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*Reports of Meetings of Experts and Equivalent Bodies*

# **Joint IOC-JGOFS CO<sub>2</sub> Advisory Panel Meeting**

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## 1. WELCOMING

Chairman Andrew Watson opened the eighth session of the IOC-JGOFS Advisory Panel on Ocean CO<sub>2</sub> at 08:30, 16 January 1999 at the Tsukuba Centre, in Tsukuba, Japan. He welcomed the members and expressed his appreciation to Professor Shizuo Tsunogai for hosting the meeting and for arranging the 2<sup>nd</sup> International Symposium on Ocean CO<sub>2</sub> scheduled for the following week. Watson thanked him for the generous financial support that Tsunogai had secured from a Japanese grant that made it possible to underwrite a good part of the travel costs for participants coming to Tsukuba for the meeting and the Symposium. The complete list of participants can be found in Annex II.

Tsunogai also welcomed the Panel members and informed the meeting that 25 years ago, the city of Tsunogai did not exist. It was designed as a model Science City, decentralized from the ever increasing crowded conditions in Tokyo, to provide the Ibaraki region with a national centre for high-level research and education. Tsukuba Science City is expected to expand in the future to play a new role in establishing a large, interdependent urban complex, complementary to the Tokyo metropolitan area.

## 2. ADOPTION OF THE AGENDA

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

## 3 RECENT EVENTS AND UPDATES

### 3.1 GOOS/OOPC

A. Alexiou brought the attention of the Panel to noteworthy events related to the continuing development of GOOS. A comprehensive 150-page colour document titled *The Global Ocean Observing System Prospectus 1998* was issued during the IOC Executive Council in November 1998. It provides in one place the background, vision, design, present state, principles of involvement and framework for implementation.

A major achievement was the creation of the GOOS Initial Observing System, which unites the main global observing sub-systems supported by the IOC, WMO and (in the case of coral reefs) the IUCN, and includes measurements from ships, buoys, coastal stations and satellites. Significantly, the included TAO moored buoy array in the tropical Pacific is now maintained under operational funding by NOAA.

WMO and IOC have approved the creation of a Joint Technical Commission for Oceanography and Meteorology (JCOMM) to replace the existing Commission for Marine Meteorology (CMM). It will be responsible for coordinating data of all kinds collected at sea from the upper ocean and the lower atmosphere and for developing, implementing and maintaining operational data collection and dissemination systems to meet requirements of GOOS, GCOS and WCRP.

There are now established Panels for all the modules of GOOS. Thorkild Aarup filled a new position to provide senior scientific support for the Coastal Panel. Draft plans for each module are expected by the end of this year (1999). Progress in implementing GOOS at present is predominantly through efforts of the Ocean Observations Panel for Climate (OOPC). The OOPC gave birth to GODAE, the Global Ocean Data Assimilation Experiment, designed to demonstrate the power of integrating satellite and *in situ* data, the power of model assimilation, and the value of a global system capable of working in real-time. As part of GODAE, a project called Argo is being developed to provide global real-time coverage for the first time of upper ocean temperature and salinity. Argo plans call for the deployment of 3000 profiling floats rising from 2000 m to the surface every 14 days, all measuring

temperature, and a special set making both temperature and salinity (CTD) measurements. The OOPC in a joint action with the Upper Ocean Panel of CLIVAR plan to convene the First International Ocean Observations Conference in St Raphaël, October 18-22, 1999.

L. Merlivat observed that GODAE does not include carbon measurements and she believed this shortcoming was due to lack of representation by ocean carbon experts on the OOPC or the GODAE steering team. She encouraged participation in GODAE planning by the ocean carbon observing community.

### 3.2 SEQUESTRATION OF CO<sub>2</sub> IN THE OCEAN

Up till now, the Panel has taken no position on CO<sub>2</sub> sequestration in the ocean, choosing instead to keep an eye on developments. Takashi Ohsumi noted there has been much work in this field since the last meeting and the Tsukuba symposium has several papers on the subject. Taro Takahashi reported that the US Department of Energy and the National Science Foundation recently met to develop a "road map" for fostering research and development. One panel considered issues concerned with CO<sub>2</sub> dumping into the ocean and into the earth's crust. He suggested the Panel take a more pro-active roll in evaluating these types of experiments. An independent impartial assessment of these activities seems to be missing.

Ohsumi has been asked to initiate a scientific workshop with the objective of providing useful information to the IPCC and to plan the next steps for these types of studies. He offered the possibility of inviting members of the Panel to participate. At present he plans to have some parts of the workshop open and others closed.

Clearly, CO<sub>2</sub> sequestration is becoming increasingly important for several countries and the Panel agreed the scientific community has to be entirely involved. Takahashi, Wong, Merlivat, Ohsumi, and Alexiou met separately off-line to consider an appropriate course of action for the Panel. They concluded that a sub-panel should be formed to look in more detail at ocean sequestration and over the next year or to prepare a state-of-knowledge report. The sub-panel should include at least a biologist and a modeler. The aim will be to provide an overview, from the perspective of ocean CO<sub>2</sub> scientists, of the scientific issues which proposals for CO<sub>2</sub> sequestration experiments raise, namely:

- How cost-effective may it be for reducing the impact of fossil fuel CO<sub>2</sub> on the climate?
- What is the likely chemical fate of injected CO<sub>2</sub> over time?
- Will the likely biological impact be large?
- What are the legacies for future generations?

The audience for the report will be the sponsors of the Panel and other members of the marine science community.

The group agreed that it is critical that the report be perceived as impartial and thus it could not rely too heavily on scientists who are already funded by industry sources to research this topic. Takahashi, Ohsumi, Watson, Wong, and Alexiou guardedly agreed to be on the sub-panel but not to chair it. Subsequent attempts to persuade a qualified individual from the participants at the symposium to chair it were unsuccessful. Appointing a chair and other members remains as an action item for the intersessionary period. Takahashi agreed to circulate a list of chapter or topic headings as a way of getting the process started.

### 3.3 PICES PLANS

C.S. Wong informed the Panel that the focus of PICES (Pacific ICES) is the region north of 30° N. The programme acquires long-term data on salinity, nutrients, CO<sub>2</sub>, mixed-layer depth, phytoplankton, zooplankton, squid stocks, pelagic fisheries, etc. Indications are that with warming, more fresh water is available to the coastal surface waters increasing the stratification and depressing

upwelling. This results in less nutrients supplied to coastal areas, probably portending lower biological productivity. The ramifications to C uptake are unclear.

The Panel was informed by Alexander Bychkov, Assistant Executive Secretary of PICES, of the work of the newly constituted PICES Working Group 13 on "Carbon Dioxide in the North Pacific". The task of this Working Group, to coordinate studies of carbon dioxide in the North Pacific (particularly those of the various PICES member nations), is an important one. The Panel members were particularly impressed by the range of work planned for the future in the North Pacific, and believed that the measurements proposed will complement these data that have been collected so far under the auspices of JGOFS and of various national programmes.

In particular, the Panel was pleased to hear that Working Group 13 plans to organize two specific international workshops. The first of these, a technical workshop (planned for April 1999 in Tsukuba, Japan) is aimed at improving the CO<sub>2</sub> measurement capability of scientists from the various PICES member nations. This will be very important to help ensure that future CO<sub>2</sub> data, collected in the North Pacific region, are of the high quality needed for biogeochemical studies. The second workshop, planned for the year 2000, is a data workshop involving scientists from the various PICES member nations. It will provide an excellent opportunity to initiate a multi-national synthesis process aimed at bringing together the various CO<sub>2</sub> data sets from around the North Pacific. This will be a major contribution to improving our overall understanding of the processes affecting the carbon cycle in the North Pacific.

The Panel would like to congratulate PICES on initiating what seems to be a very effective international Working Group, and wish to offer their encouragement in these important activities.

### 3.4 MODELLING ISSUES

Fortunat Joos provided a briefing on two currently debated issues related to CO<sub>2</sub> modelling and observations in the ocean. The first is the global-warming issue related to the marine carbon-cycle feedback. This is a potentially important positive feedback loop in the climate system that involves atmospheric CO<sub>2</sub>, global warming, the hydrological cycle, ocean circulation, and the marine carbon cycle in a world of continued carbon emissions. The chain of events theorized starts with the assumption that rising atmospheric CO<sub>2</sub> leads to increased radiative forcing and climate warming. This leads to an increase of sea surface temperature (SST) and a reduction in high-latitude sea surface salinity (SSS) which results in a stronger hydrological cycle that could result in a breakdown of the thermohaline (i.e., density-driven) circulation of the North Atlantic. This would cause a reorganization of the marine carbon cycle, and a reduction in the surface-to-deep transport of anthropogenic carbon. This decreased oceanic carbon uptake may in turn accelerate the atmospheric CO<sub>2</sub> growth.

The importance of this potential positive feedback is, at present, under debate. Maier-Reimer and his colleagues concluded that the weakening of the surface-to-deep transport and the more effective biological utilization of surface nutrients are marginal for the evolution of atmospheric CO<sub>2</sub>. On the other hand, the calculations of Sarmiento and his colleagues suggest that a weakening of the thermohaline circulation and SST warming would reduce ocean carbon uptake by up to 50% and that such reductions are only partly offset by changes in the marine biological cycle. In a modelling study at Climate and Environmental Physics in Bern, it was found that projected atmospheric CO<sub>2</sub> increase since pre-industrial time would be about 4 % higher at year 2100 and about 20 % higher at year 2500 for simulations with, than for simulations without global warming. The reduction in ocean carbon uptake is mainly explained by the consequences of sea-surface warming, in which the projected changes of the marine biological cycle tend to compensate for the reduction in downward mixing of anthropogenic carbon, except when the North Atlantic thermohaline circulation collapses. Such a collapse slows the oceanic uptake of anthropogenic CO<sub>2</sub> significantly.

Joos concluded that two adjustments are necessary to further clarify the role of this potential feedback. First, more existing ocean models and models with isopycnal mixing and higher resolutions should be used to determine the strength of the circulation changes under global warming. Second, formulations that describe the marine biota in a more process-oriented way should be implemented in the physical geochemical models. A shortcoming of the studies mentioned above is that the marine biota were treated by the classical biogeochemical Redfield approach. Joos recommended that:

- more attention be given on how potential future changes in the ocean circulation, the marine biota, and the biogeochemical cycles can be detected by observations;
- efforts to build process-oriented models of the marine biota for inclusion into coupled atmosphere/ocean transport models are continued;
- additional modelling groups study the global-warming/marine-carbon-cycle feedback.

The second actively debated issue is the uncertainty in the magnitude of the variability in the net air-to-sea flux of carbon. Much of the recent debate of the carbon cycle community has focused on interannual and regional variability in oceanic and terrestrial carbon sources and sinks. The magnitude of interannual variability in the oceanic carbon sink is still highly controversial. Atmospheric inversion studies over the years by investigators (e.g., Francey, Keeling, Rayner, and Joos) have found an interannual variability of up to 5 GtC/yr, although the two most recent studies converge on a variability of  $\pm 1$  GtC/yr. Feely and his group at PMEL found, by analyzing their surface pCO<sub>2</sub> data, a decrease of  $0.4 \pm 0.5$  GtC/yr in the carbon efflux at the Equatorial Pacific. On the other hand, a reconstruction of the variability based on the existing oceanic CO<sub>2</sub> data by a group led by Lee, and a modelling study by LeQuere suggest almost no interannual variability. Narrowing the gap between these results remains an important objective.

#### 4. OCEAN CO<sub>2</sub> SYSTEM MEASUREMENT ISSUES

##### 4.1 STANDARDS AND REFERENCE MATERIALS

Andrew Dickson reviewed the progress in the development of Certified Reference Materials (CRMs) (natural sea water preserved and analyzed for DIC and *A*<sub>T</sub> (total alkalinity) prepared by SIO. These are now supported solely by NSF. At present his lab is working on certification for pH and perhaps pCO<sub>2</sub>. The status now is that *C*<sub>T</sub> (total phosphorous) is on track, but *A*<sub>T</sub> is still a bit problematic - very good precision has been achieved on *A*<sub>T</sub>, but problems remain in establishing accuracy to better than  $\pm 2$   $\mu$ mol/kg. Dickson showed a comparison of *A*<sub>T</sub> determination with Frank Millero's lab. On the whole, Dickson was encouraged that the comparison gave very similar results. Measurements at sea by Millero's group are made in a closed cell. The latter can vary due to changes in volume of the cells before or during a cruise. Another comparison was made with Bob Byrne (University of South Florida) who developed a simple method for *A*<sub>T</sub> using a single-step acid addition and spectrophotometric method. Byrne's results were very close to Dickson's lab. BUT, all these are tied to acid determined by or checked by Dickson's lab, so they are not entirely independent.

One significant contributor to the accuracy problem is electrode specifications. Dickson received recently a new set of electrodes that give values 1.5  $\mu$ mol/kg high and he does not know why. Another issue for the CRMs for DIC is that the Hg manometer at SIO will be moved for building renovation. All numbers are tied to this manometer, so it's not clear whether the Hg manometer link will continue to be available.

Present funding by NSF (Don Rice) remains quite good, but the standards programme future in general is very tenuous since funding is dependent on proposals. Dickson started to charge \$25/bottle which covers costs for producing CRMs although research costs are not covered.



Taro Takahashi reported some recent experience with the CRMs. He made repeat analyses (at least 80) over 30 days of pCO<sub>2</sub> at 20° in CRM Batch 36. The results show a slope of 0.025 µatm/day; this is equivalent to 0.01 µmol/kg/day. He questioned whether it is safe to assume that pCO<sub>2</sub> is constant in Dickson CRMs.

Dickson pointed out that it is not clear in situations like this exactly what is changing. Is *A<sub>T</sub>* possibly changing? Or the reference gas changing? Or???? More collaborative work and more cross-checking are needed to evaluate whether these 'trends' are the results of the CRM changing, or some quirk in the laboratory measurement affecting the result of analysis. Preliminary results suggest that DIC works well usually to within 5 µatm; *A<sub>T</sub>* shows slightly less good agreement but results are suggestive that the closed cell method has more intrinsic variability. His conclusion is that the CRMs really are working!

