Intergovernmental Oceanographic Commission
Reports of Meetings of Experts and Equivalent Bodies

Joint IOC-JGOFS CO_2 Advisory Panel Meeting

Sixth Session

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ANNEXES

1. WELCOMING

Chairman Andrew Watson opened the sixth session of the IOC-JGOFS Advisory Panel on Ocean CO_2 at 08:30, 27-30 January 1996, in Mayaguez, Puerto Rico. After welcoming the Panel members and guests he introduced the new members and asked the guests to introduce themselves. The list of participants is in Annex II. He then expressed his appreciation to Frank Millero and those from the University of Puerto Rico at Mayaguez responsible for all the thoughtful arrangements for the meeting. The Panel meeting followed directly after the conclusion of the first International Symposium on CO_2 in the Oceans which was held at the University, 22-26 January 1996.

2. ADOPTION OF THE AGENDA

It was anticipated that a number of issues would emerge from the CO_2 symposium preceding this Panel meeting that could profitably be addressed by the Panel. Moreover, the presence of members of several ocean CO_2 science teams at the symposium provided a unique opportunity to have an expanded discussion on these issues. Accordingly, it was agreed that the first day of the agenda would be open to symposium participants and would address important items that arose during the symposium. L. Merlivat and A. Poisson compiled a list of the most salient of these from the view of the Panel's interest and prepared a mini-agenda for discussion during the first day. These were incorporated in section 3 (below) of the agreed agenda (Annex I).

3. SYMPOSIUM ISSUES

3.1 THERMODYNAMIC MODELS FOR THE CARBONATE SYSTEM IN SEAWATER

Thermodynamic models for the carbonate system in seawater are used for predicting the carbonate system using limited observations, for accurate CO_2 fugacity calculations (especially in deep waters), for predicting the saturation state of seawater with respect to carbonate minerals, and for the prediction of carbonate chemistry in ocean general circulation models. The drawback to this approach is that measurements of pCO_2 on discrete samples are often made at 20°C, and a thermodynamic model is needed to obtain pCO_2 values at the *in situ* temperatures. Using different equilibrium constants gives differences in pCO_2 of tens of micro atmospheres for large temperature corrections (several degrees). For surface waters, pCO_2 measurements should be made at the *in situ* temperature whenever possible. For deep waters it is probably important to continue measuring all 4 parameters until the thermodynamic consistency is better understood.

These thermodynamic models use experimental data (measured carbonate parameters and equilibrium constants) to determine the concentration of carbonate species in seawater. Carbonate equilibrium constants have been determined several times within the last two decades because of the uncertainty of their accuracy, and there are now 5 different sets of K_1 and K_2 which are commonly used. By measuring all 4 of the carbonate parameters (total alkalinity, total CO_2, $f(CO_2)$ and pH) it is possible to assess the thermodynamic consistency of models when using the different sets of K_1 and K_2. Several presentations showed that the equilibrium constants of Roy et al. (1993) and Goyet and Poisson (1989) work best for some sets of laboratory and field data.

The question was raised about whether oceanographers should be working on these thermodynamic questions or whether they should focus principally on measuring the parameters of interest directly rather than calculating them.

The underlying intellectual question is: is there a set of universal equilibrium constants which can be used for the world oceans? It seems likely that there is some universality within certain limits. The constants do have systematic errors and biases because they are derived from experimental measurements as well. An additional uncertainty is that of the conservative behaviour for boron. A. Dickson pointed out that boron conservativity is in fact uncertain by a few percent, so this will affect the uncertainty in alkalinity. At high pH, there is about 100 µmol of boron alkalinity, so any percentage error in boron appears as a significant error in alkalinity. In deep water, the contribution of boron alkalinity is less (since the boric acid pK is about 9) so any errors in alkalinity are smaller.

Although the constants have become much better determined, and the level of internal consistency has improved dramatically, A. Dickson and F. Millero pointed out that it is important to assess our current uncertainty and the limitations of the predictions; therefore, it is important to continue this work.

Until these questions of the uncertainties can be resolved it will be important to handle data consistently, i.e., to choose one set of constants for any data synthesis exercises or use in models. Complete documentation for calculated values is also important, i. e., how the data were corrected and which constants were used for the corrections.

References:

Hansson I. (1973) A new set of acidity constants for carbonic acid and boric acid in seawater. *Deep-Sea Res*. **20**, 461-478.

Mehrbach C., Culberson C. H., Hawley J. E., and Pytkowicz R. M. (1973) Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol. Oceanogr*. **18**, 897-907.

Millero F. J. (1979) The thermodynamics of the carbonate system in seawater. *Geochim. Cosmochim*. Acta **43**, 1651-1661.

Dickson A. G. and Millero F. J. (1987) A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Res*. **34**, 1733-1743.

Goyet C. and Poisson A. (1989) New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity. *Deep-Sea Res*. **36**, 1635-1654.

Roy R. N., L. N. Roy, K. M. Vogel, C. Porter-Moore, T. Pearson, C. E. Good, F. J. Millero and D. J. Cambell (1993) Determination of the ionization constants of carbonic acid in seawater in salinities 5 to 45 and temperatures 0 to 45 ^{0}C. *Mar. Chem*. **44**, 249-267.

Millero F. J. (1995) Thermodynamics of the carbon dioxide system in the oceans. *Geochim. Cosmochim. Acta*, **59**, 661-667.

Inventories of ^{14}C

It is important to carefully evaluate bomb-radiocarbon inventories and distribution in the ocean, since current assessments of ocean ventilation time scales and ocean carbon uptake are based principally on models tuned or validated with the observed radiocarbon distributions. Furthermore, the relationship between gas exchange coefficients and wind speed is currently tuned to match the data derived from the global bomb-radiocarbon inventory. T-H. Peng presented results of a recent update of the calculations of bomb-produced radiocarbon inventories at the time of GEOSECS. The new estimates are based on a refined analysis of the GEOSECS data taking into consideration an empirical relationship between radiocarbon and silica to separate the bomb signal from the natural radiocarbon background in the Southern Ocean. The global inventories of this update agree reasonably well with earlier estimates. Uncertainties in the calculated inventories stem both from the scarcity of observations and the difficulty of separating the bomb-radiocarbon signal from that of natural radiocarbon. Additionally, the total inventory (number of atoms) in a 5-degree latitude band is calculated by multiplying the specific inventory (atoms/m^2) by the surface area. This is not fully correct because the cross-sectional area of the ocean decreases with depth. As bomb-^{14}C penetrates deeper with time, the error introduce by this simplification will increase as well. The global total inventory only (e.g., as obtained by summing all inventories of the latitudinal bands), was corrected by 8% to account for the decreasing ocean area with depth.

Comparisons of new ^{14}C data in the Atlantic with GEOSECS data suggest that ^{14}C inventories in the oceans are decreasing rather than increasing, as expected from ocean model assessments. However, the calculation of ocean inventories from the recent measurements is still very preliminary and needs further refinement before any firm conclusion can be drawn. Furthermore, the 1993 Atlantic data are scarce (5 stations, 8 points per station), mostly from surface waters, and the sampling locations are not identical to the GEOSECS locations.

There are also significant uncertainties in the model assessments of the bomb radiocarbon distribution as indicated by a model intercomparison exercise by J. Orr. The particulars (extent and geographical location) of

predicted ^{14}C uptake often differ significantly between the models. On the other hand, F. Joos showed a favourable comparison of 10 different models which predict industrial carbon emissions given different cases of atmospheric CO_2 stabilization profiles (Enting et al., 1994). The similar results obtained from this exercise are impressive because the models vary significantly in their parameterization of the ocean dynamics and the terrestrial processes. Using further tracers holding time information (e.g., CFCs - but not T and S), in the models is essential as an additional check on the ocean ventilation time scales.

3.3 NEW TECHNOLOGY

Certified Reference Materials (CRMs) for dissolved inorganic carbon (DIC) measurements are a major contribution to oceanography thanks to A. Dickson's work. Being able to use these materials as alkalinity reference materials would be an additional significant advance. A. Dickson reported that he is optimistic that the CRMs for DIC analysis can also be used as alkalinity CRMs. Initial testing indicates that alkalinity values are stable and he is now working on a strategy for assessing accuracy. Work in F. Millero's laboratory gives a historical basis for providing alkalinity values for past CRMs.

In situ pCO_2 measurement capability has advanced primarily through incremental improvement rather than completely new technology, but the technology is still not yet mature. It is still not possible to deploy entirely autonomous instruments from airplanes, so there is still a need for ship-based measurements. However, new microtechnology and unattended monitoring is perhaps the bridge to that goal. Current challenges include the measurement of important ancillary parameters (temperature, salinity, nutrients, DIC, etc.) and assessment of data accuracy, particularly because of drift problems. Because this technology is expensive to develop, consideration should be given to the possibility of adapting instrumentation developed for medical and other applications to the dynamic range and precision required for oceanographic purposes.

An additional challenge of the *in situ* monitoring technology includes the interpretation of the data. The community has made significant progress toward assessing what the flux of CO_2 is into the oceans. One of the next major questions is how that flux will change in the future. *In situ* measurements should help to improve our understanding rather than just quantifying. However, it is not clear how to handle such large data sets, how to interpolate data between ship tracks, how to use the autonomous data in conjunction with satellite data, and whether the statistical nature of the variability of the autonomous observations is consistent with the models. The focus of oceanographic measurements historically has been on smaller independent data sets. It will be important to develop strategies for integrating these data with ship and satellite data and to design process study experiments to increase our understanding. The amount of *in situ* data is currently fairly small, but this is expected to change over the next few years. A workshop (perhaps in 1999 or 2000) would be useful to bring people together to talk about autonomously collected data and assimilation of large data sets.

3.4 BATS TIME SERIES

The BATS time series data are a good illustration of a fine data set, but the data offer some surprises and challenges to interpretation. For example, the ocean carbon budget cannot yet be balanced, despite including the hypothesized effects of horizontal advection. Nor can biological activity account for the observations. The thorium results indicate that sediment trap methods would have to be off (in undertrapping or overtrapping) by a factor of 10 or more, not the 2 or 3 that is generally considered reasonable. Although DIC varies seasonally by about 30-45 µmol/kg, pCO_2 is relatively constant throughout the year. It seems clear that interpretation of this valuable data set depends on more information about the dynamics and biology of the site. Clearly, any future plans for time series stations should include a more interdisciplinary approach in which the physics, geochemistry and biology are all addressed. A workshop to address general time series station issues may be useful and was proposed as a special ASLO session.

3.5 CO_2 SINK IN THE NORTH PACIFIC

C.S. Wong presented data at the symposium which indicated that the North Pacific might be a sink for CO_2 of about 1 gigaton of carbon per year (GtC/yr). Though he subsequently modified that number downward to 0.6 GTC/yr, he pointed to other data which support the hypothesis of a substantial North Pacific sink. Takahashi et al. (1993) suggested a 0.1 GtC/yr sink, and Landrum et al. (in press) used Takahashi's data combined with other data to determine a North Pacific sink of 0.2 - 0.7 GtC/6 months. Tans et al. (1990) however suggested that the North Pacific is a 1 GtC/yr source of CO_2. If, instead, the North Pacific is a 0.6 GtC/yr sink, the terrestrial sink changes by 0.7 GtC/yr since it is inferred from ocean uptake numbers. Because the net terrestrial

uptake of carbon is constrained by ocean observations, it will be important to firmly establish the source/sink of the North Pacific.

