complex Investigation of the Black Sea. Kiev, Naukova Dumka, 1980, p.165-188.