#### 4.2 VARIABILITY IN THE CARBON/NUTRIENTS SYSTEM

C.S. Wong offered a hypothesis that the biological pump controlling CO<sub>2</sub> is not in steady state, but operates intermittently, as, e.g., during ENSO events. SKAUGRAN data along the great circle route from Canada to Japan show seasonal changes of DIC and nitrate in different water masses. Of the 1.4 GtC change, roughly 1 GtC is new production and 0.4 GtC uptake. During ENSO events one sees larger fluxes of POC and PON in sediment traps, from 10 to 25% increase in deep waters. The C:N ratio decreases from 12 (variable) at 200 m, to 9.5 at 1000 m and to about 8.6 at 3899 m. The Redfield ratio is not constant. Suggested forcing mechanisms for this phenomenon might be the differences during ENSO years of increased light availability, and more fresh water drainage from western North America.

Shizuo Tsunogai showed a table to compare North Pacific, South Pacific and North Atlantic water which have very different *A<sub>T</sub>* and phosphorous but very similar *C<sub>T</sub>*. He recommended that observation programmes should pay greater attention to obtaining high quality nutrient data particularly in deep water.

Takahashi reported on an Antarctic study where diatoms grow in nutrient rich waters, feasting on P. This study suggests that P is more variable than for nitrogen and that P may be much more variable than previously thought. N variability is well known because of denitrification processes. He also reported that WOCE data showing that nutrients agreement on crossings are poor. This suggests that CRMs are needed for making nutrient measurements in order to address and sort out any variability of the Redfield Ratio vs. problems with measurements. The inconstancy of Redfield ratios looms as a bigger issue in future and is just starting to be addressed on the measurement side.

Andrew Watson noted that although nutrients have been measured for a long time, no CRMs have been used because no international cooperation on this issue has ever been agreed. WOCE also didn't have such exacting standards because the criteria for evaluating water masses is much less exacting than for biogeochemistry analyses. WOCE protocols describe a method where laboratories make their own standards and the comparability is not as good as supposed. Although the accuracy standard is relatively low by C- community standards (~0.5%), this is still not being routinely met. Watson noted that C measurements can be useful in pointing up problems with nutrient measurements in deep waters where one would expect less variability. However, because the Redfield Ratio is not as robust as previously believed he expressed doubt that the high-quality C data set could be used to correct for nutrient analysis problems.

#### 4.3 STATUS OF KNOWLEDGE OF THE THERMODYNAMICS OF THE CO<sub>2</sub> SYSTEM

Andrew Dickson led the discussion on this topic which focused on the discrepancies resulting from employing different sets of dissociation constants when calculating pCO<sub>2</sub> from measurements of total dissolved inorganic carbon,  $C_T$ , and of the total alkalinity,  $A_T$ , of a water sample. He illustrated the dimensions of the problem with the use of several plots of calculated pCO<sub>2</sub> over a range of temperatures and pressures using different sets of constants and fingered the subtle but important uncertainties that can arise with current practice.

Clearly, an accurate knowledge of the thermodynamics of the carbonic acid system in sea water is crucial to our understanding of the behaviour of carbon dioxide in sea water (see e.g., Brewer *et al.*, 1997). In particular, Dickson demonstrated the accuracy required for thermodynamic consistency whenever a particular property needs to be calculated from measurements of other related properties, e.g. the estimation of the partial pressure of CO<sub>2</sub> in air that is in equilibrium with a sample of sea water, pCO<sub>2</sub>, from measurements of the total dissolved inorganic carbon,  $C_T$ , and of the total alkalinity,  $A_T$ , of a water sample. This calculation is particularly important for ocean models which transport  $C_T$  and  $A_T$ , but which need to calculate pCO<sub>2</sub> at the sea surface so as to represent air-sea exchange processes.

Numerous determinations of these dissociation constants in sea water media have been published over the years: by Buch (Buch *et al.*, 1932; Buch, 1938); Lyman (Lyman, 1956), Moberg (Moberg *et al.*, 1934); Hansson (Hansson, 1972; Hansson, 1973a; Hansson 1973b); Mehrbach (Mehrbach, 1973; Mehrbach *et al.*, 1973); Goyet & Poisson (1989); and Roy (Roy *et al.*, 1993). Furthermore, a number of evaluations of these measurements have been published (Dickson & Millero, 1987; Edmond & Gieskes, 1970; Gieskes, 1974; Johansson & Wedborg, 1982; Millero, 1979; 1995; Plath *et al.*, 1980; Skirrow, 1965; 1975). In each case the authors have recommended “best” values for the dissociation constants, and often the constants are represented in these papers by interpolating equations or tables.

In addition, a number of investigators have assessed the “thermodynamic consistency” of the various published values for these dissociation constants with analytical measurements made on sea water samples (Clayton *et al.*, 1995; Dickson, 1977; Lee, 1996; Lee & Millero, 1995; Lee *et al.*, 1996; 1997; manuscript; Lueker, 1998; Lueker *et al.*, 1999; McElligot *et al.*, 1998; Millero *et al.*, 1993; Murphy, 1996; Stoll *et al.*, 1993; Takahashi *et al.*, 1976; Wanninkhof *et al.*, 1999). Furthermore, a number of such studies presently remain unreported (personal communications with Dave Chipman (LDEO), Bob Key (Princeton), Arne Körtzinger (IfM, Kiel) and Stephany Rubin (LDEO).

The results of these examinations are, as yet, not conclusive. At present, current opinion “favours” the use of the Mehrbach constants for the calculation of the pCO<sub>2</sub> of surface sea water samples from measurements of  $C_T$  and  $A_T$  (i.e., for pCO<sub>2</sub> values below about 500–600 µatm). At higher pCO<sub>2</sub> values (corresponding to higher  $C_T/A_T$  ratios) significant discrepancies may exist (Lueker, 1998; Lueker *et al.*, 1999).

Typically, pH measurements have not been found to be consistent with the other measurements and the Mehrbach constants. Recent studies by Byrne *et al.* (1999) and by Lee *et al.* (m/s), however, suggest that this is not necessarily always the case and that the observed problems may have been due to errors in the calibration of the indicator dye used to determine pH. These errors in turn resulted from the use of slightly erroneous values for pH for buffers made from tris in synthetic sea water (see DelValls and Dickson, 1998).

**Cautionary notes**

Although there seems to be a consensus appearing that the Mehrbach constants are “right” -- or at least better than the other published sets of constants, it is appropriate to be cautious. First, the actual functions used to calculate the equilibrium constants,  $K_1$  and  $K_2$  are typically those provided by Dickson & Millero (1997). These are based on correcting the original data of Mehrbach *et al.* (1973) to the *sea water pH scale*. They are thus not on the same pH scale as the boric acid constants of Dickson (1990) which are based on the *total hydrogen ion pH scale*. Leuker *et al.* (1999) report new interpolating functions based on correcting the original data directly to the total hydrogen ion scale:

$$\begin{aligned} \text{p}K_1 &= 3633.86/T - 61.2172 + 9.67770 \ln T - 0.011555S + 0.0001152S^2 \\ \text{p}K_2 &= 471.78/T + 25.9290 - 3.16967 \ln T - 0.0178S + 0.0001122S^2 \end{aligned}$$

The root mean square deviation of the pH scale corrected data from these functions is 0.0055 in  $\text{p}K_1$  and 0.0100 in  $\text{p}K_2$ . (Note, these are still significant uncertainties for the calculation of  $\text{pCO}_2$  from  $C_T$  and  $A_T$ ).

Second, the majority of the studies that support the use of the “Mehrbach constants” are based on computing  $\text{pCO}_2$  from  $C_T$  and  $A_T$ . Strictly, this only tests the ratio  $K_1/K_2$ , not the individual values of  $K_1$  and  $K_2$ . (It is the computations that use pH data that test these constants individually, and, as yet, the calibration of pH measurements made using indicator dyes has not been confirmed independently of the work by Clayton & Byrne (1993).

Third, the behaviour of the constants has not been well tested over a range of temperatures and values of  $\text{pCO}_2$ , i.e., the ratio  $C_T/A_T$ . This results from the fact that field measurements of pH and of  $\text{pCO}_2$  of discrete samples are typically made at a single temperature (20 or 25 °C) and thus do not provide a full test of the constants over a variety of conditions. Finally, the laboratory experiments of Lueker (1998), and to a lesser extent those of Lee (1996), suggest that there is a problem using the Mehrbach constants at  $\text{pCO}_2$  values above 500  $\mu\text{atm}$ . The reasons for this are not at all clear - no simple adjustment of the equilibrium constants serves to fit the measured data, which seem to be reliable.

Thus, the support for the wholesale adoption of the Mehrbach constants is based largely on the degree of agreement with the means of a large number of field measurements. This essentially assumes that the field measurements are perfectly accurate. As certified reference materials are only available presently for measurements of  $C_T$  and  $A_T$ , it is probably only for these parameters that unambiguous statements can be made about the likely accuracy in the typical field situation.

The problem is that, at first glance, the Mehrbach constants seem the least carefully measured of the various sets available (Mehrbach, Hansson, Goyet, Roy); if they are not that bad, certainly they are not strikingly better than the others! Why then are the others “wrong”? A significant part of this problem probably results from a desire to over-interpret the original measurements of the constants which have a number of errors and uncertainties (some acknowledged in the original papers, some not) and to assume that the fitted functions that are published are in some way immune to such problems. They are not! All the calibration errors that have plagued field measurements can (and do) also occur for laboratory measurements of equilibrium constants.

Dickson concluded that these remaining uncertainties are significant and thus it would be appropriate for the Panel to consider forming an international group of experts charged with:

- (i) Carrying out a careful review of the present literature describing measurements of the dissociation constants  $K_1$  and  $K_2$  in sea water. This should probably be undertaken by an international group of experts who should examine as far as is possible the original reported measurements.

- (ii) Arranging for a series of studies to be made independently in several laboratories, which could be used to compute accurate estimates of  $K$  and  $K_2$  in sea water under appropriately chosen conditions ( $S$ ,  $T$ ,  $C_T/A_T$ ). Extreme care will, of course, need to be taken to ensure that the calibrations of all measurements contributing to these estimates are well understood.
- (ii) Proposing new equations for the dissociation constants (as a function of  $T$  and  $S$ ), along with a careful estimate of the uncertainties involved.

Kitack Lee presented the results of the related work that he and Frank Millero had done. They came up with similar conclusions, that the calculated pCO<sub>2</sub> for surface waters from  $A_T$  and  $C_T$  are more consistent with Mehrbach at low pCO<sub>2</sub> (e.g., << 500 µatm), but are more consistent with Roy at high pCO<sub>2</sub> (e.g., > 500 µatm). They concluded that if this is true, none of the presently available carbonic acid dissociation constants are consistent with measured pCO<sub>2</sub> over the wide range of pCO<sub>2</sub> (250 to 1800 µatm). The cause of this difference is not certain and requires further study. The details of Lee's presentation are found in Annex III.

*Post Meeting Recommendation.* Alain Poisson and Catherine Goyet, after due consideration of this issue, prepared a joint letter that was distributed subsequent to the Panel meeting containing a recommendation to address and resolve the problem. They concluded that the issue is important enough to establish an international group of experts to oversee a carefully planned set of measurements to be conducted in selected laboratories in several countries. Their complete comments contained in the letter are in Annex IV.

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## 5. GLOBAL pCO<sub>2</sub> DATA SET

### 5.1 GLOBAL FLUX ESTIMATES FROM pCO<sub>2</sub> DATA

Taro Takahashi presented a new map of ocean CO<sub>2</sub> fluxes which shows a net change in the ocean uptake from 1.2 GtC/yr (Takahashi *et al.*, 1997) to 2.1 GtC/yr, making the new estimate more concordant with the estimates based on models. This new map improves upon the results presented in the Takahashi *et al.* (1997) paper. The reasons behind the significant difference are threefold. Firstly, the latest calculations incorporate new data that have become available in the Indian and Southern Ocean. The new map indicates a stronger sink in the Southern/Indian Ocean, but a weakening of the North Atlantic sink. The areal extent of the Kuroshio is also larger in the new map. There are many unsurveyed regions, so that a great problem exists when trying to summarize global data, although progress is being made to fill in regions and seasons of few data. When the measurement locations are examined (30 years of data), it appears that the ocean is well sampled. However, when the data are examined with the goal of building a climatology, it becomes clear that monthly data are sparse, especially in the eastern Pacific, Indian and Southern Oceans.

A second reason for the revision is due to recent advances in assessing gas transfer velocity across the air-sea interface. Flux calculations require a determination of gas transfer velocity across the air-sea interface. This term is usually parameterized from wind speed, but the functional form of the parameterization has been an active research question. Eddy correlation measurements of WHOI and AOML in the past year indicate, after normalization, that direct flux measurements show good agreement with Wanninkhof equation 1 parameterization, which was used in calculating these new fluxes.

Thirdly, 20% of the change is due to the increase in atmospheric CO<sub>2</sub>. Fluxes are calculated from  $\Delta p\text{CO}_2$  ( $p\text{CO}_{2\text{sw}} - p\text{CO}_{2\text{atm}}$ ). Atmospheric increases are well documented by the global sampling network. Ocean increases are expected to lag behind atmospheric CO<sub>2</sub> increases for some regions, therefore ocean carbon uptake is expected to increase from this imbalance alone.

This new uptake assessment seems large relative to the model assessments (~2 GtC/yr), particularly since a riverine flux correction (+0.7 GtC/yr) would bring the total to 2.7 GtC/yr. However, the model estimates of carbon uptake are largely based on atmospheric data with a mean date of roughly 1980. If the increase in oceanic pCO<sub>2</sub> lags the atmospheric increase, new model assessments of ocean carbon uptake may likewise be increased.