The uncertainty in assessing the role of the North Pacific may result from a general shift in water circulation patterns resulting from shifts in climate or from undersampling. C.S. Wong pointed out that there are documented changes in the depth of upwelling off California which implies that pCO_2 may be lower. Could these changes also be occurring on a larger scale and account for some of the differences in the carbon uptake estimates for the North Pacific?

Undersampling may also account for the differences in assessing carbon uptake by the North Pacific. Takahashi's data set for the North Pacific was limited in some regions, particularly the subtropics. More recent data collections have provided greater seasonal coverage and observations taken during storm events. At this point there are no quantitative data to indicate the variability of pCO_2 in the North Pacific on time scales of days to months or years to decades. Some of the symposium presentations suggested that short-term variability may be much higher than expected. If the variability is as high as suggested, the question arises as to whether the magnitude of the ocean source/sink can be determined by measuring delta pCO_2. R. Wanninkhof pointed out that the variability of CO_2 uptake based on atmospheric data is 3 GtC/yr. The time scales of this variability are uncertain, and enhanced uptake in one year may be compensated within 1-2 years. Although the ocean carbon uptake may not be confirmed by measurements of delta pCO_2 for the entire ocean, it may be possible to reach a conclusion for particular regions with focussed observational programs and emphasis on process studies and modeling exercises to understand the variability. Understanding pCO_2 variability will ultimately be important to assessing or predicting any future climate shifts.

Another question in assessing basin-wide carbon uptake is the role of the coastal seas. S. Tsunogai stated that the importance of the coastal seas must be considered for global carbon budgets. Although only a small percentage of the total ocean area (8%), these areas may have an effect larger than expected because of the high transport of carbon from coastal regions. An important question is how representative one coastal system is for coastal systems in general.

The discussion concluded by emphasizing the importance of the pCO_2 inventory to assessing the magnitude of the northern hemisphere ocean source/sink and to determining the uncertainties on that estimate.

Overall, the symposium was well received, interesting and successful. The focus of this meeting was principally on inorganic carbon in the oceans. Some expressed the view that it would be worthwhile to include participants studying the atmosphere and organic carbon in the oceans for future symposia. It would also be useful to include presentations of process studies which are needed to understand and then predict the evolution of the oceanic carbon cycle.

4. RECENT EVENTS AND UPDATES

4.1 BUDGET CUTS AND IMPLICATIONS

The timing of this meeting coincided with the peaking of the budget impasse that was occurring in December 1995 - January 1996 between the U.S. Congress and the President. What little was known about the future Departmental budgets was that there would be major hiccups in the funding of ocean CO_2 programs in FY1996 and beyond. The unsettling questions were how deeply would anticipated cuts in the USA affect ongoing ocean CO_2 programs, and further, what could be expected in other countries. Individuals from the various nations represented at the meeting were asked to give a snapshot view of their funding possibilities for ocean CO_2 activities.

USA. Though a termination of the Department of Energy (DOE) funding for ocean survey work was recommended for 1996, community support, political pressure, etc., won an extension of funding for one year, at a reduced level, to complete the Indian Ocean Survey and to get data into CDIAC. The situation for 1997 is uncertain. Closing down of the U.S. Government was having negative impacts even in the National Science Foundation where funds were only minimally affected. Grants needed to conduct scheduled operations were not being processed in time even though approved. The NOAA budget was among those that were not settled at the time but cuts in the order of 40% were anticipated in ocean CO_2 related projects.

U.K. The UK went through its budget-wringer process several years ago and funding continues to be squeezed. UK scientists are trying to convince the business community of the importance of CO_2 work but with little success. The situation was not optimistic even should a change in government occur. The European Commission may prove to be a source of future funding.

France. So far, the situation in France is not as dramatic, but it is one of slowly decreasing ocean R&D funding in general. France too, is hoping the EEC will prove to be a source of funding.

Switzerland. Funding is generally fairly stable and looks to remain so in the next few years.

Germany. The CO_2 support has been part of overall JGOFS funding which ends in October 1996. It is expected that the North Atlantic Programme of general circulation studies will pick up the support of CO_2 activities after that. Additionally, some institutions will continue CO_2 studies on the basis of their regular budget.

Norway. There is reason for some optimism for CO_2 funds in a general background of declining support for research.

Canada. The so called "green fund" money will disappear next year. The Energy R&D fund will continue to support CO_2 work. The funding for CO_2 disposal, e.g., pumping CO_2 into oil wells for storage, exists as a potential source of support.

Japan. There is a larger inertia for funding - it is difficult to increase or decrease. At present, the curve for CO_2 studies is above the mean and on the rise. S. Tsunogai's lab has fared very well with support for new permanent equipment and there is a generally positive climate for marine science expansion.

Russia. Both the present situation and future outlook for support of global change related sciences, e.g., environmental and climate studies, are bleak.

New Zealand. A nascent CO_2 program is just beginning to ramp up with the recent funding of a five-year program.

The chairman summed things up by concluding that except in a couple of countries the funding trend is not very good. A discussion followed on possible actions that could be taken individually or as a group that might have some impact on reversing this trend. Letter writing was considered to have minimal effect; but on the other hand, if no one screams, the impression may be given that there is no pain. It was concluded that the most useful letters would be those from prominent informed individuals who no longer depend on research grants and thus have no ulterior personal-gain motive.

4.2 GOOS UPDATE

A. Alexiou informed the Panel on the latest developments in GOOS. In a word, progress is slow - there is lack of people and dollar resources but there are bright spots in some countries and some regions. There is now an active European initiative, EuroGOOS, and a Northeast Asian regional GOOS, NEARGOOS. A priorities agreement meeting originally scheduled for May of 1996 has been postponed for a year in order to prepare a more comprehensive background document for the meeting. The Ocean Observations Panel for Climate (OOPC) has been established and is scheduled to hold its first meeting in March. This Panel expects to further the work of its predecessor, the Ocean Observing System Development Panel (OOSDP). Alexiou is providing staff support for the OOPC too, and performs a liaison function between this CO_2 Panel and the OOPC. He stated that if this Panel can agree on a set of carbon measurements and acceptable technology for making them operationally, then their recognition by the OOPC as basic to GOOS, could affect funding in a positive way in some countries.

5. INVENTORY OF pCO_2 DATA

A. Poisson reported on the work of the sub-panel (A. Poisson, A. Dickson, and H. Inoue) established to assemble an inventory of ocean pCO_2 data acquired by scientists around the world. A report, titled "Inventory of pCO_2 Data Collected in the World Ocean", prepared by the sub-panel with the assistance of F. Louanchi, had been distributed to the Panel prior to the meeting. The sub-panel plans to send the report to all the scientists that contributed information. The chairman thanked the sub-panel members for their report and congratulated them on the progress they had made with this very difficult task.

A discussion took place on what should be the next step. The sub-panel suggested sending a request for the data to be sent to CDIAC with the appropriate metadata and information on the type of equilibrator, the method of analysis, calibration, etc. This raised the important question of how to assure the individual rights of investigators are protected. A related issue is that investigators with large data sets want to publish their data in a formal fashion, perhaps have it peer reviewed, and to receive recognition by citations and references when the data are used by others in their published papers. CDIAC has done something like this in the past. The Panel agreed this would encourage the submission of data to CDIAC. It was suggested that one way of providing similar recognition for owners of small data sets would be to lump them together in special publications that could also be referenced. A problem with this is that individually archived data sets are not entirely comparable. The Panel agreed that a very carefully crafted letter should be sent to invite people to send their data in to a collection volume that would show the names of contributors. Principle Investigators with large quality controlled data sets should have the option of separate reports by CDIAC that can be cited with the P.I. as the author. Of course, in this case, the contributors would be expected to write full reports describing the data, calibration, etc.

The users of large amounts of data are modelers who don't have the expertise to assess data sets individually. This underscores the need to develop and promulgate standard analysis and reporting procedures.

A sample of a proposed form for scientists to use in submitting data to CDIAC was introduced by A. Kozyr. It was designed to elicit information from those with time, language, or other constraints so that data would be put in the data base with a minimum amount of pain. Otherwise their data may never get into the public domain. It was suggested that the form be modified to allow (and encourage) more explanatory text to ensure that sufficient information can be entered regarding how data were collected and analyzed. The information specifically requested on the form by the simple fill-in-the-box method should be regarded as the absolute minimum of documentation required. Guidance should be provided in the letter about what other kind of information should be provided.

The bottom line of this discussion was agreement that the number one priority issue is obtaining the data. Investigators should be encouraged to provide a detailed report, but nevertheless, to send the data numbers even if a report is not provided. CDIAC could suggest how the data sets should be cited when used in other published material.

6. OCEAN CO_2 SYSTEM MEASUREMENT ISSUES

6.1 INTERCOMPARISON EXERCISE

A. Dickson reported that the pCO_2 intercomparison exercise was fairly successful and that a written report is half done. This report is expected to be distributed for review to the Panel and to the participants of the intercomparison exercise by mid-September 1996. The final report is expected to be completed by the end of 1996.

A. Watson further mentioned that a pCO_2 intercomparison exercise at sea is now planned in the North Atlantic Ocean in June 1996. This exercise will complement the earlier exercise.

S. Tsunogai presented results from the Japanese pCO_2 intercomparison exercise, which showed differences of up to 10 uatm and response time delay of about ten minutes between the different types of equilibrators. The experiment exposed problems of systematic errors from different calibrations and baseline drift. More information on the Japanese intercomparison is included in the national report from Japan in Annex V.

A common, salient conclusion that emerges from all these experiments is that the uneven performance of equilibrators is a possible contributor to the troublesome lack of comparability of data from different investigators.

C.S. Wong raised the question of what the best strategy is for determining delta pCO_2 considering that atmospheric gradients and variability occur. For ships of opportunity, the ships seek following winds and CO_2 from stack gases can contaminate the observations. The answer depends on what type of platform, personnel, etc., are available. This underscores the need to agree on and emphasize what to report along with the data.

6.2 STANDARDS

Andrew Dickson provided an update on the status of standards and reference materials for alkalinity, ^{13}C and other parameters important to the ocean CO_2 budget. A brief review of these remarks are given below.

TCO_2. The program has produced and distributed certified reference materials (CRMs) for dissolved inorganic carbon (TCO_2) to investigators around the world. These have been used extensively during the JGOFS/WOCE and JGOFS/NOAA cruises over the last five years. For example, 52 shipments were sent to 23 laboratories in 11 countries (3500 bottles) during 1994. These CRMs have provided a method of evaluating the at-sea measurements of all the cruises. The field results typically agree with the certified value to 2 µmol/kg. The panel believes this service should continue in the future to assure that reliable TCO_2 data are acquired in future measurements.

