OBSERVING TRACERS AND THE CARBON CYCLE

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ABSTRACT - A program for repeated sampling of tracers and variables essential for quantitative understanding of the carbon cycle is recommended within CLIVAR/GOOS. The program is critical to our monitoring and understanding of climate change both natural and anthropogenic. The objectives are: the quantification of changes in the rates and spatial patterns of oceanic carbon uptake, fluxes and storage of anthropogenic CO_2, the detection and possible quantification of changes in water mass renewal and mixing rates, and providing a stringent test of the time integration of models natural and anthropogenic climate variabilityc. The strategy is to put in place a global observing network for tracers and CO_2 to document the continuing large scale evolution of these fields. hydrographic lines are advocated, although it is realized that there has to be a limit on these observations due to logistical and resource constraints. Thus, there is the need to supplement these observations with time series and autonomous measurements to provide detail in the temporal evolution of the fields.

1. THE OBJECTIVES

A program for repeated sampling of tracers and the carbon cycle is recommended within CLIVAR/GOOS. The measurement program presented here is based upon: widespread consensus expressed in various reports that have proceeded this document, cost effectiveness, and obtaining data that are critical to our monitoring and understanding of climate change both natural and anthropogenic.

The role of the oceanic uptake and storage of CO_2 will be affected by, and eventually will have an irrevocable feedback on the earth’s climate. Reorganization of the thermohaline circulatin as a result of climate change [Broe 97]; [Sarm 98] will clearly manifest itself in the tracer fields. Transient tracers provide renewal rates of water masses and information on mixing, and offer a powerful constraint to the evolution of the anthropogenic CO_2 signal in the ocean. The subsurface ocean processes including fluxes and storage rates have a direct impact on the ocean’s ability to take up atmospheric CO_2. There are still large volumes of the oceans that are untouched by anthropogenic CO_2 and transient tracers (e.g., deep Pacific, Angola Basin). If we succeed in monitoring the future rise of anthropogenic CO_2 and tracers (CFCs, tritum/helium-3, ^{14}C, SF_6, 180) in the oceans including these basins, much will be learned from the data including:

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- the identification and possible quantification of changes in the oceanic uptake, fluxes and storage of anthropogenic CO_2

- contributions to the quantification of changes in water mass renewal and mixing rates

- providing a stringent test of the time integration of models of ocean circulation and climate variability both natural and anthropogenic

2. PREVIOUS MEASUREMENTS

The ocean takes up about 30% of the atmospheric CO_2. About one-third of this uptake occurs in the high latitude North Atlantic (for latitudes higher than 50ºN) associated with the thermohaline circulation [Taka 97].

In an analogous way to CO_2, the transient tracers (CFCs, tritum/helium-3, ^{14}C, SF_6) enter the ocean at the air/water boundary. Their delivery to the ocean is constrained by known boundary conditions, allowing quantitative use of these tracers. Their oceanic distributions are analogous to that of a signal imprinted upon the ocean (e.g. a climate signal) with the additional advantage that they contain information about the rates of the penetration process over the past several decades.

Data of increasingly higher quality have been collected for the carbon cycle and some of the tracers dating back a few decades to the GEOSECS program (and even before), the Transient Tracers in the Oceans, the WOCE and JGOFS. The later two data sets in particular have produced unprecedented high quality data with global coverage for the 1990s. In addition to measuring the changes, these data have contributed to quantitative estimates of oceanic processes including uptake and fluxes of CO_2, renewal times and mixing rates. The following is intended to highlight some of these contributions for the transient and stable isotope tracers::

A. Identification of newly-ventilated water masses and variability in their rates of formation

Transient tracers provide the only means of reliably identifying the most recently formed component of a subsurface water mass. For example, hydrographic data have clearly shown that North Atlantic Deep Water (NADW) is a complex mixture of water masses with different sources. However, it is the anthropogenic transient tracer data that show which source waters have been in closest and most recent contact with the atmosphere and hence would be most susceptible to change due to a variable climate. The inventories of transient tracers in a water mass are directly correlated with the formation rates of the water mass [Smet 99]. The CFC inventories for the WOCE data can be compared to prior and future data sets to assess variability in formation rates.