The new data represent an increase of 10-20% in the number of data points. However it is not strictly the number of points that is important. Randomly removing data points has little effect on the uptake conclusion, but if the coverage in whole areas is changed, the results are strongly affected. For this new map, the additional points were not added to a random distribution of data, but they provided new information in previously unsurveyed regions. It seems likely that additional data in some regions, e.g., the subtropics, will not significantly change the carbon uptake results, but it isn't clear how new data in more dynamic regions may affect the uptake results. Just by adding a few points in the most sensitive

areas where data is sparse, the sink increased from -1.2 to -2.1 GtC/yr. Will additional data in key regions and/or seasons where no data exist, continue to revise the results? Alain Poisson showed some new data for the eastern sub-Antarctic Southern/Indian Ocean (not yet incorporated into this new map) which suggest that there may be a larger sink in the eastern sub-Antarctic and Southern/Indian Ocean than shown in the new map. Additional data 'holes' are the southeastern Pacific, and winter data generally. The time and space scales of pCO<sub>2</sub> variability have not yet been explored systematically, but this type of analysis may provide useful insights on the sampling strategy required to obtain accurate regional means for pCO<sub>2</sub>.

The importance of carbon uptake in shelf regions was also raised. This analysis employs a broad brush climatological approach with a 4° x 5° grid. Sparsity of data necessitates this coarse-grid approach, but it results in a dilution of the effects of coastal regions that cannot be directly addressed. This approach is also sensitive to the parameterization of fluxes from wind data. There are uncertainties still remaining in determining the gas exchange velocity across the air-sea interface. The recent direct flux assessments are a step forward, but should be treated with caution since a number of corrections for water vapor and heat must be made to derive the final results. Small errors can produce large effects, therefore, the flux calculations have significant uncertainties. Additionally, the gas exchange velocity is a function of other factors - duration of storms, sea state, organic films, etc. It is not clear how additional research on these questions will affect our estimates of ocean carbon uptake calculated from fluxes.

The change in C uptake estimates from CO<sub>2</sub> flux by 0.9 GtC/yr is substantial, and leads to questions of how much more this number might change with additional data. The next steps in reducing the uncertainty on this ocean carbon uptake value are unclear - whether to focus strictly on undersampled regions and seasons, to design a sampling strategy based on the time and space scales of pCO<sub>2</sub> variability, to improve parameterizations from satellite data, or to outfit an array of buoys with chemical sensors. It seems clear that a geographical sampling emphasis such as this one is important. Although there is a current focus on terrestrial CO<sub>2</sub> research, it should be pointed out that oceanic measurements are the only direct evidence for the magnitude of the terrestrial sink since the heterogeneity of the terrestrial carbon uptake makes accurate quantification even more difficult than for the ocean.

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## 5.2 INVENTORY OF pCO<sub>2</sub> DATA

Alain Poisson and Alex Kozyr reported that some new data have been submitted to national data centres as a result of the inventory effort to ferret out C data. But, of the 46 investigators identified as having pCO<sub>2</sub> data, only 6 have supplied their data to CDIAC. Perhaps a personal contact is needed in order to get data submitted, especially for data collected some time ago. There is a person in the Bergen JGOFS office, Beatrice Bellino who is willing to make the effort to actively track down the data through personal contacts. It was agreed that Poisson would turn over the inventory report to Beatrice, and Kozyr would be the further contact person. Data submitted so far also need to be converted to the same measurement type, so some treatment is necessary before the data can be readily compared.

### 5.3 WHAT NEXT WITH pCO<sub>2</sub> DATA

Watson stated that since there are still few data available, we need a plan. He suggested a start be made by collecting the data as the investigator intended and then look at all the data as a whole later. Better to do this rather than start to exclude data sets *a priori*. Some discussion took place on what quality criteria might be used to decide on rejecting/accepting data in the global database. For example, should concurrent observations of atmospheric pCO<sub>2</sub> be a requirement? Which atmospheric data should be used if the observed data disagree with the Tans sampling network? Watson expressed mixed feelings about his own atmospheric pCO<sub>2</sub> data - data on some legs agree with the atmospheric monitoring network very well; the data on other legs may disagree by 2-3 ppm. Perhaps the water dryer apparatus was not working properly or there was a leak in the lines. The bottom line is that there are no criteria currently in place to decide on quality of data.

Watson believed that for the CDIAC database the data should be accepted as is to get it in the system and avoid its being lost. A decision on whether data should be excluded can be taken later. CO<sub>2</sub> measurements have been funded on basis that the data will be used to better evaluate the ocean sink. So unless data are archived we are failing in that responsibility. If data are of variable quality, they must be accompanied with a large amount of metadata as well to make sense of it. But for now, the main objective should be to get P.I.s to just provide the data.

## 6. IRON ENRICHMENT INVESTIGATIONS

Watson informed the Panel that he was headed for New Zealand immediately after the Ocean CO<sub>2</sub> Symposium to board a ship in Wellington to participate in the Southern Ocean Iron Release Experiment (SOIREE). The experiment was planned at a location 62 or 63° S, 2500 km southwest of New Zealand, about 500 km from the Antarctic ice. This poorly studied region is perhaps the only High Nitrate - Low Chlorophyll (HNLC) region where the effects of adding iron could bring about changes in algal biomass that might significantly alter the magnitude of the oceanic sink for atmospheric carbon. The equatorial Pacific region of HNLC is not a good candidate because of the relatively low mixing rates there between surface and deep waters. The Southern Ocean, on the other hand, exhibits rapid exchange between the surface and the deep, it forms 20% of the world ocean, and it has a major influence on world climate. Watson pointed out that the Ross Sea is not typical of waters of the Southern Ocean. It is much more productive and enjoys more fair weather.

C.S. Wong informed the Panel about plans for an iron experiment proposed by the PICES Advisory Committee in the sub-Arctic Northeast Pacific, the third large regional water mass that exhibits HNLC. During El Niño years there is increased productivity here because water runoff increases and thus there is more iron washed into the ocean. There is also a correlation of productivity with the peak in 1992 of volcanic dust.

## 7. EMERGING TECHNOLOGIES

Andrew Dickson notified the panel that a US consortium led by Dr. T. Dickey (University of California, Santa Barbara) has been funded through the National Ocean Partnership Programme to deploy an instrumented buoy in the sub-Arctic North Pacific in the vicinity of Station P. The observations planned include bio-optical instruments (Dickey, UCSB), fluorescence/absorption (wetlabs Instruments), air-sea ΔpCO<sub>2</sub> (Chavez, MBARI), nitrate osmo-analyser (chavez, MBARI), pH (Byrne, USF) and pCO<sub>2</sub>/Carioca buoy (Wanninkhof, NOAA/AOML).

The buoy deployment will be carried out by the NOAA/PMEL buoy group who are responsible for the TAO array. The calibration of the buoy measurements is being organized by Richard Feely



(NOAA/PMEL) and will involve a shipboard survey made at the time of deployment and, it is hoped, a later visit to the buoy site. This deployment is expected to last one year from late 1999-2000. The data will be telemetered to shore on the NOAA GOES satellite and will be available in near real time.

Dickson also informed the Panel that YSI instruments (Ohio, US) are developing the pCO<sub>2</sub> sensor invented by Dr. Q. Watt (Tufts University) for use in a buoy-mounted system. They hope to have test buoys in the water in 1999.

Takashi Kimoto reported that a rapid response (within 1 minute) flow-through type pCO<sub>2</sub> equilibrator was designed for underway pCO<sub>2</sub> monitoring from VOS. The equilibrator can, in principle, remove the pressure effect. This pCO<sub>2</sub> system is now continuously operating on the *S/V SKAUGRAN* by the National Institute of Environmental Studies (NIES) in Japan and the Institute of Ocean Science (IOS), Canada. The Japanese Meteorological Agency (JMA) developed an air-sea CO<sub>2</sub> monitoring buoy that has been operating for over six months in the East-China Sea. New automatic C<sub>T</sub> and A<sub>T</sub> have been developed for JGOFS time-series monitoring, the reproducibility of the system being  $\pm 1 \mu\text{mol/kg}$  for both variables. The Japanese Agency for Marine Science and Technology (JAMSTEC) is now developing a large biogeochemical monitoring platform for continuously measuring upper surface ocean processes.

Liliane Merlivat showed new pH data collected with the CARIOCA buoy. A calibration exercise was undertaken near Bermuda and comparisons of the buoy data together with data collected at the BATS station were made in June/July 97, showing good correlations of the variations of temperature and pCO<sub>2</sub>. A good agreement was found between the CARIOCA and the BATS pCO<sub>2</sub> data. During the GASEX 98 experiment, 2 buoys were launched and followed during three legs in cooperation with NOAA scientists who measured pCO<sub>2</sub> onboard their ship. Good agreement was found between buoy and ship pCO<sub>2</sub> data when they were normalised to the same temperature. A new version of the CARIOCA buoy is nearing completion which will include a pH instrument measuring optical absorbance of a solution of a dye-sea water mixture; a prototype was used in the Greenland Sea from 19 to 24 of August 98. The calculated A<sub>T</sub> and the C<sub>T</sub> using buoy pCO<sub>2</sub> and pH data together with Goyet and Poisson's constants of carbonic acid, agree at  $\pm 2.5 \mu\text{mol/kg}$  with data measured onboard the ship.

A. Watson reported on the IMCORP (Instrumentation for Marine CO<sub>2</sub> from Remote Platforms) EU project in which L. Merlivat and Truls Johannessen are also engaged. The pCO<sub>2</sub> will be measured using a LI-COR + equilibrator system, C<sub>T</sub> with a LI-COR + stripper/syringe pump system developed by C. Goyet, and pH by a Flow Injection Spectrophotometer. The three systems will be incorporated in the same platform by late 99.

T. Takahashi reported on a pumping "SeaSoar" system that has been developed at the Lamont-Doherty Earth Observatory (LDEO) of Columbia University to allow continuous sampling and measurements of the upper water column between water depths of 15 and 200 meters. The SeaSoar is a towed undulating vehicle or "fish" (manufactured by the Chelsea Instrument, UK). LDEO have added to the fish an *in situ* CTD, a sensor array and a positive-displacement water pump for continuous delivery of seawater samples for ship board chemical analyses. The pump delivers seawater aboard the ship continuously at a rate of about 6 liters/min. The temperature, salinity, PAR (photosynthetically active radiation), oxygen and bio-fluorescence are measured using *in situ* sensors installed on the fish. On the other hand, pCO<sub>2</sub> and the concentrations of C<sub>T</sub>, phosphate, nitrate and silicate are measured aboard the ship in the pumped water using fast response analyzers specifically developed for this project. The temperature and salinity of the pumped water are also measured in the pumped water aboard the ship continuously using sensors identical to those installed on the fish. Annex V contains additional descriptive and performance details of the SeaSoar.

Roger Francey informed the Panel of the development of a new CO<sub>2</sub> analyzer system based on a LI-COR, but using a low flow rate of 15 mL/min, and improved long-term precision. With this new

analyzer system his lab can get precisions of  $\pm 7$  ppb. The instrument has a stable near-linear response. As one demonstration of the new capabilities, big differences in CO<sub>2</sub> in a high pressure cylinder of air are found (typically ppm in the short term, 0.05 ppm in the long term) when different frequently-employed regulators are used. Potential applications include monitoring for southern ocean circulation changes.

## 8. ATMOSPHERIC CO<sub>2</sub> ISSUES

Roger Francey stated there is lots of room for improvement in making carbon concentration and carbon isotope measurements in the atmosphere. Observations obtained from the Cape Grim atmospheric observatory, north-west Tasmania, continue to show relatively low inter-annual variability in  $\delta^{13}\text{C}$ , which has been interpreted in publications by Francey *et al.* (1995) and Rayner *et al.* (1999) as resulting in most of the CO<sub>2</sub> inter-annual variability being attributed to oceanic uptake. Particularly in the 1980's, systematic differences between  $^{13}\text{C}$  measurement laboratories were large, which was used to justify the use of a single well-calibrated southern hemisphere station to represent the world. Variations of ocean C flux in Francey *et al.* were estimated to be  $\sim 4\text{--}5$  GtC/yr. Using the same data but a 3D transport model, Rayner *et al.* estimated ocean variability at around 1-2 GtC/yr. Recently Rayner has added 5 more  $\delta^{13}\text{C}$  stations from the CSIRO network and still found variability on the same order of magnitude. A small part of the difference between the two studies comes from Rayner using larger  $^{13}\text{C}$  disequilibrium terms (which differ from the Peter Tans derived values used earlier; the new estimates of disequilibrium are based on comparing decadal oxygen and  $\delta^{13}\text{C}$  trends), the rest appears to be due to the ability of the 3D model to accommodate larger global  $\delta^{13}\text{C}$  variability than measured at the limited number of sites. Francey noted that the data indicate there are spatial gradients in longitude but models are not really accounting for this at present.

*Post meeting clarification. It now appears that inconsistent smoothing, both statistically and from atmospheric mixing, of the atmospheric  $\delta^{13}\text{C}$  data compared to CO<sub>2</sub> data may have contributed more than anticipated to over-estimation of interannual variability in ocean carbon fluxes from atmospheric inversion methods.*

Nevertheless, according to CSIRO  $\delta^{13}\text{C}$  atmospheric data and Rayner *et al.*'s inverse model, subtropical regions are estimated to take up most of the carbon: - 0.6 GtC/yr for the subtropical North Pacific to  $\sim 45^\circ\text{N}$ , - 0.8 for the South Pacific, - 0.1 for the Southern Ocean, - 0.6 for the North Atlantic, and - 0.3 for the subtropical South Atlantic.

Takahashi provided a comparison of results of Rayner *et al.*'s work and his own. The biggest difference was in the Southern Ocean where Takahashi calculated a value of - 0.6 GtC/yr.

Francey's laboratory is focusing on measurement errors. There are few examples of data merging from different CO<sub>2</sub> laboratories, let alone from  $\delta^{13}\text{C}$  laboratories. In a series of WMO round-robin measurement exercises involving 16 laboratories during the period 1991-1993, CO<sub>2</sub> measurements of 3 different concentrations differed from NOAA's by up to 0.6 ppm. A similar exercise involving 24 laboratories during 1994-1997 produced smaller, but still significant differences. For example, Japanese data were about 0.3 ppm high relative to NOAA so one can't really merge the data. A precision target for merging binned (in time or region) CO<sub>2</sub> data for inversion studies has been set at 0.1 ppm.

With regard to  $\delta^{13}\text{C}$  measurements, a typical precision for individual measurement is 0.03 *per mil*. The target for a binned average is smaller, at 0.01 *per mil*. (The latitudinal gradient is around 0.2 *per mil*. The 1980 differences between Scripps and CSIRO were more than 0.1 *per mil*).