TA. Although the reference material is not yet certified for total alkalinity (TA), Millero and co-workers (Millero et al., 1993, 1995, 1995, and 1996; Lee and Millero, 1995) have shown that the material is stable for TA (2 µmol/ kg) and pH (0.002). Dickson has been working to develop an analytical approach that can be used to certify the CRM's for alkalinity. He has been able to reduce the background levels of TA for NaCl solutions to about 2 µmol/kg which can be compared to levels of 10 to 30 µmol/kg on most other studies on these mixtures. This NaCl has then been used to prepare standard solutions for alkalinity based on standard tris (NIST SRM 723), borax, and sodium carbonate which can be used to standardize HCl solutions. The values obtained agree well with those measured by direct coulometric titration. He has also developed a method that can be used to determine the TA of seawater by adding an excess of acid to pH < 4, stripping the CO_2 and titrating to pH = 3.0. The equivalence point is calculated using a modified Gran approach. The precision is 0.7 µmol/kg and comparison with the solutions of standard bases suggests that the accuracy is within 2 µmol/kg. He hopes to use this method to certify the TA of the CRM's in the near future. [Note: A. Dickson reported (August 1996) that this work has been completed, and that his laboratory are now certifying these reference materials for total alkalinity.]

^{13}C. Recently Dickson and Wong have examined the use of the CRMs as a standard for ^{13}C. Although the precision of the individual laboratory measurements is often as good as 0.01 in delta ^{13}C, the measurements by various groups differ by as much as 0.1 in delta ^{13}C. The average values found for the CRM used for the intercomparison (about 1.5) are close to the values of surface waters in atmospheric equilibrium. Since the values of delta ^{13}C are different for each sample, each individual batch would need

certification. Since the cost of preparing seawater standards is high, this type of certification will probably not occur regularly, though it might be possible to reserve particular batches for use as delta ^{13}C standards. The panel believed that scientists making these measurements should be encouraged to use the CRMs to allow measurement compatibility to be ascertained.

pH and pCO_2. As mentioned above a number of workers have shown that the CRM's are quite stable for pH (0.002) as well as for discrete pCO_2 measurements (2 µatm). Although these measurements can be standardized by other methods, the monitoring of the CRM's for these parameters can be useful in doing quality control of the data and in examining the thermodynamic consistency of the measurements.

References:

F.J. Millero, J.Z. Zhang, K. Lee, and D.M. Campbell, Titration alkalinity of seawater, Mar. Chem., **44**: 153-165, 1993.

F.J. Millero, W. Yao, K. Lee, J.-Z. Zhang and D.M. Campbell. The Carbonate System near the Galapagos Islands. University of Miami Technical Report No. RSMAS-95-001, 1995.

F.J. Millero, J.-Z. Zhang, K. Lee, J. Aicher, S. Mane, S. Olivella, D.O. Medina, and P.A. Steinberg, pH and total alkalinity measurements in the North Atlantic, Univ. Miami Tech. Rpt. No. RSMAS 95-004, 1995.

K.Lee and F.J. Millero, Thermodynamic studies of the carbonate system in seawater, Deep Sea Res., **42**, 2035-2061, 1996.

F.J. Millero, W. Yao, K. Lee, J-Z. Zhang, and D.M. Campbell, Carbonate system in the waters near the Galapagos Islands, Deep Sea Res., submitted, 1996.

F.J. Millero, Thermodynamics of the carbon dioxide system in the oceans, Geochim. Cosmochim. Acta, **59**, 661-667, 1995.

7. MODELLING THE CARBON CYCLE

Fortunat Joos briefly reviewed the variety of modeling approaches used in carbon cycle modeling. Transport in the ocean is modelled using GCMs, 1- and 2-D models. The ocean ventilation behaviour of these models is tested or tuned using transient tracer distributions (e.g., ^{14}C, Freons, ^{39}Ar). Because different ventilation mechanisms (e.g., convection vs. advection) operate on different timescales, a variety of tracers with differing time-dependence are required for model testing, not just radiocarbon. With respect to modelling the uptake of anthropogenic CO_2, a perturbation approach is frequently used. Alternatively, a full carbon cycle model including biology can be employed, with new production being parameterized and constrained in several different ways. Tests of the models' representation of biological processes include distributions of biogeochemical tracers (e.g., nutrients, oxygen, CO_2) as well as paleo-oceanographic data. In order to evaluate potential feedbacks on future CO_2 uptake, model representations of paleo-oceanographic carbon-cycle changes will be particularly useful. Joos emphasized that up to the present the uptake of CO_2 has depended much more on the circulation than on how one formulates the C cycle itself. The assumption till now has been that of a steady state CO_2 cycle.

The usefulness of ^{13}C data for model calibration was emphasized, and the panel concurred that data collection for ^{13}C data should be expanded. The panel also recommended that models and time-series data be examined to guide the design of ^{13}C sampling programs, and that such programs should carefully consider the scientific goals which are being addressed. Measurements of ^{13}C in the ocean should be closely coordinated with potential users of such data in the atmospheric, paleo-oceanographic and biological oceanography communities. The data should be used to improve understanding of the processes which control the ^{13}C distribution (temporal/spatial) within the ocean. This understanding is required to guide the interpretation of the ocean sediment ^{13}C record using models, which in turn can be used to quantify

feedbacks in the ocean-atmosphere-biosphere-sediment carbon cycle. This discussion served as a lead-in to Section 8.6.

8. THE OCEAN CARBON BIOLOGICAL PUMP

There has been a continuing debate regarding the role of the biological pump, its role in sequestering anthropogenic carbon and the potential biological feedback effects resulting from increased atmospheric CO_2 and greenhouse warming. Change of carbon in the mixed layer is dependent on mixing and new production. This is illustrated in the following function:

$$\partial C_m/\partial t = K_t(C_{tc}-C_m)-N_p$$

where: C_m = carbon in the mixed layer
C_{tc} = Carbon in the thermocline
K_t = Exchange rate of carbon that controls mixed-layer renewal: t = 1-2 years time scale.
N_p = New production from carbon input due to climate induced physics + new production from terrestrial input of carbon/nutrients to the ocean)

According to C.S. Wong, there are a number of small terms that may affect the new production term which often are not considered by modelers (e.g., riverine DOC and POC, aeolian POC and PIC, and riverine DIC and $CaCO_3$), and which in the aggregate amount to about 0.7 GtC/yr. Redfield ratio deviations and human induced changes (such as sewage and fertilizer) can also affect this value (by as much as 0.3 perhaps). Furthermore, there may be some climate induced changes in new production which are episodic and are estimated to be 10-15% of total new production, i.e., 0.7. The total of all these factors comes to about 1.7GtC/yr.

Joos cautioned that it was important to make assessments consistent with goals and time scales. Over long time scales the short-time-scale perturbations are in the averaged ocean signal. The impact of the biological pump is a function of the nonlinear interplay of organic matter fluxes, gas exchange, and carbon chemistry. Changes in biology will not cause a change in the removal rate of atmospheric CO_2 by a constant factor, but will set a new background equilibrium state. Different biologically induced scenarios ranging from biological response to fertilization of the ocean (iron or nutrients) can only delay the effect of anthropogenic CO_2 release to the atmosphere. This seems to be a consistent result from all models.

T. Johannessen suggested this conclusion may be biased by the possibility that current models may be tuned to be more sensitive to circulation changes (i.e., physics) rather than biological changes. D. Wallace noted that since the CO_2 atmospheric concentration ranges from 180 ppm (for a fully effective biological pump, i.e., all nutrients utilized) to 500 ppm (for a "dead" ocean), there is some potential for biology to change the ocean carbon cycle, but in the end, circulation changes will dominate. Watson added that although only about 15% of the surface ocean has nutrients, it is misleading to base estimates on area alone. Polar regions, where most nutrients are, are connected to deep water so they may have a disproportionately large effect on setting the steady state of atmospheric CO_2. Joos added that something to consider in the future is that if circulation does change, biology may change and the Redfield ratios may change, which were not considered in his analysis.

Watson concluded that, at present, it is not possible to implicate biology in changes in ocean carbon uptake, but long-term changes in biological cycling may dominate over the long term (glacial-interglacial).

9. STATUS OF THE GLOBAL CO_2 SURVEY

Catherine Goyet reviewed the current status of the US component of this Survey. Surveys of the Pacific, South Atlantic and Indian Oceans are now almost complete. The Survey of the North Atlantic remains to be conducted, and is contingent on uncertain WOCE plans and funding levels. JGOFS-supported work on

Process Studies in the Equatorial Pacific and the Arabian Sea have been completed, and proposals are pending for CO_2 measurements during the Southern Ocean study. There will be no US-supported JGOFS Process Study in the North Atlantic Ocean.

The Panel briefly reviewed the status of Global Survey activities in other countries. Within France, there are no current long-term plans for new field work with the exception of the continuation of a ship-of-opportunity program between Le Havre and Tahiti (via Panama) which will run until 1997, a program in the equatorial Atlantic, and the extension of a program between La Reunion and the French subantarctic islands in the southwestern Indian Ocean which will include subsurface measurements. Likewise within Germany, planning is year-to-year. Within the UK, WOCE line A23 was recently completed with CO_2 and discrete-pCO_2 measurements: coverage was limited as only one analyst was aboard. In the Indian Ocean two JGOFS cruises included TCO_2 and discrete pCO_2 data. In Norway, there will be some CO_2 work aboard future NORDIC WOCE cruises as well as in the CARDEEP program in the Nordic Seas. Japan has supported CO_2 measurements on P2 and along 165 E, with a fairly complete suite of measurements. In Canada, WOCE lines in the Western Pacific, along P1W and P15N have been supported for CO_2 measurements as well as repeat sections (2-4 times per year) along Section P in the northeast Pacific. In the Atlantic, repeat measurements have been made, and will continue, on WOCE line A1 in the Labrador Sea, as well as on a recent Trans-Arctic cruise. Within Russia, there are no current plans for major expeditions, however CO_2 measurements and sediment trap deployments are being made as part of a monitoring program around a sunken nuclear submarine in the Norwegian Sea.

9.1 AIR SEA INTERACTION

Rik Wanninkhof presented an overview of a recent analysis by Taro Takahashi and his collaborators of a large multi-year, global pCO_2 data set that combined data sets of Takahashi, Weiss, the NOAA laboratories and others to create a seasonal pCO_2 field. A detailed description of their approach is given in Annex III. This study sought to compile high-quality, accessible data and utilize innovative interpolation, extrapolation and averaging approaches in order to estimate the global air-sea CO_2 flux. The approach was presented at the Revelle Memorial Symposium, and will be published in that Symposium's proceedings. With this new approach, the global uptake of CO_2 in 1990 was estimated to be between 0.7 to 1.3 GtC/year depending on the gas exchange formulation chosen. This estimate is appropriate for non-El Nino years, and does not include corrections for a thermal skin-effect or riverine input. The panel noted that this estimate is not inconsistent with other estimates derived using alternative approaches, and that it is not greatly different from the estimate based on global pCO_2 data (only) published by Tans, Fung and Takahashi in 1990. This overall agreement between an early estimate based on a very limited data set and interpolation approach and the much larger data set used in this new approach, was considered to be encouraging. On the other hand, as the delta pCO_2 fields become better constrained, the large difference between the empirical gas-exchange vs wind-speed relationships, and the various available wind products themselves become a more dominant problem.