Since 1991, CSIRO and NOAA have been operating a unique “operational intercalibration” where 4 times *per* month measurements of CO<sub>2</sub>, δ<sup>13</sup>C, δ<sup>18</sup>O, CH<sub>4</sub>, CO, N<sub>2</sub>O and H<sub>2</sub> from both laboratories on actual Cape Grim air samples are electronically compared via ftp. Unanticipated systematic errors have been detected and continue to emerge. Regulators on high-pressure cylinders are a problem. CSIRO and NOAA have established intercomparability to ~0.02 ppm in CO<sub>2</sub> using high-pressure cylinders, but sampling from the same low pressure flask in the “operational intercalibration” has shown consistent differences of ~0.2 ppm. However, with the ongoing well documented difference between the two laboratories, for most species most of the time, high precision merging of data from the two networks (NOAA has the largest global network, CSIRO the second largest) appears close to realization.

Based on this experience, Francey's lab, with NOAA, have proposed an international calibration strategy which addresses these problems, can service many more laboratories and can be operated at reasonable cost. It is called GLOBALHUBS, involving 4 regional centres which remain tightly intercalibrated and can provide well characterised air to laboratories in their region. They are seeking international funding for this programme.

Francey's lab is trying to get more regional information. Vertical sampling over the southern oceans indicates a vertical gradient of almost 1 ppm exists from the surface to 8 km. By comparing tracers at higher atmospheric levels, contamination of the upper air can be identified from biomass burning signatures. CO and CH<sub>4</sub> data are being used to pin-point where the contamination occurs. Clearly, climatologies are contaminated by biomass burning. The contribution of biomass burning to CO<sub>2</sub> concentration above the Cape Grim region can be calculated since there is no biomass-burning contamination effect in the surface sampling. Removal of this biomass burning signal permits much better estimates of large scale air-sea exchange to the west of the sampling site off Cape Grim.

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## 9. STATUS OF <sup>13</sup>C MEASUREMENTS

Measurements of <sup>13</sup>C are valuable because they provide information about the partitioning of anthropogenic carbon between the oceanic and terrestrial sinks; they also provide a loose constraint on the absolute magnitude of ocean carbon uptake. In the paleo-oceanographic field, research is underway to determine how <sup>13</sup>C changes might be related to changes in ocean circulation. Isotopic fractionation on dissolution and biological uptake differs for <sup>12</sup>C, <sup>13</sup>C and <sup>14</sup>C. By using these differences, additional information about ocean processes can be obtained.

The potential for <sup>13</sup>C data is clear, but two issues must be addressed to utilize these data fully. The first is how to build an inventory of the existing data and available samples which could potentially be analyzed. The second is the question of intercomparability of the existing data sets and future <sup>13</sup>C data. If <sup>13</sup>C in seawater is to become part of future global C measurement programmes, this is a critical issue. Given the present interlaboratory measurement differences, a strategy is needed that will lead to minimizing these differences in order to produce a global database.

## 9.1 INVENTORY OF OCEAN <sup>13</sup>C DATA

The question is how to do it. There are 3 different types of oceanic <sup>13</sup>C data now available and which could become available:

- (i) analyzed datasets (not currently intercomparable);
- (ii) archived samples not yet analyzed (extracted and unextracted, e.g., from AMS <sup>14</sup>C analyses, WOCE sidecatch from DIC samplings);
- (iii) stray datasets which are available (not collected originally for isotope analysis; e.g., a great deal of <sup>13</sup>C data is available from time series work, and from <sup>13</sup>C analyses made as part of particle flux studies).

Some sources of analyzed data are Quay, Tilbrook, Wong, Keeling, Johannessen, Inoue, Tsunogai, and the Canada/Japan SKAUGRAN monitoring programme. These data also would require a great deal of time to inventory, perhaps a one-person year just to compile the data. At present there is no funding for this task.

**Intercomparability.** The round-robin intercomparison of <sup>13</sup>C measurements in seawater has previously been reported (5th Session Report). If results from 2 laboratories are excluded (since results were quite different from the others), the remaining 10 laboratories showed differences of up to 0.30 *per mil* between laboratories. This is 15 times larger than the signal corresponding to the expected ocean carbon uptake of 2 GtC/yr using <sup>13</sup>C data (0.02 parts *per mil*/yr). When data for pure CO<sub>2</sub> analyses are compared, the inter-laboratory differences are much smaller, suggesting that extraction is the major source of error. If <sup>13</sup>C measurements are to have a future in ocean C programmes, data from different laboratories must be able to be combined. The present inter-laboratory measurement differences constitute a formidable challenge to reaching the goal of sufficiently high quality data sets that can be merged into a global database.

**Experience of the Atmospheric Community.** The community measuring <sup>13</sup>C in atmospheric samples has also found significant inter-laboratory differences. Roger Francey discussed the inter-laboratory differences for measurements of <sup>13</sup>C in atmospheric samples obtained during the WMO round-robin exercises in 1991-1993 and 1994-97 (see Section 8). The comparison goal is 0.1 ppmil, but inter-laboratory differences were more than five times larger. The exercise also shows inter-laboratory differences in the linearity of the results. In another intercomparison exercise of four laboratories differences in linearity between laboratories were again observed. One possible contributor to these differences are tank regulators. Laboratory checks found significant differences in values obtained from the same tank, but using different regulators.

Roger Francey has suggested an approach for atmospheric <sup>13</sup>C intercalibration which may provide some useful information for the oceanic community (see Section 8). He proposes to set up 4 hub laboratories which will act as centres for distributing cylinders and collecting data. Samples from Cape Grimm would be sent to each of the hub laboratories, and then distributed regionally for round-robin comparisons. This approach is proposed instead of a single laboratory centre since the costs of freight and customs are so high. These cylinders would consist of high pressure samples containing pure CO<sub>2</sub> and natural air, as well as low pressure samples.

This exercise seems promising for providing enough information to reveal the source of the systematic problems while minimizing costs. Estimated costs are several hundred thousand dollars to set up and then an additional amount for each additional laboratory. Freight is the single largest cost. An advantage of this approach is that real geochemical information is obtained while assessing interlaboratory differences.

**Ocean Community Response.** The problems facing the oceanic community are greater because of the additional step of gas extraction from water. Although the ocean data intercomparisons are likely to have more problems initially, it seems important to tie the oceanic and atmospheric measurements to the same scale. If funding becomes available, perhaps a joint atmosphere-ocean intercalibration will be possible. At this point, the ocean <sup>13</sup>C community is perhaps not so far along as the atmospheric community. Monitoring the progress of the atmospheric intercalibration results, as well as developing a <sup>13</sup>C ocean CRM seem sensible steps at this point.

**CRMs for Oceanic <sup>13</sup>C.** One of the important tools for intercomparison is certified reference materials (CRMs), but there is currently no <sup>13</sup>C ocean CRM available. The usual procedure is to use PDB to 'standardize' the results. A CRM would provide a means of comparing extraction efficiencies between laboratories, and monitoring systematic differences.

Two possibilities for CRMs seem possible. Andrew Dickson is currently certifying seawater for DIC and TA. The water used for the current CRMs has near-natural <sup>13</sup>C levels, and initial tests show the <sup>13</sup>C levels to be stable. If he received additional funding, Dickson could develop CRMs for <sup>13</sup>C in seawater. Alternatively, the AEC could be broached on this topic since they already provide a number of standards.

No clear consensus was reached regarding the role the panel should play in addressing these difficult issues.

## 10. PANEL FUTURE DIRECTIONS

Alexiou stated that a turning point for the Panel had been reached with completion of the observational phase of JGOFS. The Panel had essentially completed its task of fostering activities leading to a high quality coherent ocean C data set from JGOFS field work. It had done its job well and congratulations were in order. He believed the Panel now needed to be reconstituted with new terms of reference (TOR) and a membership consistent with those terms. From the IOC point of view, GOOS needed advice on the "what, where, and when" of carbon system observations that should be planned in a global observing programme. Moreover, IOC was keen to continue to have a ready source of advice for dealing with emerging issues such as CO<sub>2</sub> sequestration. He invited discussion on possible future directions for an Ocean CO<sub>2</sub> Panel to serve IOC, JGOFS and SCOR.

Watson noted that JGOFS was in the process of transforming itself, moving away from measurements to a grand synthesis and modelling effort, and was looking for counsel from this Panel. He believed that there still remains considerable important work relative to measurement issues. The floor was then opened to all present to comment. The ensuing debate brought out the following points:

- The study of the carbon cycle continues to need the field work including experiments and time series.
- We need to maintain an observational capacity and continue to improve it to provide modellers with the best observations possible.
- There is a growing requirement to merge databases beyond the pCO<sub>2</sub> data set.
- A reconstituted Ocean CO<sub>2</sub> Panel should continue have a close interface with the atmospheric chemistry scientists and consider occasionally sitting together with the terrestrial CO<sub>2</sub> community.
- The scope should be well defined as to whether to include the global carbon cycle or just the ocean.
- The Ocean CO<sub>2</sub> Panel should provide a way for modellers and observationalists to interact. These groups need each other. Modellers can spot flawed data and advise on priorities for where data are needed; conversely, high quality observations can be used to identify model weaknesses.

- Modellers can't be trusted to not misuse data. Some experimenters are needed to keep them honest.
- The atmospheric community has modelling more integrated with the observationalists.
- Mitigation is the future for obtaining funds; the Panel could involve itself in such activities.
- The Panel should move closer to GOOS-type activities since GOOS has no strength in ocean chemistry.

Some discussion was devoted to consider some draft terms of reference. It was agreed that the Panel should be a source for advice on strengths and weaknesses of data, for what to measure in the future, and on new technology. It should stimulate studies and organize workshops that can focus community efforts to move our knowledge forward on front-burner issues, e.g., long-term impacts of CO<sub>2</sub> disposal options. Obtaining reliable <sup>13</sup>C measurement was also considered a basic goal. Watson agreed to take this discussion into account into developing a draft TOR to submit to JGOFS for their consideration.

## 11. NATIONAL REPORTS

Panel members were invited to give a brief report on national activities on ocean CO<sub>2</sub>.

**Australia.** Over the last year analyses have been finalised of surface fCO<sub>2</sub> data collected over a 7- year period by CSIRO Marine Research Laboratories in the Southern Ocean sector between 60°E and 150°E. They show a strong seasonality in the sub-Antarctic Zone uptake of CO<sub>2</sub> to the south of Australia, and that persistent zonal changes in CO<sub>2</sub> uptake occur in the seasonal sea-ice zone of the region. These data will fill a critical gap in the present pCO<sub>2</sub> climatology of Takahashi and others, and improve the estimate of CO<sub>2</sub> exchange in the Southern Ocean. The data are undergoing final formatting for distribution. The surface fCO<sub>2</sub> data will be sent to CDIAC in the next month or so.

The above work has motivated studies to understand the large seasonal changes in air-sea CO<sub>2</sub> exchange in the sub-Antarctic zone. The studies involve a combination of underway monitoring, sediment trap deployment and process studies. A major process study in March 1998 was aimed at understanding biological production in the region and involved 35 scientists from 5 countries.

Regional marine carbon cycle models are being developed to interpret the oceanographic data. A global marine carbon cycle model is being developed to investigate the past, present and future uptake of CO<sub>2</sub> by the ocean. The effort is exploiting both oceanographic and atmospheric data to validate and guide model development. Our model is participating in OCMIP.

The analysis of <sup>13</sup>C in water samples accumulated over several years is in progress. Data on <sup>13</sup>C seasonality in the Southern Ocean will be emerging in the next few months.

CSIRO atmospheric research on the carbon cycle (work with implications for ocean carbon) is being structured within a framework of the 3D Bayesian synthesis inversion methodology. The inversion of atmospheric mixing ratios and isotopic composition, *via* an atmospheric transport model, to derive surface fluxes is ill-conditioned, and requires additional constraints. These constraints come from "prior" information, including the spatial distribution of sources and sinks, and independent information of source strengths, characteristics and uncertainties. The methodology permits a realistic combination of the uncertainties from the various inputs, including air-sea and ecosystem fluxes, from regional to global scales. More importantly, it offers a means of assessing and maintaining global consistency between all sources of carbon cycle information.

A long-term advantage of the approach comes from exploiting the spatial integration provided by atmospheric mixing and it offers efficient, continuous monitoring of large-scale regional carbon budgets.

Some current specific areas of focus are:

- Combining the use of vertical (aircraft) profiling of the marine boundary layer, and limited area transport modelling to better relate point sampling in the boundary layer to the typical grid scale (~1000km) of global atmospheric transport models.
- Development of a new low flow (~15 ml/min) precise (~7 ppbv) analyzer for CO<sub>2</sub> measurement.
- Development of a variety of advanced strategies aimed at markedly better inter-laboratory calibration for CO<sub>2</sub>, CO<sub>2</sub> isotopes and related atmospheric species.
- Using the models developed for the interpretation of data, to assess the implication of new instrumentation and designing strategies for their optimum deployment.

**Canada.** In climate research there has been a shift away from measurement programmes toward emphasizing mitigation studies. A cut of 5% was made each year to put into CO<sub>2</sub> sequestration and iron fertilization studies. A new ship of opportunity programme from Canada to Australia is facing tough logistical problems. The sediment trap programme at Station P and the Labrador Sea line programme are continuing.

**France.** French JGOFS has been reorganized with other climate studies as part of the PROOF (PROcessus biogéochimiques dans l'Océan et Flux). Areas of concentration are in the south Indian Ocean, and buoy data in the equatorial Atlantic and Pacific; some obs are being taken in the North Atlantic. There is good interaction with the atmospheric and modelling groups. There are some ongoing C time-series measurements in the western Mediterranean with CARIOCA buoys. Official long-term funding is now assured for a 10-year programme at two oceanic observatories and the pCO<sub>2</sub> line from Reunion to 60° S will be occupied twice each year. Expansion of modelling activity is planned.

**Germany.** The JGOFS pCO<sub>2</sub> work is coming to an end. The Baltic Sea is the site for evaluating air sea exchange processes. A SOLAS meeting is planned in Kiel for January 2000.