The Panel appreciated this new and significant work and looked forward to seeing it published soon. The Chairman underscored the hope of the Panel that once published, the data used in this study could be contributed to the global inventory of pCO_2 measurements being collected by the pCO_2 sub-panel.

B. Schneider mentioned that under certain conditions (high delta pCO_2, low mixing depth, low biological activity) during winter in the Baltic Sea, the air/sea CO_2 flux can be determined directly by measurements of changes in C_T. By such studies improved parameterizations of the CO_2 exchange coefficient may be obtained. Watson added that the biological effects on gas exchange are important also. He referred to the work of Nelson Fruhe on this; Fruhe is also investigating the direct relationship of radar backscatter to the gas exchange coefficient, (instead of converting the backscatter to a wind first).

9.2 INTEGRATING DATA OF DIFFERENT TIME AND SPACE SCALES

The panel then discussed the question of how much pCO_2 data are required to accurately constrain the oceanic sink for CO_2. It was suggested that two approaches should be used to address this question:

(i) Employ models to simulate natural variability and sub-sample the model output (to some extent, this approach requires a "perfect" model);

(ii) Use bootstrap techniques in which a subset of the data can be used to test the accuracy of the interpolation and extrapolation schemes. This approach requires a large data set, which may now be within reach.

9.3 TIME SERIES OBSERVATIONS

A. Watson opened the discussion on time series observations by mentioning that these refer to fixed stations and to regularly repeated transects as well. S. Tsunogai reported on the time series observations of oceanic CO_2 parameters in Japan (see also Japan National Report in Annex V). Measurements of pCO_2 in the northwest Pacific have been performed by the Japanese Meteorological Agency (JMA) since 1961 and were extended to the equatorial region along two transects at 137 E and 155 E in 1981. Data on winter pCO_2 were presented which were below equilibrium with the atmosphere and showed an annual increase of 1.8 ppm. Since this corresponds approximately to the increase of atmospheric CO_2, no change in delta pCO_2 with time occurs. In contrast, pCO_2 during summer, which is higher than the atmospheric level, did not change during recent years and suggests a decreasing degassing of CO_2. The data of the JMA time series are documented in the WMO WDCGG Data report. Other Japanese institutions involved in time series observations are the National Institute of Resources and Environment (NIRE) and the National Institute for Environmental Studies (NIES). The measurements of NIES are performed in cooperation with the Institute of Ocean Sciences (Sidney, Vancouver). C.S. Wong gave an introduction to this project which is performed under the auspices of PICES (Pacific International Council for the Exploration of the Sea) and which comprises a comprehensive set of CO_2 and supplementary parameters measured regularly along a transect in the subarctic Pacific and along two southern lines (Vancouver-Hawaii; Seattle-Hawaii) using ships of opportunity. Other Canadian activities and known time series organized by other countries are summarized in Annex IV.

9.4 WINTER DATA

At the last meeting of the Panel, T. Takahashi brought the attention of the members to the utility of winter pCO_2 data because it was significantly less noisy. He called for added effort to increase the amount of wintertime data. It was pointed out at this meeting that nutrient data are also less noisy, and that winter pCO_2 data are needed with other parameters in order to calculate the preformed values. Since they are generally scarce, the Panel should continue to encourage the collection of winter data. A. Poisson reminded the Panel that seasonal variability can be very high and must be quantified. Sufficient year-round data are needed to quantify this variability with reliability. It was questioned whether Takahashi's discrete sampling perhaps could miss the high summer variability. D. Wallace posed a question regarding increased storm activity in the winter and whether this could systematically influence pCO_2 measurements by introducing bubbles into the equilibrators. At present the effect is uncertain.

9.5 SUBARCTIC MONITORING

The SubArctic Monitoring Programme is being formulated by a Working Group to study the role of the North Pacific on climate change, including CO_2 changes, as one of the activities of the Pacific International Council for Exploration of the Seas (PICES), an intergovernmental North Pacific Marine Sciences Organization, headquartered at IOS, Sydney BC, Canada. This regional subarctic monitoring group suggested a strategy to monitor long-term, large-scale changes in the subarctic waters on relevant parameters indicating changes in CO_2, heat, circulation and biology. Two of the elements useful for the CO_2 Panel are: (i) sediment trap moorings to monitor fluxes of C, N, and Si, metals and isotopic C and N, particularly suggesting two new stations in the centres of the Alaska Gyre and the gyre south of the Aleutian-Kamchatka area; (ii) ships-of-opportunity to provide time varying and spatial coverage in subarctic waters with three proposed lines: Hawaii to Alaska, Hawaii to Seattle and Vancouver to Tokyo. The Vancouver to Tokyo programme is being implemented under a bilateral science and technology agreement between Japan and Canada by the Japanese National Institute of Environmental Studies (NIES) and the Canadian Institute of Ocean Sciences (IOS). Measurements and sample collections are being carried out on a lumber carrier M.V. SKAUGRAN about 10-12 times a year on a direct cruise track between Tokyo

and Vancouver, then following the Great Circle route through the NE Pacific, Bering Sea, NW Pacific off Kamchatka and Kurile Islands to Tokyo. Shipboard measurements include pCO_2, T, S, O_2 (by sensor), chlorophyll-a (by fluorometer). XBTs and sample collections include those for atmospheric gases for NIES (CO_2, CH_4, CO, N_2O, and ^{13}C) in S/S cylinders for 10-12 stations along the northern route; O_2/N_2 for R. Keeling; and atmospheric and oceanic ^{13}C, chlorophyll-a, nutrients of P, N, Si, DIC, TA for the ocean biogeochemistry group at IOS. Meteorological data of wind speed and direction, air temperature, SST and irradiance will be logged. Atmospheric ^{14}C will be included in future after the AMS facility at NIES, when the first gas target in the world, is in full operation. Data will be deposited both at NIES and IOS. Responsible scientists are Y. Nojiri (NIES) and C. S. Wong (IOS). The data sets will be in the public domain after publication each year of the scientific results.

10. STATUS OF ^{13}C

10.1 MONITORING OF ^{13}C

There is general agreement that ^{13}C data are valuable for constraining the ocean carbon cycle. For example, the ^{13}C time-series observations in the ocean and the atmosphere are used to differentiate the uptake of anthropogenic CO_2 by the ocean and the terrestrial biosphere. The unanswered question is: given the difficulty of measuring ^{13}C in the ocean, what is the relative importance and just how important is it to pursue in lieu of other measurements.

At present, the sample throughput for ^{13}C is relatively limited. The panel urged, as it has done previously, that the AMS-^{14}C measurement programs which routinely measure ^{13}C should be optimized to ensure that the ^{13}C measurement precision and accuracy are adequate for scientific applications of ^{13}C data. It was agreed that modelers would be requested to examine and comment on the sampling density frequency and accuracy of ^{13}C observations for the data set to be really useful. In addition, the panel reiterated its previous statement of support for ^{13}C monitoring programs in the ocean and the atmosphere as important to leading to better understanding of the carbon cycle.

At this point it was noted that current plans for the North Atlantic Ocean work during the US component of WOCE does not include any plans for either ^{13}C or even ^{14}C sampling. The Chairman offered to write a letter to the National Science Foundation asking that support for carbon isotope work not be neglected during this study.

10.2 SUB-PANEL ON ^{13}C

The discussion shifted towards the current availability of ^{13}C data that have already been collected. The situation was unclear, and the Panel appointed a sub-panel to examine this question. The sub-panel members are Wong (Chairman), Tsunogai and Johannessen. They are charged with preparing an inventory of ^{13}C data sets in a similar manner to the sub-panel on pCO_2 data. D. Wallace would act as an intermediary with US investigators if necessary. The panel will solicit information from the paleo-oceanography community in addition to tracer and CO_2 chemists.

Terms of reference for the Sub-Panel on ^{13}C are: To compile an inventory of measurements of delta ^{13}C in oceanic waters containing sufficient information to allow the relative roles of natural and anthropogenic temporal changes in the atmospheric, oceanic and terrestrial carbon reservoirs to be assessed quantitatively.

11. OTHER PANEL-RELATED CLIMATE TOPICS

11.1 IPPC REPORT

The section of the new (1995) IPCC Report on "marine biotic responses to environmental change and feedbacks to climate change" has been criticized as lacking depth. The difficulty is that uncertain feedbacks in the longer term (circulation, nutrient inputs, etc.) make it difficult to assess future changes

in the magnitude of the current sources and sinks. The Panel pondered the question of how to narrow the uncertainties on the impact of feedback mechanisms.

D. Wallace believed it was important to work on testable hypotheses and, since the issue is decadal, to focus on process studies that could be done in the context of time series. He suggested a couple of issues that might be addressed: What are the factors controlling the Redfield ratio and its variability? What controls the relative rain rate of soft to hard tissue carbon. Though it would be difficult to imagine how the C:N:P ratios might change, he envisioned that it would be straight-forward to imagine how the hard/soft ratio might change since this is species dependent and different organisms are responsible.

F. Joos emphasized the importance of models getting the high-latitude oceans right for long-term feedback. Processes there influence the global circulation. He reminded the Panel that one weakness of the models is due to the lack of information about the Southern Ocean and that it was very difficult to come up with a global ocean model when such a large region is so poorly modelled.

A. Watson noted that the IPCC Report helps to finger the weaknesses in our knowledge of the ocean carbon cycle and this points the way to studies that will be important in the future. He concluded we still have a long way to go in describing and quantifying the dynamics of the carbon cycle in the ocean.

11.2 OTHER GREENHOUSE GASES

A. Alexiou gave some background for placing this item on the agenda. He stated that the Panel's participation in preparing the "state of knowledge" background document for the last Malta meeting on ocean CO_2 has proven to be very valuable. It was made a part of the Malta meeting report and given wide distribution. Feedback has been very positive. Because the subject of other greenhouse gases has been receiving more press lately, G. Kullenberg, Executive Secretary of the IOC, was considering the possibility of another Malta-type meeting of experts on the state of knowledge of the role of the ocean in greenhouse gases other than CO_2. He was looking for counsel from the Panel.

R. Weiss reported on the role of the oceans in the global budgets of important atmospheric trace gases other than CO_2. These gases, both natural and anthropogenic, are of important environmental concern because they alter the earth's longwave radiation balance through the "greenhouse effect" or because they lead to the production of free radicals in the lower stratosphere which catalytically destroy the earth's protective ozone layer and thus increase ultraviolet radiation at the earth's surface.

Nitrous Oxide (N_2O). This gas is the principal natural modulator of the ozone layer through the photolytic production of stratospheric NO, and it is also an important greenhouse gas. The oceans release about a third of the total natural flux of N_2O to the atmosphere, the remainder being of terrestrial origin. Anthropogenic sources, either through the enhancement of biological production or through direct industrial production, add an amount equal to roughly half of the global natural sources.