**Japan.** The MIRAI vessel is scheduled to work in the North Pacific in the winter of 1999-2000 to observe gas exchange rates and other components of the carbon system. An AMS for <sup>14</sup>C is to be installed. The SKAUGRAN sampling programme will be phased out and a new ship of opportunity programme starting on a new vessel (40-50°N). Work is ongoing to develop an autonomous system that will require less monitoring. At present, nutrients and pH right can not be measured but space will be staked out on the new ship for this in the future. JMA also has funding for VOS programme from Japan to Mexico (20-30°N). Both these programmes are 3-year programmes.

The KNOT (Kyodo North Pacific Ocean Time-series) station at 44°N and 155°E had 13 visits in 1998. At this site CO<sub>2</sub> system and primary production measurements are taken. It is difficult to access in winter, but the MIRAI can easily go there even in winter. Plans to develop a model are in the works. To satisfy a need for an E-W line in the North Pacific there is a plan to reoccupy a 47° N line done in the 1980's. Also the P2 line from Japanese WOCE programme will be done. The Niri programme includes observations of the CO<sub>2</sub> system and biology in the southern region off Japan in the western Pacific. Tsunogai's chemistry group are participating in the Okhotsk programme which is focused on the formation of intermediate water. Complete water column measurements are being made at Station K.

**New Zealand.** Three separate programmes focused on carbon observations are being conducted, two by the National Institute for Water & Atmospheric Research (NIWA) in Wellington and the third by NIWA jointly with University of Otago.

Atmospheric Trace Gases Programme. This research programme is operated by NIWA (Wellington) and incorporates measurements of CO<sub>2</sub> and other greenhouse gases (CH<sub>4</sub>, N<sub>2</sub>O, non-methane hydrocarbons, aerosols) at the Bering Head site near Wellington. The measurement suite includes <sup>13</sup>C in atmospheric CO<sub>2</sub> and CH<sub>4</sub>.

Measurement of <sup>13</sup>C and <sup>14</sup>C in seawater DIC. This research programme (also operated by NIWA) involves measurement of both isotopes in seawater samples, to date collected mainly over the Chatham Rise east of New Zealand. The group also collaborates with CSIRO, making measurements of <sup>14</sup>C in CSIRO-collected samples.

Ocean-Atmosphere Programme. This is a joint research programme of NIWA and the University of Otago which commenced with initial government funding in 1996. It is currently funded through to mid-2002. The programme has 4 objective areas:

- (a) *Dimethylsulfide.* This objective is concerned with DMS measurements in surface waters, and with measuring rates of gas exchange by eddy correlation and tracer release methods.
- (b) *Numerical modelling.* The development and testing of a 1-dimensional model for CO<sub>2</sub> cycling in the water column.
- (c) *CO<sub>2</sub> chemistry.* This objective, which is operated primarily from the Centre for Chemical & Physical Oceanography, University of Otago, is focused on measurement of the CO<sub>2</sub> system in New Zealand waters with a view to defining air-sea exchange of CO<sub>2</sub>. The initial 2 years of research were focused largely on method development and validation. Methods now in regular use are continuous *in situ* surface-water pH and *f*CO<sub>2</sub>, as well as alkalinity on discrete samples. These methodologies have been used on 2 cruises south-east of New Zealand to the Polar Front, with a 3<sup>rd</sup> cruise planned for mid-1999. From 2000, attention will focus on subtropical waters further north.

Within the context of method development, the Otago group have investigated temperature and dye corrections for pH measurements, and are developing a novel coulometry-based method for alkalinity. They have also developed Windows-based software for computation of CO<sub>2</sub> equilibria in seawater.

In addition, the group has established a time-series transect across the Otago continental shelf which traverses subtropical and sub-Antarctic waters (the Subtropical Convergence). This involves monthly sampling for salinity, temperature, pH, *f*CO<sub>2</sub> and fluorescence (continuous measurements) plus discrete samples at 10 stations for alkalinity, nutrients and pigments.

- (d) *Penetration of <sup>14</sup>C into deep waters.* This involves measurements of <sup>14</sup>C in samples collected by CSIRO. See above.

Contacts. Further details of the University of Otago group's activities are available from Professor Keith A Hunter <khunter@alkali.otago.ac.nz> or from the Web site:  
<<http://neon.otago.ac.nz:801/chemistry/research/coru/coru.htm>>.

**Russian Federation.** Because of the economy problems in Russia, financial support for almost all of the scientific programmes concerning CO<sub>2</sub> in the ocean has stopped. Practically from the beginning of 1999, the few scientific groups still functioning are operating with some funds left over from last year. Most of these groups are in:

- Moscow (led by Dr. P. Makkaveev) - the collection of the archive data, the study of the variability of the carbon system and the investigation of the western Arctic Seas;
- Vladivostok (led by Dr. I. Semiletov and Dr. P. Tischenko) - development of methods of



measurement and calculation of the carbon system, the investigation in the Far East Seas and the eastern Arctic section;

- Gelendjik (led by Dr. J. Lukashov and Dr. E. Yakushev) - the modelling of the carbon cycle and investigations in the Black and Azov Seas.

The main directions of the investigations are:

- study of the carbon cycle in the Arctic Seas;
- study of the role of the Arctic (its seas and its lands) in the global carbon cycle;
- study of the carbon equilibrium in the anoxic waters;

The administrative strategic goals are:

- to find financial support for the investigations;
- to make the investigations of the carbon system concurrently and cooperatively with work being undertaken by commercial organizations.

**United Kingdom.** UK has no formal CO<sub>2</sub> programme at all. *Ad hoc* measurements will be made in the Southern Ocean related to the iron fertilization experiments.

**United States.** The US is now in a dormant stage for major field programmes, looking inward trying to decide where to move in ocean CO<sub>2</sub>-related experiments. There are three major ongoing planning activities. One addresses carbon cycle science in a very broad sense that will provide a direction for connecting GCMs and small scale measurements, i.e., an omnibus strategy document on how to coordinate everything, including CO<sub>2</sub> sequestration. Some of the principals involved are Wofsy, Sarmiento, Doney and Keeling; the report will go to NSF, NOAA, DoE.

A second activity is the development of a CO<sub>2</sub> Sequestration Strategy. The report will be a roadmap on how to do the research and will become Chapter VI in the omnibus report.

The third is a workshop on basic research needs to address industry, policy and socio-economic issues as well as science. The carbon cycle is one chapter of the report and Takahashi is principal author for that.

Continuing bits and pieces of other CO<sub>2</sub> work include NOAA's small effort in underway measurements in connection with servicing buoys with CO<sub>2</sub> sensors near the equator; there is a programme to develop geochemical buoys in the North Pacific; NSF is funding the JGOFS synthesis and modelling work; and the HOT and BATs time-series stations are continuing their observations. Some US scientists are collaborating with Russian scientists on a cruise on a Russian ship in the Sea of Okhotsk that will make CO<sub>2</sub> observations. They will look at waters in the coastal region responsible for intermediate water formation.

**Other Countries.** Meeting participants contributed brief comments on work being done in countries not represented at the meeting. The Netherlands are making skin T measurements as part of routine CO<sub>2</sub> measurements. Korea, Taiwan and Russian scientists have data on the formation of intermediate water formation near the Japan Sea. There is a shallow straight surrounding the sea, so O<sub>2</sub> is high. The data indicate that in 1960 formation of deep water stopped. It is believed that CO<sub>2</sub> accumulation in deep water decreased since then.

## 12. SYMPOSIUM ASSESSMENT

The Panel meeting was scheduled in conjunction with the 2nd International Symposium on Ocean CO<sub>2</sub> held in Tsukuba, Japan, 16-22 January 1999. As with the first such conference held in Mayaguez

Puerto Rico in January 1996, the Panel lent its full support to this conference. A number of current and past members of the Panel were scheduled as keynote speakers. The 112 papers on the programme demonstrated striking progress in a number of areas including advances made in observing techniques, global carbon models, determining air-sea fluxes, quantifying biological processes, data management, and experiments in CO<sub>2</sub> sequestration.

The last day of the Panel meeting took place on the afternoon and evening of the third day of the Symposium. Therefore, the Panel had a chance to form impressions and to compare this second symposium with the first one in Mayaguez. Opinions were invited from the meeting participants on how they viewed the first three days of the symposium. Comments are summarized below.

This Symposium featured more synthesis as opposed to measurements. The payoff from WOCE and JGOFS is evident.

The number of measurements made by the Japanese community is impressive. The SKAUGRAN data set is impressive, and the basis for a number of papers. The Government of Japan is learning how to fund universities and other research institutes.

The additional data now available changes the values of C uptake significantly. This can be viewed as an encouraging result or a disappointment. The problem remains unsolved. More analyses are being done on existing data sets to find what the probable uncertainties are on the measurements. Binning may bring out the systematic errors, but coverage in particular geographical areas is still an issue. International comparisons of data and models should be made on an annual basis and it would be useful to make comparisons on a monthly time scale.

The constraints on the terrestrial sink come from atmospheric and ocean data. The terrestrial community is still very distant from estimating terrestrial uptake directly. The uncertainties in the ocean uptake could be narrowed significantly if funding could be obtained for a programme providing a large number of measurements for a year, say, order of 1000 buoys, plus satellite observations and a good atmospheric transport model.

There was some disquiet about the status of modelling. Modellers still use <sup>14</sup>C as a CO<sub>2</sub> tracer and to test models even though C and <sup>14</sup>C behave differently. This a growing source of error as <sup>14</sup>C decreases and anthropogenic C increases. Models have not yet incorporated topography that influences circulation. This is significant for ocean CO<sub>2</sub> sequestration. Models also give a poor representation of real upwelling distribution. There is a mismatch between model results and observations of upwelling and it is not all at the equator. For these reasons, confidence in the model-derived thermohaline circulation is not high.

### 13. NEXT MEETING

If there is to be another meeting of the CO<sub>2</sub> Panel it was suggested that it be held in conjunction with another international event. The SOLAS meeting in Kiel in January 2000 was suggested as one possibility; JGOFS meetings in Norway in April 2000 and in Brest in July 2000 were others. It was noted that the next Atmospheric CO<sub>2</sub> meeting would be held in 2001; it was recommended that the next International Ocean CO<sub>2</sub> symposium be considered for 2002/3.

## **ANNEX I**

### **AGENDA**

- 1. WELCOMING**
- 2. ADOPTION OF THE AGENDA**
- 3. RECENT EVENTS AND UPDATES**
  - 3.1 GOOS/OOPC
  - 3.2 SEQUESTRATION OF CO<sub>2</sub> IN THE OCEAN
  - 3.3 PICES PLANS
  - 3.4 MODELLING ISSUES
- 4. OCEAN CO<sub>2</sub> SYSTEM MEASUREMENT ISSUES**
  - 4.1 STANDARDS AND REFERENCE MATERIALS
  - 4.2 VARIABILITY IN THE CARBON/NUTRIENTS SYSTEM
  - 4.3 STATUS OF KNOWLEDGE OF THE THERMODYNAMICS OF THE CO<sub>2</sub> SYSTEM
- 5. GLOBAL pCO<sub>2</sub> DATA SET**
  - 5.1 GLOBAL FLUX ESTIMATES FROM pCO<sub>2</sub> DATA
  - 5.2 INVENTORY OF pCO<sub>2</sub> DATA
  - 5.3 WHAT NEXT WITH pCO<sub>2</sub> DATA
- 6. IRON ENRICHMENT INVESTIGATIONS**
- 7. EMERGING TECHNOLOGIES**
- 8. ATMOSPHERIC CO<sub>2</sub> ISSUES**
- 9. STATUS OF <sup>13</sup>C MEASUREMENTS**
  - 9.1 INVENTORY OF OCEAN <sup>13</sup>C DATA
- 10. PANEL FUTURE DIRECTIONS**
- 11. NATIONAL REPORTS**
- 12. SYMPOSIUM ASSESSMENT**
- 13. NEXT MEETING**

ANNEX II

LIST OF PARTICIPANTS

I. CO<sub>2</sub> PANEL MEMBERS

Andrew G. **DICKSON**  
Marine Physical Laboratory  
Scripps Institution of Oceanography  
University of California, San Diego  
9500 Gilman Drive  
La Jolla, CA 92093-0902  
USA  
Tel: (1-619) 534 2582  
Fax: (1-619) 456 9079  
E-mail: adickson@ucsd.edu

Liliane **MERLIVAT**  
University Pierre et Marie Curie  
LEDUC Tour 14, 2ème étage  
4, place Jussieu  
75252 Paris Cedex 05  
FRANCE  
Tel: (33 1) 44 27 70 72  
Fax: (33 1) 44 27 38 05  
E-mail: merlivat@lodyc.jussieu.fr

Alain **POISSON**  
Laboratoire de Physique et  
Chimie Marines  
University Pierre et Marie Curie  
Tour 24 Case 134  
4, place Jussieu  
75252 Paris Cedex 05  
FRANCE  
Tel: (33 1) 4427 4869  
Fax: (33 1) 4427 4993  
E-mail: apoisson@ccr.jussieu.fr

Taro **TAKAHASHI**  
Lamont-Doherty Earth Observatory  
Columbia University  
Palisades, N.Y. 10964  
USA  
Tel: (1-914) 365 8537  
Fax: (1-914) 365 2312  
E-mail: taka@ldeo.columbia.edu

Shizuo **TSUNOGAI**  
Laboratory of Marine &  
Atmospheric Geochemistry  
Div. of Ocean & Atmospheric  
Sciences  
Hokkaido University  
Sapporo 060  
JAPAN  
Tel: (81 11) 706 2368  
Fax: (81 11) 726 6234  
E-mail: mag-hu@eoas.hokudai.ac.jp

Andrew **WATSON**  
School of Environmental Sciences  
University of East Anglia  
Norwich NR4 7TJ  
UNITED KINGDOM  
Tel: (44 1603) 456 161 (standard)  
(44 1603) 593 761 (direct)  
Fax: (44 1603) 507 719  
E-mail: a.j.watson@uea.ac.uk

C S. **WONG**  
Centre for Ocean Climatic Chemistry  
Institute of Ocean Sciences  
9860 W. Saanich Rd.  
P.O. Box 6000  
Sidney, BC V8L 4B2  
CANADA  
Tel: (1-604) 363 6407  
Fax: (1-604) 363 6476  
E-mail: cswong@ios.bc.ca

II. CO<sub>2</sub> MEMBERS NOT ATTENDING

Truls **JOHANNESSEN**  
Geophysical Institute,  
Allegt. 70,  
University of Bergen  
N-5007 Bergen  
NORWAY  
Tel: (47 55) 21(58) 2615  
Fax: (47 55) 96(58)0566  
E-mail: truls.johannessen@gfi.uib.no  
or: truls@gfi.uib.no

**Fortunat JOOS**

Physikalisches Institut C-14 Lab.

Universität Bern

Sidlerstrasse 5

CH-3012 Bern

SWITZERLAND

Tel: 41 31 631 44 61

Fax: 41 31 631 44 05

E-mail: joos@climate.unibe.ch

**Petr N. MAKKAVEEV**

P.P. Shirshov Institute of Oceanology

Russian Academy of Sciences

Krasikova St. No. 23

Moscow 117218

RUSSIAN FEDERATION

Tel: (7 095) 124 7742 (Work)

(7 095) 412 4334 (Home)

Fax: (7 095) 124 5983

E-mail: mkkaveev@ecosys.sio.rssi.ru

**Frank J. MILLERO**

Rosenstiel School of Marine &

Atmospheric Sciences

4600 Rickenbacker Causeway

Miami FL

33149-1098

USA

Tel: (1-305) 361 47 07

Fax: (1-305) 361 47 11

E-mail: fmillero@rsmas.miami.ed

**Graeme PEARMAN**

CSIRO/Division of Atmospheric Research

PMB 1

Mordialloc, Victoria 3195

AUSTRALIA

Tel: (61 3) 586 76 50

Fax: (61 3) 586 75 53

E-mail: gip@dar.csiro.au

**Douglas WALLACE**

Abteilung Meereschemie

Institute für Meereskunde

Universität fuer Kiel

Dusternbrooker Weg 20

D - 24105

GERMANY

Tel: 49 431 597 3810

Fax: 49 431 565876

E-mail: dwallace@ifm.uni-kiel.de

**III. INVITED GUESTS**

**Dr. Alexander BYCHKOV**

Assistant Executive Secretary

N Pacific Marine Science Org (PICES)

c/o Institute of Ocean Sciences

9860 West Saanich Road

P.O. Box 6000

Sidney, British Columbia

CANADA V8L 4B2

Tel: (1-250) 363-6364

Fax: (1-250) 363-6827

E-mail: bychkov@ios.bc.ca

**Roger J. FRANCEY**

CSIRO Atmospheric Research

PMB#1 Aspendale

Vic. 3195

AUSTRALIA

Tel: 61 3 9239 4615

Fax: 61 3 9239 4444

e-mail: roger.francey@dar.csiro.au

**Catherine GOYET**

WHOI

Woods Hole MA 02543

USA

Tel: 1-508 548 1400 x2552

Fax: 1-508 457 2193

E-mail: cgoyet@whoi.edu

**Keith A. HUNTER**

Centre for Chemical & Physical Oceanography

Department of Chemistry

University of Otago

P.O. Box 56, Dunedin

NEW ZEALAND

E-mail: khunter@alkali.otago.ac.nz

**Takashi KIMOTO**

Kimoto Electric Co. Ltd

3-1 Funahashi-cho, Tennoji-ku, Osaka-shi

Osaka, 543-0024

JAPAN

E-mail: tkimoto@kimoto-electric.co.jp

*also working at:*

Research Institute of Oceano-Chemistry (RIOC)

Osaka Office

3-1 Funahashi-cho

Tennoji-ku

Osaka 543-0024

JAPAN

E-mail: tkimoto@rioc.or.jp

Alexander **KOZYR**  
CDIAC's Oceanographic Data Analyst  
The University of Tennessee  
Pellissippi Research Facility  
10521 Research Drive, Suite 100  
Knoxville, TN 37932  
USA  
Tel: (423) 974-8408  
Fax: (423) 974-8448  
E-mail: [akozyr@utk.edu](mailto:akozyr@utk.edu)

Kitack **LEE**  
NOAA/AOML/OCD  
4301 Rickenbacker Causeway  
Miami FL 33149  
USA  
Tel: (1-305) 361 4389  
Fax: (1-305) 361 4392  
E-mail: [lee@aoml.noaa.gov](mailto:lee@aoml.noaa.gov)

Paulette P. **MURPHY**  
PMEL/NOAA, Bldg. 3  
7600 Sand Point Way NE  
Seattle, WA 98115  
USA  
Tel: 206 526-6217  
E-mail: [murphy@pmel.noaa.gov](mailto:murphy@pmel.noaa.gov)

Yukihiro **NOJIRI**,  
Leader, Global Warming Mechanism Laboratory  
National Institute for Environmental Studies  
Tsukuba, Ibaraki 305  
JAPAN  
Tel: +81-298-50-2499,  
Fax: +81-298-50-2569  
E-mail: [nojiri@nies.go.jp](mailto:nojiri@nies.go.jp)

Takashi **OHSUMI**  
Central Research Institute  
of Electric Power Industry  
1646 Abiko,  
Abiko-City  
Chiba 270 1194  
JAPAN  
E-mail: [ohsumi@criepi.denken.or.jp](mailto:ohsumi@criepi.denken.or.jp)

Bernd **SCHNEIDER**  
Baltic Sea Research Institute  
Seestrasse 15  
D-18119 Rostock-Warnemuende  
GERMANY  
Tel: 49 381 519 7 320  
Fax: 49 381 519 7 302  
E-mail: [bschneider@io-warnemuende.de](mailto:bschneider@io-warnemuende.de)

#### IV. IOC SECRETARIAT

Arthur G. ALEXIOU  
Senior Assistant Secretary IOC  
IOC/UNESCO  
1, rue Miollis  
75732 Paris  
France  
Tel: 33-1 4568 4040  
Fax: 33-1 4568 5812  
E-mail: [a.alexiou@unesco.org](mailto:a.alexiou@unesco.org)

## ANNEX III

THERMODYNAMICS OF THE CARBONATE  
SYSTEM IN SEA WATER

by

Frank J. Millero and Kitack Lee

**The Reliability of  $K_1/K_2$  ( $pK_2-pK_1$ ) Ratio**

When the field and laboratory measurements of  $pCO_2$ ,  $A_T$  and  $C_T$  were examined (Millero *et al.*, 1993; Lee *et al.*, 1996; Lee *et al.*, 1997; McElligott *et al.*, 1998; Lueker, 1998; Wanninkhof, *et al.*, 1999), the constants of Mehrbach *et al.* (1973) (referred to henceforth as MEHR) gave the best consistency. These observations indicate that the  $K_1/K_2$  ( $pK_2-pK_1$ ) ratio of MEHR is more reliable than that of the constant of Goyet and Poisson (1989) and Roy *et al.* (1993) (referred to henceforth as GP and ROY). One should keep that in mind that the calculation of  $pCO_2$  from  $A_T$  and  $C_T$  requires reliable values of  $K_1/K_2$  ratio of carbonic acid. MEHR made direct measurements of  $pK_1$  and  $pK_2$  in real seawater while others used artificial seawater. Since there are small differences in  $pK_1$  (0.002-0.01) among the various workers, a large part of the differences in the ratio of  $K_1/K_2$  is due to errors in the determination of  $K_2$ .

Two independent laboratory (Lee *et al.*, 1996; Lueker, 1998) and field studies (Lee *et al.*, 1997; Wanninkhof *et al.*, 1999) indicate that the calculated  $pCO_2$  for surface waters from  $A_T$  and  $C_T$  are more consistent with MEHR at low  $pCO_2$  (e.g.,  $<< 500 \mu atm$ ), but are more consistent with ROY at high  $pCO_2$  (e.g.,  $> 500 \mu atm$ ). If this is true, none of the presently available carbonic acid dissociation constants are consistent with measured  $pCO_2$  over the wide range of  $pCO_2$  (250 to 1800  $\mu atm$ ). The cause of this difference is not certain and requires further studies. At low temperature, ROY and MEHR both give a reliable prediction of  $pCO_2$ , because difference in  $K_1/K_2$  ratio between ROY and MEHR at temperatures lower than 5°C is significantly smaller than those at other temperatures.

**The Reliability of  $pK_2$** 

Recent laboratory and field measurements of pH, and  $C_T$  (Millero, 1993; Millero, 1995; Lee and Millero, 1995; Lee *et al.*, 1997; McElligott *et al.*, 1998) are internally consistent with the carbonic acid dissociation constants of Goyet and Poisson (1989) (referred as GP) and ROY. However, the deviations (measured - calculated) increase with increasing  $A_T/C_T$  ratio (X) of the samples. When the same sets of constants (GP and ROY) are used, the deviations are larger for samples with high X (or low  $pCO_2$ ), but negligible for samples with low X (or high  $pCO_2$ ). The observed X dependence of the deviations between the measured and calculated values (pH,  $A_T$  and  $C_T$ ) is reduced using MEHR, although the overall agreement is poorer than using ROY. These observations suggest that an adjustment of  $\sim 0.01$  to 0.015 in  $pK_2$  of GP and ROY be required to yield deviations near zero for the oceanic conditions since this magnitude of errors in  $pK_2$  affects a given calculated parameter differently depending upon the value of X.

Recently DelValls and Dickson (1998) found that spectroscopic pH values calculated from reported  $pK_2$  of m-cresol purple (Clayton and Byrne, 1993) needed to be increased at all temperatures and salinities by 0.0047. This adjustment in pH makes measurements of pH,  $A_T$ , and  $C_T$  more internally consistent with MEHR at least at 20 and 25°C. It also implies even larger adjustment ( $\sim 0.015$  to 0.02) in  $pK_2$  of ROY and GP.

DelValls and Dickson (1998) did not make spectroscopic measurements on the buffers used to re-determine the emf of TRIS. This needs to be done before any conclusive adjustments can be made on the spectroscopic pH measurements made in the laboratory and field. Note that the examination of the internal consistency using pH,  $A_T$ , and  $C_T$  evaluate the reliability of various equations of  $pK_2$  only, not  $pK_1$ .

### The Reliability of $pK_1$

The measured values of  $pCO_2$  in the field were consistently lower by about 1% to 4% than those calculated from the input of pH and  $A_T$  (or  $C_T$ ), when the constant of MEHR (1%), ROY (3%), GP (3.5%), and DM (4%) were used (Millero *et al.*, 1993; Lee *et al.*, 1997; McElligott *et al.*, 1998). Part of the difference could be due to errors ( $\sim 0.0047$ ) in pH measurements. If pH values were adjusted by 0.0047 as recommended by DelValls and Dickson (1998), MEHR would give most reliable prediction of  $pCO_2$  from the input of pH- $A_T$  (or pH -  $C_T$ ). These observations suggest that the first dissociation constant ( $pK_1$ ) for carbonic acid of MEHR is most consistent with the field measurements, because only a reliable  $pK_1$  is needed to calculate  $pCO_2$  when pH- $A_T$  (or pH- $C_T$ ) is used as an input combination. However, three independent studies (GP, ROY, and DM) agreed to  $\pm 0.003$  (Millero, 1995) but differ from MEHR by about 0.01 in  $pK_1$ . We cannot rule out the possibility that  $pK_1$  of GP, ROY, and DM might have a small error of 0.01, which is within the range of experimental precision for  $pK_1$  of GP, ROY, and DM. The small error of 0.01 in  $pK_1$  can cause significant differences in the calculated  $pCO_2$  depending upon the level of  $pCO_2$  of samples.

Finally it should be pointed out that variations of  $K_1/K_2$  as a function of  $X$  ( $C_T$  or  $pCO_2$ ) are apparent using the constants of MEHR or ROY. Two possible causes can be responsible for this: (1)  $pK_2$  is a function of  $X$  or (2)  $pK_0$  is a function of  $X$  in real seawater. Model calculations do not support variations in  $K_1/K_2$  when  $C_T$  gets higher. Is the  $pK_2$  in real seawater different from the artificial seawater? Does the coupling between borate and carbonate (McElligott and Byrne, 1998) cause the  $pK_2$  to be different in real seawater compared to artificial seawater? The  $pK_0$  was measured in acidified seawater with pure  $CO_2$  equilibration. Is the value of  $K_0$  a function of  $pCO_2$ ? At present we cannot state with certainty what causes the apparent variation of  $K_1/K_2$  with  $C_T$ .

The recent emf measurements (DelValls and Dickson, 1998) on "tris", which is used to calibrate  $pK_2$  of m-cresol purple, differ by 0.0047 from the earlier emf measurements of Ramette *et al.* (1977). If this is correct, the constants of MEHR proved to be internally consistent with pH- $A_T$ - $C_T$  over the wide range of  $X$  and with  $pCO_2$ - $A_T$ - $C_T$  only at high  $X$  (or low  $pCO_2$ ). However, at low  $X$  (or high  $pCO_2$ ),  $K_1/K_2$  ratios of MEHR do not appear to be as reliable as the values determined by ROY. Further studies need to be done to unravel this discrepancy.

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ANNEX IV

COMMENTS FROM C. GOYET AND A. POISSON  
ON  
THE APPARENT DISSOCIATION CONSTANTS OF CO<sub>2</sub> IN SEA WATER

Dear Panel Colleagues,

As clearly indicated by several studies, there are still some ambiguities on the determination of the most appropriate set of apparent constants of CO<sub>2</sub> in seawater. Right now there is no clear evidence that one set is more appropriate than another and the debate can go on further for years until additional scientific research and experiments are done. Therefore, to resolve this issue we suggest the following:

**1. A careful review of the measured apparent dissociation constants  $K_1$  and  $K_2$ .** This has to be done by an international "well weighted" group of experts. The CO<sub>2</sub> Panel could ask the international bodies to reactivate such a group. Joris Gieskes from SIO, who was the chairman of JPOTS, could be approached to form this group.