Methane (CH_4). This gas is an important greenhouse gas, for which the present-day oceans play a relatively minor role in the global natural budget. However, very large amounts of methane are believed to be sequestered in the form of methane-water clathrates in high-latitude, shallow marine sediments, and there is concern that global climatic warming could have a very large positive feedback through the release of this methane should these clathrates become unstable at higher temperatures. In addition to its importance as a greenhouse gas, methane is the principal sink of tropospheric hydroxyl (OH) radical, and through this affects nearly all tropospheric chemistry. Tsunogai noted that ocean CH_4 is increasing at the same rate as that in the atmosphere. He suggested that changes in ecosystems could be important to changes in levels of CH_4 and dimethyl sulphide. He believed there was a link to CO_2 because of the link with biology.

Methyl Halides. Methyl chloride (CH_3Cl) is probably produced primarily in the oceans, and is the principal natural source of ozone-destroying stratospheric chlorine, but its oceanic and atmospheric budgets are not well understood. Methyl bromide (CH_3Br) was previously believed to be produced primarily in the oceans, but current thinking is that the oceans represent a net sink for atmospheric CH_3Br. Since this compound is also an important anthropogenic agricultural fumigant, and since stratospheric bromine is

about 80 times more effective at destroying ozone than stratospheric chlorine, there is considerable interest in learning more about the atmospheric CH_3Br budget, and especially about the ocean's role in this budget. Methyl iodide (CH_3I) is also believed to be of important oceanic origin, and iodine is a potent stratospheric ozone-destroyer, but the lifetime of this gas in the troposphere is short and its budget is not well understood.

Dimethyl Sulphide (DMS). This gas is important to climate, although strictly not as a greenhouse gas, because it is the principal natural precursor of atmospheric sulphate aerosol, which, in turn, plays an important role in cloud nucleation. DMS is biologically produced in the marine photic layer, and is released to the atmosphere by air-sea gas exchange. C.S. Wong discussed some experiments that suggested the DMS climate biofeedback effects may have been underestimated in the past. These experiments indicate that perhaps up to 1/3 of the sulfur in coastal regions might be biogenically produced.

Hydrohalocarbons (HCFCs and HFCs). There is a wide range of these compounds which are coming into use as replacements for the anthropogenic chlorofluorocarbons (CFCs) now banned under the Montreal Protocol. Unlike the CFCs, these compounds contain hydrogen-carbon bonds that make them vulnerable to chemical attack by tropospheric OH radical. Also, unlike the CFCs, many of these compounds are probably chemically reactive in seawater, so that oceanic destruction may be a significant component of their atmospheric budgets.

With regard to Kullenberg's proposition to consider holding a Malta meeting on other greenhouse gases, A. Watson noted that the knowledge base of the members of this Panel was specific to ocean CO_2 and was probably not the right group to comment on or undertake the task of preparing a background document for such a meeting. One of the reasons for the Panel's success was that it maintained its narrow focus and till now it made good sense to do so. However, the time may be close approaching when consideration should be given to widening its scope. The chairman asked the members to give some thought to the question of how to do this (e.g., dissolve the Panel and organize a new one; widen the interests of this one; other approaches).

11.3 AEROSOLS

Alexiou introduced this agenda item by presenting a summary of a paper by T. Bates. Atmospheric aerosol particles affect the earth's radiative balance directly through the backscatter of solar radiation and indirectly as cloud condensation nucleii (CCN). The global-mean radiative forcing due to aerosol particles is calculated to be of the same order of magnitude (about 2 watts/m^2) but of opposite sign due to the forcing produced by CO_2 and other greenhouse gases. Unlike CO_2, however, because of a lack of globally distributed data and a clear understanding of the processes, they have been poorly characterized in climate models. Although atmospheric sulphate in the northern hemisphere is clearly dominated by anthropogenic emissions, over the remote oceans atmospheric sulphate is derived mainly from atmospheric oxidation of biologically produced DMS.

Watson stated that the new IPCC Report has a large section on this subject and that it is an active research question. Watson wondered whether this was another area that might be covered in a Panel with a wider scope. Investigating the role of marine biota in generating cloud condensation nucleii would appear to involve a JGOFS-like process study. He envisioned some kind of perturbation experiment (perhaps with isotopically labelled sulfur) to count CCN would be helpful.

12. IRON ENRICHMENT INVESTIGATIONS

A. Watson presented results of the second iron enrichment experiment in the Galapagos area in July 1995. The first test indicated a large effect of the added iron on the biology but only the beginning of a reduction in the surface-water CO_2 levels which stopped after three days. The second test, on the other hand, produced stunning results. For this second experiment, a second dose of iron was added three days after the first. The fertilized patch did not subduct and was tracked for 18 days. The pCO_2, initially in the 500 µatm range, dropped by 30 µatm after 4 days, by 60 µatm after 10 days and by 100 µatm (the lowest observed drawdown) after 13-16 days, and the bloom continued to grow. F. Millero hypothesized that the different results could be due to the fact that the iron solution in test-1 was effectively removed from the system by quickly adhering to particles in the sea water, before the biology could respond. With

the second injection in test-2, the biology had time to respond and production, when well underway, was able to keep the iron in the system and sustain the production. The trick is to keep the iron in the system in bioavailable form.

Test-2 clearly established that iron enhances productivity and CO_2 drawdown in the equatorial Pacific. The question remains, however, given that there are many controls on a biological system, of how dominant a control iron will be for other systems in other ocean regions. It is planned to address this question in a future experiment in the Southern Ocean.

C.S. Wong revealed plans for a different kind of iron fertilization experiment near Station P in conjunction with Japanese power companies. This will involve adding iron to cylindrically curtained volumes of seawater, 2-3 meters in diameter and 20-30 meters deep, with sediment traps below, to determine the ecosystem response. Wong indicated experiments are also being planned for the Southern Ocean and the equatorial Pacific.

13. CO_2 DISPOSAL IN THE OCEAN

T. Johannessen presented an update of European activities. European countries involved in this research are Norway (in co-operation with Japan) and the United Kingdom. The main cost difficulty in CO_2 ocean disposal is the expensive first step of CO_2 separation from the fossil fuel source. The cost of the next step of disposal in the ocean is much lower. Some approaches under consideration include the dumping in sea water of high-density CO_2 solutions, pure liquified CO_2, solid CO_2 hydrates, and solid CO_2. Solid CO_2 will sink slowly. On the basis of experiments done in Japan, it is estimated that 50% of a solid block would reach the deep ocean (i.e., 3000 m where the melted liquid CO_2 becomes heavier than the ambient seawater). Some method would be needed to get it below that depth so it could sink to the deep ocean.

S. Tsunogai presented the Japanese plans for studies in 1995-1997. These studies include a baseline study of the deep sea environment and a land-based study to identify the optimal design of diffusers for maximum dispersion of the injected liquid CO_2 droplets within the wake region behind a towed pipe of the discharge ship.

C. S. Wong reported that there was an International Energy Agency (IEA) Ocean Circulation Workshop last August 1995, and that he is Chairman of the Engineering Committee on Oceanic Research (ECOR) Oceanic CO_2 Disposal Committee. Studies of CO_2 residence times in the oceans suggest that the most appropriate place to dump CO_2 in the deep ocean would be in the South Pacific Ocean. But it should be kept in mind there is some uncertainty in our assessment of diffusivity and consequently of residence times as well.

B. Schneider mentioned that there was no further planning in Germany to work on this subject. Germany's initial research raised strong doubts about the practicality, given the serious environmental issues raised and the inadequate science base.

The panel agreed that, at present, the expense estimates and potential environmental impacts are reason for skepticism. However, there is inadequate knowledge on which to recommend any action on this issue except to continue the necessary ocean research to increase the knowledge base.

14. NEW TECHNOLOGIES

Liliane Merlivat presented data collected from CARIOCA buoys in the Mediterranean and the eastern equatorial Pacific. The Mediterranean buoy includes in-situ measurements of O_2 and N_2 as well as pCO_2. The depth-resolved measurements in the Mediterranean (2m and 8m) show the potential influence of near-surface stratification and large temperature differences (6^oC) on fixed-depth pCO_2 measurements. Indications exist of long-period variations in the pCO_2 (40 µatm in 2-3 days) of the equatorial Pacific.

A. Watson described the IMCORP system (Instrument for Marine CO_2 from a Remote Platform). This is an EEC project to develop instrumentation for measuring total CO_2 and total alkalinity on ships of opportunity and buoys.

Truls Johannessen described proposed measurements in the Central Greenland Gyre (using CARIOCA for pCO_2), which will include a combination of hydrographic cruises including CO_2 measurements, vertical profiling moored CTD measurements, and a deliberate tracer-release experiment to be conducted in the Greenland Gyre.

D. Wallace discussed an array of moored instruments that are to be deployed on the continental shelf off the East Coast of the United States. This array, supported by the US Department of Energy's Ocean Margins Program will include a "control-volume" array (8 x 8km; 30m of water) which will be densely instrumented with a combination of ADCPs to measure currents and zooplankton biomass; moored conductivity-temperature sensors; moored oxygen and pCO_2 sensors (DeGrandpre-type: SAMI-CO_2); moored nutrient analyzers (MBARI); moored fluorometers; and moored Fast-Repetition Rate fluorometers to measure the in-situ photosynthesis rate. The array dimensions are designed according to observed correlation lengthscales of biological and chemical parameters in order that convergence and divergence of biological and chemical parameters can be determined from the control-volume time-series data. This represents a unique attempt to resolve ocean variability explicitly in order that processes can be examined in-situ. The experiment commences with mooring deployment on or around February 1, 1996.

15. NATIONAL REPORTS

Panel Members were invited to very briefly cover in oral presentations their nations' ocean CO_2 activities and to submit more detailed written summaries as appropriate for this report. These are included in Annex V.

16. FUTURE GOALS

The original goal of the panel was basically to serve as a board of experts to oversee the world survey of ocean CO_2. This work is approaching completion and will end by about the year 2000. Accordingly, the future of the Panel was made an agenda item during this session in order to begin a dialogue that could stimulate thinking intersessionally of the options and perhaps lead to a recommendation to the sponsors during the next session. The question addressed this time was whether this Panel should be disbanded or given new goals. An alternative would be to create a new Panel with new terms of reference and new membership. Consideration of this question had already surfaced during earlier discussions on greenhouse gases other than CO_2 (section 11.2), and CO_2 disposal in the ocean (section 13). The value of a forum to enhance interaction between data managers, observationalists, and modelers was another topic.

17. NEXT MEETING

The Panel considered two proposals to host the next meeting. S. Tsunogai offered to host the next International Ocean CO_2 Symposium and a meeting of this Panel in the October 1997 - March 1998 time frame. B. Schneider offered to host the Panel meeting in June 1997 in Warnemuende when the weather could be expected to be reasonably decent. An important consideration for setting the date of this Panel's meeting is the date of the Fifth session of the WMO Carbon Dioxide Conference in Australia in 1997. Without knowledge of a firm date for that Conference, the Panel tentatively decided to accept the offer from Germany and to ask Tsunogai to consider a later 1998 time frame for his proposal for a joint Ocean CO_2 Symposium and Panel meeting arrangement as was held in Puerto Rico. (It was determined subsequent to the meeting that the WMO CO_2 Conference would be held in Cairns, 8-12 October 1997 and would pose no serious conflict with the planned June Panel meeting in Warnmuende.)

ANNEX I

AGENDA

1. WELCOMING

2. ADOPTION OF THE AGENDA

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3.2 INVENTORIES OF ^{13}C
3.3 NEW TECHNOLOGY
3.4 BATS TIME SERIES
3.5 CO_2 SINK IN THE NORTH PACIFIC

4. RECENT EVENTS AND UPDATES

4.1 BUDGET CUTS AND IMPLICATIONS
4.2 GOOS UPDATE

5. INVENTORY OF pCO_2 DATA

6. OCEAN CO_2 SYSTEM MEASUREMENT ISSUES

6.1 INTERCOMPARISON EXERCISE
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7. MODELLING THE CARBON CYCLE

8. THE OCEAN CARBON BIOLOGICAL PUMP

9. STATUS OF THE GLOBAL CO_2 SURVEY

9.1 AIR-SEA INTERACTION
9.2 INTEGRATING DATA OF DIFFERENT TIME-SPACE SCALES
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9.4 WINTER DATA
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10. STATUS OF ^{13}C

10.1 MONITORING OF ^{13}C
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11. OTHER PANEL-RELATED CLIMATE TOPICS

11.1 IPCC REPORT
11.2 OTHER GREENHOUSE GASES
11.3 AEROSOLS

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13. CO_2 DISPOSAL IN THE OCEAN

14. NEW TECHNOLOGIES

15. NATIONAL REPORTS

16. FUTURE GOALS

17. NEXT MEETING

ANNEX II

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ANNEX III

USING PCO_2 DATA TO CALCULATE CO_2 FLUX OVER THE GLOBAL OCEAN

Submitted by Rik Wanninkhof

The utility of a comprehensive global pCO2 data set is seen in a publication of Takahashi et al. (1996) in which they combined datasets from Takahashi, Weiss, the NOAA laboratories and others to create a seasonal global pCO2 field. Even with over 13000 6-hour averaged data points (binned in 4 by 5 degree boxes), large spatial and temporal gaps remain (see figure x which shows the distribution of all the data and the distribution for two individual months). All the pCO2 data were normalized to 1990 assuming that the surface ocean pCO2 keeps up with the atmospheric trend between 45°S and 45°N while the sub-polar regions increase their air-water partial pressure difference (delta pCO2) at the same rate as atmospheric increase.

To extrapolate the data over time and space, the data were incorporated into a monthly surface-water advection model of Bryan and Lewis (1979) of NOAA/GFDL. This computational scheme was checked by comparing the observed and climatological SST in each box, and between model SST and climatological SST for boxes where no measurements were available. No bias was apparent for both exercises and the standard deviation for the first exercise (climatological vs. observed) was 1.5°C while the standard deviation between climatological and model data was 2.4°C. The delta pCO2 for each month was converted to a monthly flux for each box by using the monthly climatological winds from Esbensen and Kushnir (1981) and three different relationships between gas exchange and wind speed (Liss and Merlivat, 1986; Tans et al., 1990; Wanninkhof, 1992). The resulting annual global fluxes for 1990 are 0.7, 1.0, and 1.3 GtC/yr.

The research clearly shows the utility of a large scale synthesis of global pCO2 datasets as currently being undertaken by the IOC-JGOFS sub-panel. The data used in this study probably constitute less than half the total data available to date. The extrapolation scheme is unique but obviously not perfect as indicated by the standard deviation between model and climatological SST. Using an advection model makes it difficult to place uncertainty limits on the calculated fluxes. Other extrapolation methods, such as objective analysis techniques, do offer (statistical) uncertainty estimates but objective analysis does not take advantage of knowledge about geochemical behavior and thus probably overestimates the uncertainty.

The current estimated annual uptake is very similar to that provided by a more limited dataset of Tans et al. (1990). Using the same gas exchange-wind speed relationship for both studies yields a flux of 1.6 GtC/yr for the 1990 study and 1.3 GtC/yr for the current work. Much of this difference can be reconciled by the fact that the current study excludes El Niño years which decreases the estimated uptake by 0.2 to 0.5 GtC/yr. It is not clear if the good agreement between studies is fortuitous or if the global delta pCO2 maps are adequate to constrain air-water fluxes. Clearly, however, the large differences between the empirical gas-exchange vs. wind-speed relationships, and differences in global wind speed products becomes a more vexing problem now that the delta pCO2 fields are becoming better constrained.

References

Bryan, K., and L.J. Lewis, A water mass model of the world ocean, J. Geophys. Res., 84, 2503-2517, 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, Corvalis OR, 1981.

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.

Takahashi, T., R.A. Feely, R. Weiss, R. Wanninkhof, D.W. Chipman, S.C. Sutherland, and T.T. Takahashi, An estimate of net air-sea flux of CO2 for the global oceans 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, 1996.

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

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

ANNEX IV

INVENTORY OF TIME SERIES
compiled by Bernd Schneider

This inventory consists of the existing CO_2 times series stations and sections that participants at the sixth session of the IOC-SCOR Advisory Panel on Ocean CO_2 were aware of. It is not purported to be a complete list of all time series in the world.

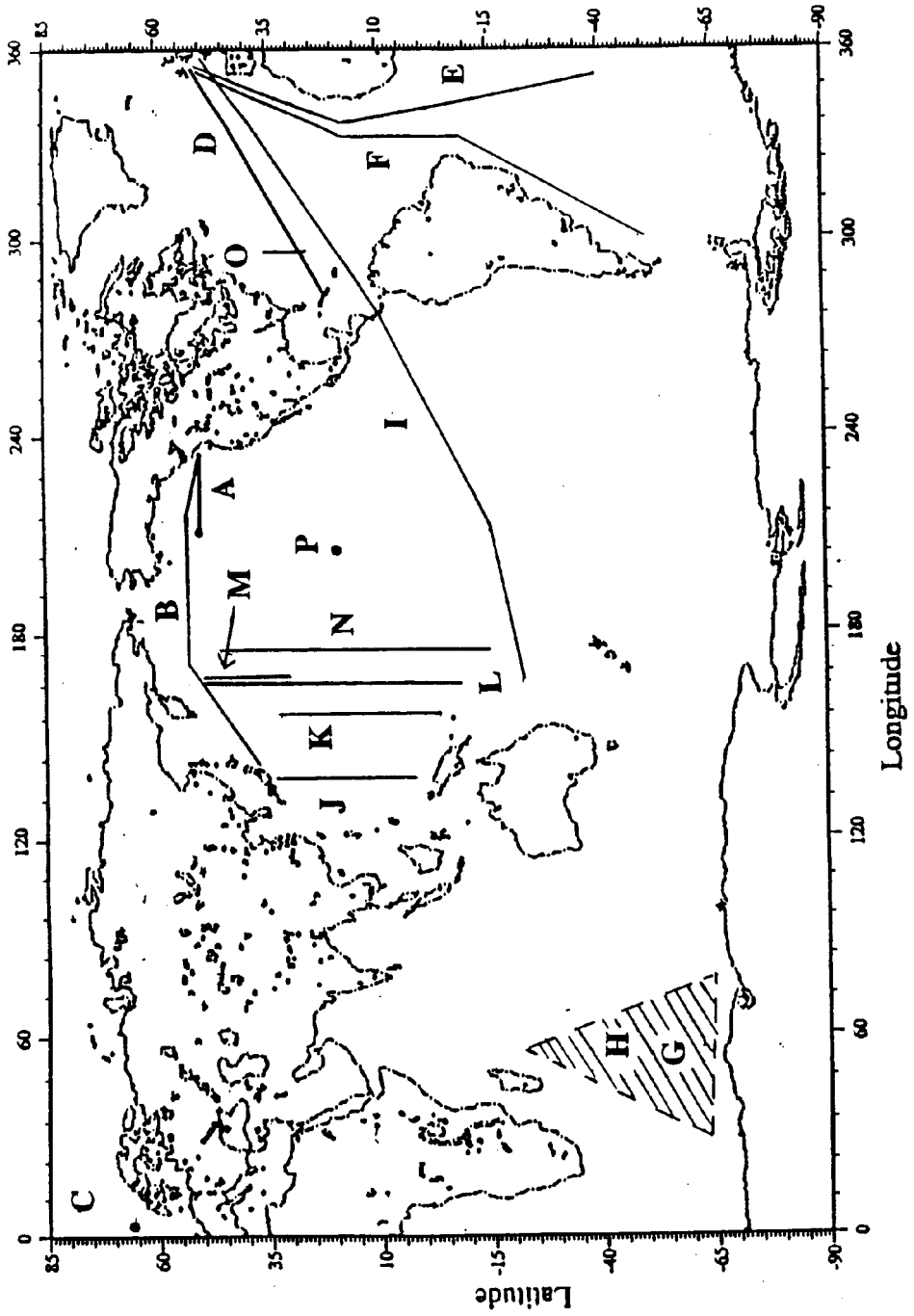

Figure 1: Location of Time Series Stations Listed in the Following Table

Country, Institution		Location, Acronym	Frequency, Period	CO_2 Parameters	Supplementing Variables	Remarks
Canada: IOS	A	Vancouver-Station P (50°N, 145°W)	3-4/yr 1989-cont.	pCO_2 (water,air), C_T, A_T	nutrients, O_2, T,S	research vessel
	B	Vancouver-Japan[1]	12/yr 1995-cont.	fCO_2 (water,air) C_T, A_T, C-13 (water, air)	nutrients,chloroph. T, S air: CH_4, N_2O	ship of opportunity [1] joint project with NIES (Japan)
Norway:	C	Station M (Norwegian Sea)	varying[1] 1988-cont.	pCO_2 (air), C_T	nutrients, O_2, T, S C-13 (occasionally)	[1] in dependence on the season either daily, weekly or monthly
U.K.: PML	D	UK-Jamaica	9/yr May 1994-Aug1995	pCO_2	T	ship of opportunity
	E	UK-Tenerife-St. Helena	9/yr June 1994-cont.	pCO_2	T	ship of opportunity
	F	UK-Falkland Isl.	2/yr (spring/fall) 1995-cont.	pCO_2	nutrients, T, S chlorophyll,optical parameters	research vessel