An analysis should take into account only the data themselves; not the estimated  $K_i$  from a fit to the data. In areas ( $S, T, C_T/A_T$  ranges) where the data from different sets are in agreement within the standard error of measurement, these data can be "averaged". In the other areas ( $S, T, C_T/A_T$  ranges) where the data from different sets do not agree, additional measurements should be made.

**2. Measurements of  $K_1$  and  $K_2$  in the identified  $T, S, X$ , ranges.** Measurements should be made independently by several laboratories in different countries (a minimum of 3) on the same agreed upon  $S, T, C_T/A_T$ . Cross Checks of the preparation of artificial seawater must be organized between these laboratories. For example, each lab would prepare enough artificial seawater to perform a duplicate measurement of  $K_1$  and  $K_2$  (1 measurement in his/her lab, and 1 measurement in another lab).

The calibration of all the other parameters such as  $S, T, C_T/A_T$ , should also be checked between the measuring labs to minimize the uncertainty from those parameters.

**3. An international convention.** This could be proposed to the bodies by the group of experts. We strongly believe that such detailed analyses of the data and carefully planned and executed experiments constitute the only way to unequivocally resolve this issue. In particular, additional measurements should be made in the low temperature range since large areas of the ocean (Arctic and Antarctic Oceans as well as deep waters in all oceans) are at temperatures below 3C.

Best regards

Catherine Goyet and Alain Poisson

## ANNEX V

### THE LAMONT-DOHERTY EARTH OBSERVATORY SEASOAR

"SeaSoar" is the system that has been developed at the Lamont-Doherty Earth Observatory (LDEO) of Columbia University to allow continuous sampling and measurements of upper water column between water depths of 15 meters and 200 meters. The SeaSoar is a towed undulating vehicle or "fish" (manufactured by the Chelsea Instrument, UK), whose position in water is controlled by changing the attack angle of its main wing. LDEO have added to the fish an *in situ* CTD, a sensor array and a positive-displacement water pump for continuous delivery of seawater samples for ship board chemical analyses.

The water sampling pump is powered by 460 volt three-phase AC, which is supplied from the ship to the fish through conductors embedded within the towing cable. The towing cable is 500 meters long (3/4" o.d.) and is made of high-tensile-strength Kevlar. It houses a Nylon tubing (5/16" i.d.) for the water sampling, and a number of conductors which are used for supplying electric power to the pump as well as for the electronic data transmissions. The pump delivers seawater aboard the ship continuously at a rate of about 6 liters/min. The temperature, salinity, PAR (photosynthetically active radiation), oxygen and bio-fluorescence are measured using *in situ* sensors installed on the fish. On the other hand, pCO<sub>2</sub> and the concentrations of total CO<sub>2</sub>, phosphate, nitrate and silicate are measured aboard the ship in the pumped water using fast response analyzers specifically developed for this project. The temperature and salinity of the pumped water are also measured in the pumped water aboard the ship continuously using sensors identical to those installed on the fish. A comparison of the salinity measured in the pumped water using the shipboard sensor with that measured using the *in situ* sensor on the fish allows a precise determination to be made of the transit time of water samples pumped through the 500-meter long sampling tube.

The fish is towed at a lateral speed of about 6 knots (11.1 km/hr) with one surface-to-deep-to-surface cycle of about 30 minutes (i.e., 5.5 km for one full cycle). This corresponds to a fish speed of about 0.2 m/sec vertically and 3 meters/sec horizontally. Because of this fast motion of the fish, rapid measurements of various properties are required. The pCO<sub>2</sub> in the pumped water was measured using a combination of a fast-flowing IR CO<sub>2</sub> analyzer with a newly developed rapid response gas-water equilibrator which uses a bundle of fine tubes made of hydrophobic gas-permeable membranes. The e-folding response time for the equilibrator has been estimated to be about 2 seconds and the pCO<sub>2</sub> data are recorded once every 2 seconds (or at a rate of 0.5 Hz). The total CO<sub>2</sub> concentration (TCO<sub>2</sub>) is determined using a combination of an IR CO<sub>2</sub> analyzer with a newly developed rapid gas extractor similar to (but much smaller than) the one used for the rapid response pCO<sub>2</sub> equilibrator. In order to optimize for a precision at +/- 0.2 % or better in TCO<sub>2</sub>, a rate of analysis of about 30 seconds per sample is required. Therefore, two such units are used concurrently to improve the analysis rate to one determination for each 15 seconds. The macro-nutrients (nitrate, phosphate and silicate) are measured using a Lachat Quickchem Model 8000 unit modified for rapid determinations. A special fast reduction column for nitrate-nitrite analyses has been developed, and the computer software has been extensively improved. As a result, a measurement rate of one analysis per 12 seconds has been attained for nitrate; and that of one analysis per 24 seconds for phosphate and silicate with an analytical precision of about +/- 0.5%.

The pumping SeaSoar system was deployed in the Ross Sea during the US JGOFS/ AESOPS Ross Sea Process IV cruise (November-December 1997) along four repeated transects one week apart along 76° 30' S between 169° E and 179° E longitude. Each transect covered a distance of about 250 km for a depth range of 15 meters to 200 meters in about 20 hours. Mesoscale variations were observed ranging from about 5 km to 30 km for all the properties measured. A persistent intrusion (about 15 km wide and 30 meters thick) of modified circumpolar deep water was observed at a depth of about 100 meters. This was identified by a pronounced temperature maximum at about 175° E. Furthermore, this intrusion was overlain near the surface by a lens of the freshest water seen in the region. Nearly vertical

density contours bracketing this feature imply strong flow to the north at its western boundary and to the south at its eastern boundary. With only two-dimensional coverage, however, LDEO could not determine whether this is part of a meandering current or an eddy. The lens of low salinity water yielded the most stably-stratified surface waters along the whole transect, and contained abundant macronutrients in the euphotic zone. However, this location was found to be one of a minimum in chlorophyll and nutrient utilization. In contrast, on the both sides of this low salinity zone, it was observed that pCO<sub>2</sub> and nutrients in upper layers (down to about 50 meters on the average) were drawn down by the onset of the spring bloom. The west side was dominated by diatoms, which utilized greater proportions phosphate, whereas the east side was dominated by phaeocistis, which utilized lesser proportions of phosphate compared to nitrate. Factors which regulate the preference of one species to another or determine the onset of phytoplankton blooms remain unclear.

## ANNEX VI

### LIST OF ACRONYMS

<b>AEC</b>	Atomic Energy Commission
<b>AMS</b>	Accelerator Mass Spectrometer
<b>AOML</b>	Atlantic Oceanographic and Meteorological Laboratory
<b>BATS</b>	Bermuda Atlantic Time Series Station
<b>CARIOCA</b>	A French pCO <sub>2</sub> Measuring Buoy
<b>CDIAC</b>	Carbon Dioxide Information Analysis Centre (USA)
<b>CLIVAR</b>	Climate Variability and Predictability
<b>CMM</b>	Commission for Marine Meteorology (WMO)
<b>CRMs</b>	Certified Reference Materials
<b>CSIRO</b>	Commonwealth Scientific and Industrial Research Organization
<b>CTD</b>	Conductivity-Temperature-Depth Probe
<b>DIC</b>	Dissolved Inorganic Carbon
<b>DMS</b>	Dimethylsulphide
<b>DOE</b>	Department of Energy (USA)
<b>ENSO</b>	El Niño and the Southern Oscillation
<b>GCOS</b>	Global Climate Observing System
<b>GODAE</b>	Global Ocean Data Assimilation Experiment
<b>GOES</b>	Global Operational Environmental Satellite
<b>GOOS</b>	Global Ocean Observing System
<b>HNLC</b>	High Nitrate - Low Chlorophyll
<b>IfM</b>	Institute für Meereskunde, Kiel
<b>IOC</b>	Intergovernmental Oceanographic Commission (UNESCO)
<b>IOS</b>	Institute of Ocean Science
<b>IPCC</b>	Intergovernmental Panel on Climate Change
<b>IUCN</b>	International Union for the World Conservation of Nature
<b>JAMSTEC</b>	Japan Marine Science and Technology Centre
<b>JCOMM</b>	Joint WMO-IOC Technical Commission for Oceanography and Marine Meteorology
<b>JGOFS</b>	Joint Global Ocean Flux Study
<b>JMA</b>	Japan Meteorological Agency
<b>KNOT</b>	Kyodo North Pacific Ocean time-Series (Japan)
<b>LDEO</b>	Lamont-Doherty Earth Observatory
<b>MBARI</b>	Monterey Bay Aquarium Research Institute
<b>NIES</b>	National Institute of Environmental Studies (Japan)
<b>NIWA</b>	National Institute for Water and Atmospheric Research (New Zealand)
<b>NOAA</b>	National Oceanic and Atmospheric Administration (USA)
<b>NSF</b>	National Science Foundation (USA)
<b>OCMIP</b>	Ocean Community Model Intercomparison Project
<b>OOPC</b>	Ocean Observations Panel for Climate
<b>PAR</b>	Photosynthetically Active Radiation
<b>POC</b>	Particulate Organic Carbon
<b>PON</b>	Particulate Organic Nitrogen
<b>PICES</b>	North Pacific Marine Science Foundation
<b>PMEL</b>	Pacific Marine Environmental Laboratory
<b>POC</b>	Physical Oceanography Committee
<b>PROOF</b>	PROcessus biogéochimiques dans l'Océan et Flux
<b>SCOR</b>	Scientific Committee on Oceanic Research
<b>SIO</b>	Scripps Institution of Oceanography (University of California, USA)
<b>SOIREE</b>	Southern Ocean Iron Release Experiment

<b>SOLAS</b>	Surface Ocean Lower Atmosphere Study
<b>SSS</b>	Sea Surface Salinity
<b>SST</b>	Sea-Surface Temperature
<b>TAO</b>	Tropical Atmosphere-Ocean Array
<b>TOR</b>	Terms of Reference
<b>UCSB</b>	University of California, Santa Barbara
<b>VOS</b>	Voluntary Observing Ship
<b>WCRP</b>	World Climate Research Programme
<b>WHOI</b>	Woods Hole Oceanographic Institution (USA)
<b>WMO</b>	World Meteorological Organization
<b>WOCE</b>	World Ocean Circulation Experiment