Country, Institution		Location, Acronym	Frequency, Period	CO_2 Parameters	Supplementing Variables	Remarks
France:						
LPCM	G	western Indian Ocean/Antarctic Sector MINERVE	1985-cont.	pCO_2 (water,air) pH	nutrients, O_2, T,S	research vessel
LPCM	H	south of Kerguelen Islands KERFIX	variable 1990-1993	pCO_2, pH, C_T, A_T	nutrients, O_2, T, S, chlorophyll	fixed station
LODYC	I	Le Havre-Panama-Tahiti-Noumea	4/yr 1991-1997	pCO_2 (water, air)	fluorescence, T, XBT	ship of opportunity
Japan:						
IMA	J	137°E 3°-34°N	2/yr (winter/summer) 1981-cont.	fCO_2 (water, air) C_T	nutrients, T, S, fCH_4	R/V Ryofu Maru
	K	155°E 4°S-30°N	1/yr (summer) 1990-1996	-"-	-"-	-"-
	L	165°E 10°S-50°N	1/yr (autumn) 1997 (start)	-"-	-"-	-"-
	M	165°E 30°N-50°N	1/yr (spring) 1997 (start)	-"-	-"-	-"-

Country, Institution		Location, Acronym	Frequency, Period	CO_2 Parameters	Supplementing Variables	Remarks
Japan:						
NIRE	N	175°E 15°S-48°N	1/yr 1990-cont.	fCO_2, C_T, A_T, pH, C-13, C-14	nutrients, primary prod.,sedim.traps, sediments, T, S	R/V Hakurei Maru
NIES[1]	B	Japan[2]-Vancouver	12/yr 1995-cont.	fCO_2 (water,air) C_T, pH, C-13 (water,air), A_T	nutrients, chloroph. T, S in air: CH_4, N_2O	ship of opportunity [1]joint project with IOS (Canada) [2]different harbours
USA:						
BBS	O	Bermuda BATS	12/yr 1987-cont.	pCO_2, C_T, A_T	nutrients, biomass T, S	fixed station
UH	P	Hawaii HOTS	12/yr 1990-cont.	pCO_2, C_T, A_T, pH	nutrients, biomass O_2, N_2, Ar	fixed station

ANNEX V

NATIONAL REPORTS

CANADA

Pacific work included the start of analytic work on samples for DIC, TA checks on WOCE line P1W and P15 N in 1993 and 1994 respectively, and $^{13}C/^{12}C$ extractions on these and previous cruises 1991, 1992 in the NW Pacific in co-operation with Russia.

In 1995, the field programmes were: (i) repeat oceanography on WOCE Line P and Station P, three times a year to Station P (50N, 145W) with shipboard pCO_2 measurements and sample collections for DIC, TA and ^{13}C. Freon profiles were measured at Station P and other stations on line P to study freon and delta ^{13}C penetration; (ii) a winter expedition to Okhotsk Sea of SIO and UW (Steve Riser), PMEL (Bullister). Samples were collected of DIC, TA and ^{13}C; (iii) ship-of-opportunity programme was initiated in March 1995 for a bilateral Canada-Japan programme between the National Institute for Environmental Studies (NIES) and the Ocean Biogeochemistry Group (primarily called Centre for Ocean Climate Chemistry) of IOS. A lumber carrier, the **M.V. SKAUGRAN**, is making 10-12 crossings per year from Tokyo, Japan to Vancouver, Canada, then back to Tokyo via the great circle route through the NE Pacific, Bering Sea, waters of Kamchatka and Kurile Islands, with two technicians on board. Shipboard measurements were made for air and surface sea water pCO_2, fluorescence, T, S and O_2 (by sensor), XBT. Sample collections included those for DIC, TA, nutrients (P, N, Si), atmospheric ^{13}C and oceanic ,^{13}C fluorescence, (IOS) and for atmospheric trace gases (CO_2, CO, CH_4, N_20, ^{13}C) at NIES; $0_2/N_2$ for SIO; (iv) Arctic-95: Samples were collected for $^{13}C/^{12}C$ from the Beaufort Sea and Chukchi Seas in the Arctic; (v) WOCE P-15S: Samples were collected for three stations for intercalibration (University of Washington (Paul Quay) and IOS (Wong) to ensure compatibility between P-15N and P-15S. Intercalibration work was conducted between eleven laboratories for ^{13}C comparison using sea water prepared at SIO. Another intercalibration was done between IOS and Hokkaido University for pCO_2, TA, DIC and ^{13}C.

FRANCE

Work on oceanic carbon in France is funded under three different programmes: National Programme for Study of the Climate: Programme Nationale d'Etude du Climat (PNEDC); JGOFS; and WOCE.

1. PNEDC

1.1 DEVELOPMENT AND FIELD TEST (MEDITERRANEAN SEA AND PACIFIC OCEAN) OF AN AUTONOMOUS BUOY FOR THE MEASUREMENT OF PCO_2, CARIOCA

1.2 ECOA PROGRAMME:

Measurements of pCO_2 are made on a ship of opportunituy four times a year along the line Le Havre-Panama-Tahiti-Noumea, across the Atlantic and the Pacific. This is a time series.

1.3 MINERVE PROGRAMME:

Measurement of surface $_pCO_2$ were performed in 1996 along four cruises between Cyprus and La Réunion in February; La Réunion, Djibouti and Marseille in March/April; Djibouti and La Réunion in July and between La Réunion, South of Kerguelen Archipelago (58^0S) and La Réunion in October/November. Surface and deep samples were analyzed for TCO_2 and TA during this last cruise. Three cruises are planned in 1996 between Durban and the Antarctic Continent in February. La Réunion, Durban, Socotra and La Réunion in August and between Hobart and Terre Adélie in October.

This programme will continue two or four times a year between La Réunion and the French sud-antactic islands for several years with an extention of sub-surface measurements of temperature, salinity, oxygen, chlorophyll "a" p^H and TCO_2.

1-4c: a 1D model has been developed at the LPCM to interpolate and extrapolate the sparse data they collexted in the Western Indian Ocean.

3-1: In the Pacific Ocean: surface PCO_2 and deep TCO_2 and TA were measured by the LPCM during the Flupac and Olipac cruises between Nouméa andTahiti along the Equator.

3-2: In the Indian Ocean, TCO_2 and TA were measured by the LPCM on deep samples during the ANTARES/JGOFS cruise south of the Kerguelen Archipelago.

1.4 MODELLING:

(i) Tropical Atlantic: coupling of a biogeochemical model with the 3-D primitive equation of LODYC.

(ii) Tracers distribution (T, CFC, ^{14}C) in the 3-D model Intercomparison of 3D models for the carbon and ^{14}C uptake Data assimilation.

2. WOCE

2.1 PCO_2, TCO_2 MEASUREMENTS IN THE TROPICAL ATLANTIC (PROGRAMME ETAMBOT).

3. JGOFS

3.1 IN THE PACIFIC: EPOPE

3.2 IN THE INDIAN OCEAN: ANTARES.

JAPAN

1. Time Series Observations

Since 1990, the Japan Meteorological Agency, (JMA) has been making operational observations of fugacities of CO_2 and CH_4 in the surface water and in the surface air along two meridional lines: (1) along 137ºE between 35ºN and 3ºN twice a year, and (2) along 155ºE between 30ºN and 5ºS once a year. This effort is based on the same observation programme conducted by the Meteorological Research Institute (MRI) as a research activity from 1984. That research produced many valuable results, some of which were published in the recent Tellus (**47**, 391, 1995).

There is a plan to change the observation line along 155ºE to 165ºE between 50ºN and 10ºS, and to observe this line between 50ºN and 30ºN twice a year beginning in 1997. The plan also calls for a change in the line along 155ºE to 165ºE between 50º and 10ºS, and to observe the line between 50ºN and 30ºN twice a year starting in 1997. The intention is to measure total CO_2, pH, alkalinity and CFCs in the water column.

The North Pacific Carbon Cycle Study (NOPPACS) of the National Institute of Resources and Environment (NIRE) has been occupying a section along 175ºE between 48ºN and 15ºS once a year since 1990. The observations include the water column distributions of $f(CO_2)$, TCO_2, ^{14}C, ^{13}C, alkalinity, pH, nutrients, pigments, CFCs and biomass as well as primary production measurements and sediment trap experiments. The programme will continue after 1996 with some modifications.

The National Institute of Environmental Science (NIES) started observations of $f(CO_2)$ of surface water in March 1995 in the northern North Pacific by using the ship-of opportunity SKAUGRAN between Japan and Canada. The preliminary results show small $f(CO_2)$ values in the sub-boreal North Pacific. It

takes about two weeks for one traverse or 40 days for one cycle. The observations will continue at least for a few years.

2. Co_2 Survey

The Hokkaido University group participated in the Japanese WOCE cruises for CO_2. The observation lines were P13 along 165ºE and P2 along 30ºN. In 1996, they will observe P8 along 130ºE in the western North Pacific.

3. Process Studies

The Science and Technology Agency (STA) programme, MASFLEX (Marginal Sea Flux Experiment in the West Pacific) has been active in the East China Sea since 1992 participating in a Japan-China co-operative study. The results show a great deficit in $f(CO_2)$ of 60 ppm as an annual mean in the East China Sea surface water. This programme will end in February 1996.

4. New Vessels

RYOFU MARU of JMA will be replaced by a new vessel in 1997, which can more easily observe oceanic carbon species and extend the observation line stated above. The new vessel can be used for observations of the oceanic carbon system in winter and a committee for its use is now considering the programme.

5. New Facilities

In 1995, the Japan Foundation for the Promotion of Marine Sciences was established. It will be financially supported by STA. The Foundation created a new small Research Institute, the Mutsu Oceanographic Research Institute at Mutsu City, in northern Japan. The Institute will have an AMS (Accelerator Mass Spectrometer) for the determination of ^{14}C in seawater in 1996, which will be available to all Japanese chemical oceanographers.

6. GOOS and Japanese Intercomparison Exercises for Measurement of the Oceanic Carbon System

In view of the implementation of GOOS, Japanese oceanographers are carrying out a project under the aegis of the MESC (Ministry of Education, Science and Culture), a fundamental study for GOOS. As part of the project, the Japanese intercomparison experiments for the oceanic carbon species were carried out at the Usujiri station of Hokkaido University, 22-26 June 1995. About 20 persons from 8 institutes participated. The variables examined were: $f(CO_2)$, TCO_2, pH and alkalinity. The location was extremely favourable for the work, because the diurnal variation in $f(CO_2)$ ranged from less than 200 to more than 400 ppm. The great variation revealed the weak points of analytical methods and procedures.

Even though the equilibrators for the $f(CO_2)$ were calibrated against the same standard gases, the values measured did not coincide due to the three following reasons: A large or long equilibrator responded with some lag time. The shower-head type equilibrator without a vent gave high values. Its content was probably under reduced pressure due to sucking of air bubbles by the flowing water. Finally, the bubbling type equilibrator showed an unstable base line, although the effect of over pressure on the rising bubbles could not be determined. A wider variation obtained with a titration type method of Okayhama University is also difficult to explain.

An institute using a gas chromatographic method for the TCO_2 determination gave less precise values than those using a coulometric method. The reported values for alkalinity varied widely but in parallel from institution to institution. For the determinations of TCO_2 and alkalinity, the use of standard reference materials is therefore essential. Experiments confirmed that the spectrophotometric method is precise, and the scale including the preparation of standard solutions is important for the determination of pH.

6. Meetings and the Japanese Oceanic Co_2 Community

The Japanese oceanographic CO_2 community is now growing rapidly. After the intercomparison exercises described above, participants met in Tsukuba and decided to hold meetings periodically to discuss new findings, new technologies and future funding. The next meeting will be held August 1996 in Sapporo.

RUSSIA

The problem of CO_2 in oceans is being investigated in Russia by the two Programmes which have government's support. One of them is Russian National Research Programme "Comprehensive Investigation of Oceans and Seas". The leader of this programme: Academician Igor S. Gramborg. It comprises the following:

(i) "Physical Fields of Russian Seas and of Oceans", the leader academician Artem S. Sarkisyan.

(ii) "Chemical Patterns of Russian Seas and Oceans", leaders: Dr. Igor I. Volkov, Dr. Victor V. Sapozhnikov.

(iii) "Dynamics of Ecosystems, Biostructure and Biological Resources", leaders: Academician Mikhail E. Vinigradov, Dr. Anatoly A. Elizarov.

(iv) "Ocean and Seas Geospheres: Composition, Structure, Evolution," leaders: Dr. Anatoly N. Vishnevsky, academician Yury M. Pushckkarovsky.

(v) "The Arctic", leaders: Dr. Vladimir L. Ivanov, Dr. Ivan E. Folov.

(vi) "The Antarctic", leaders: Dr. Alexander I. Danilov, Dr. Vladimir M. Kotlyakov.

(vii) "The Seas of Russia", leader : Dr. Sergey S. Lappo.

(viii) "Economic, Political and Legal Problems of Scientific Research of Using Resources and Expanses of the World Ocean", leaders: Dr. Yury G. Barsegov, Dr. Anatoly L. Kolodkin.

(ix) "The Hardware and Techniques for Measurements", leader Dr. Rostislav V. Ozmidov.

One of the goals of the Problem Area 2 is the study of the global biogeochemical cycles of carbon in the oceans. This work is focused on the "Hydrochemical" data bank which incldes the hydrochemical parameters which have been measured since 1927 till now. This year we accomplished quality control of the pH, alkalinity, total carbon and dissolved oxygen in surface waters of the Pacific, Atlantic and Indian oceans.

Other important work in this area includes investigations of the spatial and temporal distribution of the carbon system elements in the local region of the ocean.

The Problem Area 3 includes evaluating role of the oceanic ecosystems in the global cycle of carbon and oxygen.

The second of these big Programmes is a Federal Research Programme of Russia "Global Changes of Environment and Climate". The leader of this Programme: academician N.P. Laverov. The main goals of this programme are investigations of the "greenhouse" effect, interaction between biota and the geospheres and prediction of the possible climate changes. This Programme consists of the following branches:

Branch 1 "Global changes of environment"
Branch 2 "Seismicity and related processes in the environment"
Branch 3 "Global changes of climate"
Branch 4 "Global changes effects on the biosphere"
Branch 5 "Monitoring of global environment and climate change"

Branch 6 "Ensuring a steady progress on national economy under changing climate and global changes of environment"

Branch 4 is focused on the investigation of carbon dioxide and other "greenhouse" gases. The leader of this Branch is academician G.A. Zavarzin. This Branch consists of the following Projects:

4.1 "Biogenic formation and consumption of carbon dioxide".
4.2 "Biogenic emission of greenhouse gases".
4.3 "Vegetation cover in relation to moisture variation".
4.4 "The condition of soils and landscapes in relation to global changes".
4.5 "Major changes in the biosphere of the past".
4.6.1 "Coastal ecosystems".
4.6.2 "The streams of oxygen and carbon in the ocean".
4.7 "Zonal changes in ecosystems".

Carbon dioxide in the ocean is being investigated in Project 4.6.2. "The streams of oxygen and carbon in the ocean". It is led by academician M.E. Vinogradov (Deputy Director of the P.P. Shirshov's Institute of Oceanology RAS). Scientific secretary of this Project is Dr. P.N. Makkaveev. This Project connects 5 research groups:

4.6.2.1 "The investigation and quantitative estimation of the carbon dioxide and oxygen exchange between the ocean and atmosphere" (leader Prof. Dr.O.K. Bordovsky).

4.6.2.2. "The regularity of forming and changing of the carbon flux from the upper layer to the deep waters of the ocean" (leader: academician M.E. Vinogradov).

4.6.2.3 "The regularity of the extraction of the carbon dioxide from the building of skeletons and peculiarities of the burying them in sediments" (leader: Prof. Dr. A.A. Romankevich).

4.6.2.4 "The peculiarities of the carbon streams through the layers of the ocean waters below the photic zone and its burning in the sediments" (leader academician A.P. Lisitsin).

4.6.2.5 "The variability of the components of the carbon and oxygen cycles in the ocean evaluation" (leader Dr. A.P. Kuznetsov).

This project began in 1992. This year a primary consideration was the determination of the correlation between the surface chlorophyll concentration measured by satellite data and the ecosystem peculiarities which specify the formation and the intensity of the carbon flux from the aphotic zone into the deep ocean layers. The existence of in time connection between the measured from the satellite peculiarities of the various community elements of the aphotic zone was demonstrated for the communities of North Atlantic open regions. Then the same investigations were provided for the Pacific ocean.

Along with this investigation in the area of this Project were done other works:

4.6.2a The investigation of the detritus flux in the Norwegian Sea and central tropical Atlantic.
4.6.2b The development of a mathematical model of the carbon flux in the oceans biological community.
4.6.2c The investigations of the carbonate equilibrium of the Black Sea waters and in the waters of the mixed sea-river zones in the Kara Sea.

For the investigation of the carbon fluxes in the ocean, various sediment traps were placed in the Norwegian, Barents and Kara Seas.

SWITZERLAND

The University of Bern continues to investigate the climate system, the global carbon cycle, and in particular the links between the relatively fast exchanging carbon reservoirs (marine and terrestrial biospheres, ocean, sediment, atmosphere) by both measuring climate parameters and by modeling.

For the ocean modeling, a hierachy of transport models are used, i.e., 1-dimension (1-D) box-diffusion type models and dynamical 2-D and 3-D models. Interactions between ocean circulation, carbon cycle and the climate system are typically assessed on time scales of decades to centuries to study the anthropogenic perturbations as well as on the long time scales of glacial-interglacial cycles to study natural climate variations.

Within the European programme 'Environment' the ocean's role in controlling observed glacial-interglacial atmospheric CO_2 variations as well as the ocean's role in linking observed northern and southern hemisphere climate variations are investigated. A special emphasis is given to modeling the distribution of ^{13}C in the climate system to allow a comparison between model results and ^{13}C observations in ocean sediments and in air-bubbles trapped in ice. This highlights the importance of appropriate ^{13}C observations in the different carbon reservoirs as a unique quantitative tool to assess potential future climate changes based on observed glacial-interglacial climate variations.

Observations of the atmospheric CO_2 and ^{13}C history since pre-industrial time are used to estimate the net uptake of anthropogenic carbon by the ocean and the terrestrial biosphere. For integrated assessment studies of global change, simplified ocean and terrestrial carbon uptake models are developed.

University of Bern continues to measure important climate parameters, such as CO_2, ^{13}C, CH_4, ^{18}O, H_2O_2, NH_4 in air bubbles trapped in ice to reconstruct past atmospheric concentrations. A new ice core will be drilled in Antarctica by a team of scientists from different groups (European programme EPICA) and Switzerland will contribute to this effort and to the processing of the core.

Argon-39 which allows one to validate ocean transport model is further measured in seawater samples.

USA

The US has four main components to its CO_2 related work which is supported by three federal agencies: the US National Science Foundation (NSF), the US Department of Energy (DOE), and the National Oceanic and Atmospheric Administration (NOAA).

(i) The US JGOFS time-series of measurements made on (approximately monthly) samples obtained from two sites, one near Hawaii and one near Bermuda. Information about these time-series stations is available on the World Wide Web (WWW) through the US JGOFS Home Page:
http://www1.whoi.edu/jgofs.html

(ii) The JGOFS "global carbon dioxide survey" undertaken on cruises of the US WOCE Hydrographic Program (as well as on occasional cooperative non-US cruises). Some information about this program is available on the WWW:

http://www.oasdpo.bnl.gov/~oasdpo/mosaic/DOECO2/

(iii) US JGOFS Process Studies during which a number of cruises are made in a particular study area over a relatively short period of time (1-2 years). Information about these Process Studies is available on the World Wide Web through the US JGOFS Home Page:
http://www1.whoi.edu/jgofs.html

(iv) The NOAA OACES (Ocean Atmosphere Carbon Exchange Studies) program which has typically been studying (and hopes to repeat) "long lines" in the various ocean basins. Again, information about this program is available on the World Wide Web:

http://www.pmel.noaa.gov/co2/co2-home.html

In addition, US federal agencies have supported work into carbon dioxide reference materials at the Scripps Institution of Oceanography, and these have been distributed widely both within the US and internationally, and into CO2 data archival at the Carbon Dioxide Information Analysis Centre (CDIAC) at Oak Ridge, Tennessee. For more information see:

http://www-mpl.ucsd.edu/andrew/CO2_QCsite/Home.html
http://cdiac.esd.ornl.gov:80/cdiac/

Work completed in 1995/1996

(i) Measurements of total dissolved inorganic carbon, total alkalinity, and pH were measured on monthly depth profiles for the Hawaii time-series site. In addition, a limited number of measurements of surface p(CO2) were made. At Bermuda, total dissolved inorganic carbon and total alkalinity were measured on monthly depth profiles, and underway p(CO2) on the various cruises.

(ii) The US WOCE Indian Ocean Survey. The CO2 measurements on this survey - total dissolved inorganic carbon; total alkalinity; and underway p(CO2) - represent a collaborative effort between a number of separate investigators over a 14-month period, and along 92,000 km of ship track. These data are currently being processed, and are expected to be submitted to CDIAC in the coming year.

(iii) The Arabian Sea Process Study cruises were completed. A number of cruises involved CO2 measurements: total dissolved inorganic carbon, total alkalinity; and underway p(CO2). Details of this program are available from the US JGOFS Home Page (see above).

(iv) NOAA undertook work in the Indian Ocean. Underway p(CO2) and underway pH was measured on a series of legs over the course of the year; in addition regular surface samples were taken for measurement of total inorganic carbon. During the OACES leg (Fremantle - Maldive Islands), additional depth profiles were measured for total dissolved inorganic carbon, total alkalinity, pH and discrete p(CO2). This leg was a WOCE Hydrographic Program repeat leg which repeated a cruise that had been carried out six months previously (section ii).

Work Planned for 1996-1997

(i) The US JGOFS time-series of measurements at Hawaii and Bermuda will continue.

(ii) The JGOFS "global carbon dioxide survey" will participate in a limited number of US WOCE cruises in the North Atlantic. The first cruise is in October 1996, and the remainder are in 1997.

(iii) The US JGOFS Southern Ocean Process Studies programme is now underway, and is expected to continue for about 2 years of field work.

(iv) There is no NOAA work planned in this time frame, the next OACES cruise is provisionally planned for 1998.

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