In this Series, entitled

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

1. Third Meeting of the Central Editorial Board for the Geological/Geophysical Atlases of the Atlantic and Pacific Oceans
2. Fourth Meeting of the Central Editorial Board for the Geological/Geophysical Atlases of the Atlantic and Pacific Oceans
3. Fourth Session of the Joint IOC-WMO-CPPS Working Group on the Investigations of 'El Niño' (*Also printed in Spanish*)
4. First Session of the IOC-FAO Guiding Group of Experts on the Programme of Ocean Science in Relation to Living Resources
5. First Session of the IOC-UN(OETB) Guiding Group of Experts on the Programme of Ocean Science in Relation to Non-Living Resources
6. First Session of the Editorial Board for the International Bathymetric Chart of the Mediterranean and Overlay Sheets
7. First Session of the Joint CCOP(SOPAC)-IOC Working Group on South Pacific Tectonics and Resources
8. First Session of the IODE Group of Experts on Marine Information Management
9. Tenth Session of the Joint CCOP-IOC Working Group on Post-IDOE Studies in East Asian Tectonics and Resources
10. Sixth Session of the IOC-UNEP Group of Experts on Methods, Standards and Intercalibration
11. First Session of the IOC Consultative Group on Ocean Mapping (*Also printed in French and Spanish*)
12. Joint IOC-WMO Meeting for Implementation of IGOSS XBT Ships-of-Opportunity Programmes
13. Second Session of the Joint CCOP/SOPAC-IOC Working Group on South Pacific Tectonics and Resources
14. Third Session of the Group of Experts on Format Development
15. Eleventh Session of the Joint CCOP-IOC Working Group on Post-IDOE Studies of South-East Asian Tectonics and Resources
16. Second Session of the IOC Editorial Board for the International Bathymetric Chart of the Mediterranean and Overlay Sheets
17. Seventh Session of the IOC-UNEP Group of Experts on Methods, Standards and Intercalibration, Monaco, 1985
18. Second Session of the IOC Group of Experts on Effects of Pollutants
19. Primera Reunión del Comité Editorial de la COI para la Carta Batimétrica Internacional del Mar Caribe y Parte del Océano Pacífico frente a Centroamérica, Aguascalientes, 1986 (*Spanish only*)
20. Third Session of the Joint CCOP/SOPAC-IOC Working Group on South Pacific Tectonics and Resources
21. Twelfth Session of the Joint CCOP-IOC Working Group on Post-IDOE Studies of South-East Asian Tectonics and Resources
22. Second Session of the IODE Group of Experts on Marine Information Management, Moscow, 1986
23. First Session of the IOC Group of Experts on Marine Geology and Geophysics in the Western Pacific
24. Second Session of the IOC-UN(OETB) Guiding Group of Experts on the Programme of Ocean Science in Relation to Non-Living Resources, Paris, 1987 (*Also printed in French and Spanish*)
25. Third Session of the IOC Group of Experts on Effects of Pollutants, Oslo, 1986
26. Eighth Session of the IOC-UNEP Group of Experts on Methods, Standards and Intercalibration, Paris, 1987
27. Eleventh Session of the Joint IOC-IHO Guiding Committee for the General Bathymetric Chart of the Oceans, Paris, 1987 (*Also printed in French*)
28. Second Session of the IOC-FAO Guiding Group of Experts on the Programme of Ocean Science in Relation to Living Resources, Rome, 1987
29. First Session of the IOC-IAEA-UNEP Group of Experts on Standards and Reference Materials, Paris, 1987
30. First Session of the IOCARIBE Group of Experts on Recruitment in Tropical Coastal Demersal Communities, Cartagena de Indias, 1987 (*Also printed in Spanish*)
31. Second IOC-WMO Meeting for Implementation of IGOSS XBT Ship-of-Opportunity Programmes
32. Thirteenth Session of the Joint CCOP-IOC Working Group on Post-IDOE Studies of East Asia Tectonics and Resources, Bangkok, 1987
33. Second Session of the IOC Task Team on the Global Sea-Level Observing System
34. Third Session of the IOC Editorial Board for the International Bathymetric Chart of the Mediterranean and Overlay Sheets, Paris, 1987
35. Fourth Session of the IOC-UNEP-IMO Group of Experts on Effects of Pollutants, Paris, 1987
36. First Consultative Meeting on RNOECs and Climate Data Services, Wormley, 1988
37. Second Joint IOC-WMO Meeting of Experts on IGOSS-IODE Data Flow, Ottawa, 1988
38. Fourth Session of the Joint CCOP/SOPAC-IOC Working Group on South Pacific Tectonics and Resources, Suva, 1988
39. Fourth Session of the IODE Group of Experts on Technical Aspects of Data Exchange, Ottawa, 1988
40. Fourteenth Session of the Joint CCOP-IOC Working Group on Post-IDOE Studies of East Asian Tectonics and Resources, Baguio City, 1988
41. Third Session of the IOC Consultative Group on Ocean Mapping, Bremerhaven, 1988
42. Sixth Session of the Joint IOC-WMO-CPPS Working Group on the Investigations of 'El Niño', Viña del Mar, 1988 (*Also printed in Spanish*)
43. First Session of the IOC Editorial Board for the International Bathymetric Chart of the Western Indian Ocean
44. Third Session of the IOC-UN(OALOS) Guiding Group of Experts on the Programme of Ocean Science in Relation to Non-Living Resources, Bordeaux, 1989
45. Ninth Session of the IOC-UNEP Group of Experts on Methods, Standards and Intercalibration, Villefranche-sur-Mer, 1988
46. Second Session of the IOC Editorial Board for the International Bathymetric Chart of the Caribbean Sea and the Gulf of Mexico
47. Cancelled
48. Twelfth Session of the Joint IOC-IHO Guiding Committee for the General Bathymetric Chart of the Oceans, Boulder, CO, 1989
49. Fifteenth Session of the Joint CCOP-IOC Working Group on Post-IDOE Studies of East Asian Tectonics and Resources, Bangkok, 1989
50. Third Joint IOC-WMO Meeting for Implementation of IGOSS XBT Ship-of-Opportunity Programmes, Hamburg, 1989
51. First Session of the IOC Group of Experts on the Global Sea-Level Observing System, Bidston, 1989
52. Fourth Session of the IOC Editorial Board for the International Bathymetric Chart of the Mediterranean, Paris, 1989
53. First Session of the IOC Editorial Board for the International Chart of the Central Eastern Atlantic, Lagos, 1989 (*Also printed in French*)
54. Third Session of the IOC Editorial Board for the International Bathymetric Chart of the Caribbean Sea and the Gulf of Mexico, Caracas, 1990 (*Also printed in Spanish*)
55. Fifth Session of the IOC-UNEP-IMO Group of Experts on Effects of Pollutants, London
56. Second Session of the IOC Editorial Board for the International Bathymetric Chart of the Western Indian Ocean
57. First Meeting of the IOC *ad hoc* Group of Experts on Ocean Mapping in the WESTPAC Area
58. Fourth Session of the IOC Consultative Group on Ocean Mapping
59. Second Session of the IOC-WMO/IGOSS Group of Experts on Operations and Technical Applications
60. Second Session of the IOC Group of Experts on the Global Sea-Level Observing System
61. UNEP-IOC-WMO Meeting of Experts on Long-Term Global Monitoring System of Coastal and Near-Shore Phenomena Related to Climate Change
62. Third Session of the IOC-FAO Group of Experts on the Programme of Ocean Science in Relation to Living Resources
63. Second Session of the IOC-IAEA-UNEP Group of Experts on Standards and Reference Materials
64. Joint Meeting of the Group of Experts on Pollutants and the Group of Experts on Methods, Standards and Intercalibration
65. First Meeting of the Working Group on Oceanographic Co-operation in the ROPME Sea Area
66. Fifth Session of the Editorial Board for the International Bathymetric Chart of the Mediterranean and its Geological/Geophysical Series
67. Thirteenth Session of the IOC-IHO Joint Guiding Committee for the General Bathymetric Chart of the Oceans (*Also printed in French*)
68. International Meeting of Scientific and Technical Experts on Climate Change and Oceans
69. UNEP-IOC-WMO-IUCN Meeting of Experts on a Long-Term Global Monitoring System
70. Fourth Joint IOC-WMO Meeting for Implementation of IGOSS XBT Ship-of-Opportunity Programmes
71. ROPME-IOC Meeting of the Steering Committee on Oceanographic Co-operation in the ROPME Sea Area
72. Seventh Session of the Joint IOC-WMO-CPPS Working Group on the Investigations of 'El Niño' (*Spanish only*)
73. Fourth Session of the IOC Editorial Board for the International Bathymetric Chart of the Caribbean Sea and the Gulf of Mexico (*Also printed in Spanish*)
74. UNEP-IOC-ASPEI Global Task Team on the Implications of Climate Change on Coral Reefs
75. Third Session of the IODE Group of Experts on Marine Information Management
76. Fifth Session of the IODE Group of Experts on Technical Aspects of Data Exchange
77. ROPME-IOC Meeting of the Steering Committee for the Integrated Project Plan for the Coastal and Marine Environment of the ROPME Sea Area
78. Third Session of the IOC Group of Experts on the Global Sea-level Observing System
79. Third Session of the IOC-IAEA-UNEP Group of Experts on Standards and Reference Materials

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80. Fourteenth Session of the Joint IOC-IHO Guiding Committee for the General Bathymetric Chart of the Oceans
81. Fifth Joint IOC-WMO Meeting for Implementation of IGOSS XBT Ship-of-Opportunity Programmes
82. Second Meeting of the UNEP-IOC-ASPEI Global Task Team on the Implications of climate Change on Coral Reefs, Miami, FL, 1993
83. Seventh Session of the JSC Ocean Observing System Development Panel, Lisbon, 1993
84. Fourth Session of the IODE Group of Experts on Marine Information Management, Washington, D.C., 1993
85. Sixth Session of the IOC Editorial Board for the International Bathymetric chart of the Mediterranean and its Geological/Geophysical Series, Jerusalem, 1993
86. Fourth Session of the Joint IOC-JGOFS Panel on Carbon Dioxide, Plymouth, 1993
87. First Session of the IOC Editorial Board for the International Bathymetric Chart of the Western Pacific, Tianjin, 1993
88. Eighth Session of the JSC Ocean Observing System Development Panel, Dartmouth, NS, 1993
89. Ninth Session of the JSC Ocean Observing System Development Panel, Melbourne, 1994
90. Sixth Session of the IODE Group of Experts on Technical Aspects of Data Exchange, Geneva, 1994
91. First Session of the IOC-FAO Group of Experts on OSLR for the IOCINCWIO Region, Mombasa, 1994
92. Fifth Session of the Joint IOC-JGOFS CO<sub>2</sub> Advisory Panel Meeting
93. Tenth Session of the JSC Ocean Observing System Development Panel, Paradise, TX, 1994
94. First Session of the Joint CMM-IGOSS IODE Sub-group on Ocean Satellites and Remote Sensing, Paris, 1994
95. Third Session of the IOC Editorial Board for the International Chart of the Western Indian Ocean, Zanzibar, 1994
96. Fourth Session of the IOC Group of Experts on the Global Sea Level Observing System, Bordeaux, 1995
97. Joint Meeting of GEMSI and GEEP Core Groups, Bermuda, 1993
98. First Session of the Joint Scientific and Technical Committee for Global Ocean Observing System, Nantes, 1994
99. Second International Meeting of Scientific and Technical Experts on Climate Change and the Oceans, Valletta, 1994
100. First Meeting of the Officers of the Editorial Board for the International Bathymetric Chart of the Western Pacific, Bali, 1994
101. Fifth Session of the IOC Editorial Board for the International Bathymetric Chart of the Caribbean Sea and the Gulf of Mexico, San José, 1994
102. Second Session of the Joint Scientific and Technical Committee for Global Ocean Observing System, Paris, 1995
103. Fifteenth Session of the Joint IOC-IHO Committee for the General Bathymetric Chart of the Oceans, Monaco, 1995
104. Fifth Session of the IOC Consultative Group on Ocean Mapping, Bremerhaven, 1995
105. Fifth Session of the IODE Group of Experts on Marine Information Management, Athens, 1996
106. IOC-NOAA *Ad hoc* Consultation on Marine Biodiversity, Paris, 1995
107. Sixth Joint IOC-WMO Meeting for Implementation of IGOSS XBT Ship-of-Opportunity Programmes, Ottawa, 1995
108. Third Session of the Health of the Oceans (HOTO) Panel of the Joint Scientific and Technical Committee for GOOS, Bangkok, 1995
109. Second Session of the Strategy Subcommittee (SSC) of the IOC-WMO-UNEP Intergovernmental Committee for the Global Ocean Observing System
110. Third Session of the Joint Scientific and Technical Committee for Global Ocean Observing System
111. First Session of the Joint GCOS-GOOS-WCRP Ocean Observations Panel for Climate, Baltimore, Md, 1997
112. Sixth Session of the Joint IOC-JGOFS CO<sub>2</sub> Advisory Panel Meeting, Mayaguez, 1996
113. First Meeting of the IOC/WESTPAC Co-ordinating Committee for the North-East Asian Regional - Global Ocean Observing System (NEAR-GOOS)
114. Eighth Session of the Joint IOC-WMO-CPPS Working Group on the investigations of "El Niño", Concepción, 1996 (*Spanish only*)
115. Second Session of the IOC Editorial Board of the International Bathymetric Chart of the Central Eastern Atlantic, Paris, 1996  
(*Also printed in French*)
116. Tenth Session of the Offices Committee for the Joint IOC-IHO General Bathymetric Chart of the Oceans (GEBCO), USA, 1996
117. IOC Group of Experts on the Global Sea Level Observing System (GLOSS), Fifth Session, USA, 1997
118. Joint Scientific Technical Committee for Global Ocean Observing System (J-GOOS), Fourth Session, USA, 1997
119. First Session of the Joint IOC-WMO IGOSS Ship-of-Opportunity Programme Implementation Panel, South Africa, 1997
120. Report of Ocean Climate Time-Series Workshop, Joint GCOS-GOOS-WCRP Ocean Observations Panel for Climate, USA, 1997
121. IOC/WESTPAC Co-ordinating Committee for the North-East Asian Regional Global Ocean Observing System (NEAR-GOOS), Second Session, Thailand, 1997
122. First Session of the IOC-IUCN-NOAA *Ad hoc* Consultative Meeting on Large Marine Ecosystems (LME), France, 1997
123. Second Session of the Joint GCOS-GOOS-WCRP Ocean Observations Panel for Climate (OOPC), South Africa, 1997
124. Sixth Session of the IOC Editorial Board for the International Bathymetric Chart of the Caribbean Sea and the Gulf of Mexico, Colombia, 1996  
(*Also printed in Spanish*)
125. Seventh Session of the IODE Group of Experts on Technical Aspects of Data Exchange, Ireland, 1997
126. IOC-WMO-UNEP-ICSU Coastal Panel of the Global Ocean Observing System (GOOS), First Session, France, 1997
127. Second Session of the IOC-IUCN-NOAA Consultative Meeting on Large Marine Ecosystems (LME), France, 1998
128. Sixth Session of the IOC Consultative Group on Ocean Mapping (CGOM), Monaco, 1997
129. Sixth Session of the Tropical Atmosphere - Ocean Array (TAO) Implementation Panel, United Kingdom, 1997
130. First Session of the IOC-WMO-UNEP-ICSU Steering Committee of the Global Ocean Observing System (GOOS), France, 1998
131. Fourth Session of the Health of the Oceans (HOTO) Panel of the Global Ocean Observing System (GOOS), Singapore, 1997
132. Sixteenth Session of the Joint IOC-IHO Guiding Committee for the General Bathymetric Chart of the Oceans (GEBCO), United Kingdom, 1997
133. First Session of the IOC-WMO-UNEP-ICSU-FAO Living Marine Resources Panel of the Global Ocean Observing System (GOOS), France, 1998
134. Fourth Session of the IOC Editorial Board for the International Bathymetric Chart of the Western Indian Ocean (IOC/EB-IBCWIO-IV/3), South Africa, 1997
135. Third Session of the Joint GCOS-GOOS-WCRP Ocean Observations Panel for Climate (OOPC), France, 1998
136. Seventh Session of the Joint IOC-JGOFS CO<sub>2</sub> Advisory Panel Meeting, Germany, 1997
137. Implementation of Global Ocean Observations for GOOS/GCOS, First Session, Australia, 1998
138. Implementation of Global Ocean Observations for GOOS/GCOS, Second Session, France, 1998
139. Second Session of the IOC-WMO-UNEP-ICSU Coastal Panel of the Global Ocean Observing System (GOOS), Brazil, 1998
140. Third Session of IOC/WESTPAC Co-ordinating Committee for the North-East Asian Regional - Global Ocean Observing System (NEAR-GOOS), China, 1998
141. Ninth Session of the Joint IOC-WMO-CPPS Working Group on the Investigations of 'El Niño', Ecuador, 1998 (*Spanish only*)
142. Seventh Session of the IOC Editorial Board for the International Bathymetric Chart of the Mediterranean and its Geological/Geophysical Series, Croatia, 1998
143. Seventh Session of the Tropical Atmosphere-Ocean Array (TAO) Implementation Panel, Abidjan, Côte d'Ivoire, 1998
144. Sixth Session of the IODE Group of Experts on Marine Information Management (GEMIM), USA, 1999
145. Second Session of the IOC-WMO-UNEP-ICSU Steering Committee of the Global Ocean Observing System (GOOS), China, 1999
146. Third Session of the IOC-WMO-UNEP-ICSU Coastal Panel of the Global Ocean Observing System (GOOS), Ghana, 1999
147. Fourth Session of the GCOS-GOOS-WCRP Ocean Observations Panel for Climate (OOPC); Fourth Session of the WCRP CLIVAR Upper Ocean Panel (UOP); Special Joint Session of OOPC and UOP, USA, 1999
148. Second Session of the IOC-WMO-UNEP-ICSU-FAO Living Marine Resources Panel of the Global Ocean Observing System (GOOS), France, 1999
149. Eighth Session of the Joint IOC-JGOFS CO<sub>2</sub> Advisory Panel Meeting, Japan, 1999