The existence in the North Atlantic of a well-ventilated water mass component of upper NADW, upper Labrador Sea Water, lying above classical Labrador Sea Water (LSW) was not known until CFC (e.g. [Weis 85]; [Fine 88]; [Smet 93]) and tritium data [Jenk 80]; [Olso 86] were collected. The tracers now reveal that this water mass is found extensively throughout the western tropical North Atlantic (e.g. [Moli 92]; [Rhei 95]; [Pläh 98]; [Andr 98]) and also in the South Atlantic (e.g. [Wall 92]). Smethie and Fine [Smet 99] have estimated a formation rate for Upper LSW of 3.4 Sv based on CFC inventories from the late 1980s to early 1990s. Classical LSW, on the other hand, contained low levels of CFCs south of the Grand Banks prior to the 1990s [Smet 93]; [Pick 98]. With the increase in the formation rate, high CFC concentrations associated with newly-formed classical LSW have been observed spreading into the eastern subpolar North Atlantic in about 5 years (Sy *et al.*, 1997), into the western North Atlantic at 46ºN in less than 5 years [Smet 93]; [Pick 98], and into the subtropics in 8-10 years [Moli 98]. Comparison of the CFC distributions along 20ºW in the eastern North Atlantic between 1988 and 1993 show an out-of-phase relationship between ventilation of classical LSW and Subtropical Underwater in response to changes in surface forcing associated with the North Atlantic Oscillation [Done 98].

There have been numerous studies of deep water formation rates within the polar regions using tracers. Bullister and Weiss [Bull 83], Smethie *et al.* [Smet 88], Heinze *et al.* [Hein 90], and Rhein [Rhei 91] calculated exchange rates between deep Greenland and deep Norwegian Seas. Schlosser *et al.* [Schl 91] showed that the formation of deep Greenland Sea water was reduced in the 1980s. Boenisch *et al.* [Boen 97] combined tracer and hydrographic data to conclude that the period from 1980 to 1994 was a time of low deep water formation rates in the central Greenland Sea. In the Southern Ocean, most of the studies of deep and bottom water formation have occurred in the Weddell Sea. Schlosser *et al.* [Schl 91] combined the CFCs, tritium, and the isotopes of helium and oxygen to infer processes and regions for the formation of Weddell Sea Bottom Water (WSBW). Mensch *et al.* [Mens 96] calculated formation rates for WSBW based on tracer data. Other regions of formation of deep and bottom waters along the Antarctic margin can be clearly identified by the CFC signal. High CFC concentrations in the bottom waters adjacent to the Ross Sea [Trum 91]; [Warn 93], the Adelie Land ice shelf [Rint 98], and the Amery ice shelf [Whit 98] confirm recent formation and ventilation. Deep water influx into the Weddell Sea from sources further east has been demonstrated by Meredith *et al.* [Mere 99].

B. Pathways, time scales and rates of water mass spreading

Pathways of newly-ventilated waters are the routes that surface-derived properties, anthropogenic CO_2, or climate signals, follow into the subsurface ocean. Since tracers enter the ocean at the surface and have been measured at high spatial resolution during WOCE, they are excellent tools to study these pathways which can be mapped in considerable detail. The pathways can be coupled with tracer-derived ages to estimate average rates of water mass spreading, ventilation (e.g., re-equilibration of dissolved gases with the atmosphere) and mixing.

The newly-ventilated component of upper LSW was first observed to be transported from the western boundary eastward along the equator on a time scale of about 20 years after a five-fold dilution by mixing with CFC-free water [Weis 85]. The tracers have been used to show that water from the DWBC is transported through a series of recirculation gyres (e.g. [Fine 88]; Pick 93]; [John 97]; [Smet 99]) on its path to the equator. As a consequence of mixing during the recirculation, the tracer-derived equatorward spreading rates are 1-2 cm/s (e.g. [Smet 93]; [Doney 94]) - an order of magnitude slower than direct velocity measurements [Fine 95]. In evaluating the southward transport of a substance by the DWBC, the effective rate is that calculated using the tracers, which is in good agreement with the Lagrangian float rates.

There are other examples of the use of tracers to estimate pathways and time scales of water mass spreading for the Pacific Ocean. Warner *et al.* [Warn 96] estimated a ventilation time scale for the North Pacific subtropical gyre of <10-25 years. Fine *et al.* [Fine 94] described the importance of low-latitude western boundary currents in transporting newly-ventilated water from higher latitudes to the western equatorial Pacific, and they point out the contribution of North Pacific Subtropical Mode Water to the Indonesian throughflow. Wijffels *et al.* [Wijf 96] used CFCs and tritium to examine tropical-subtropical exchange. For isopycnal surfaces which do not outcrop in the North Pacific ($\sigma_\theta > 26.8$), Warner *et al.* [Warn 96] confirmed that the Sea of Okhotsk is an important site for ventilation. Aydin *et al.* [Aydi 98] estimated the Alaskan Gyre contributes 1 Sv in further ventilating North Pacific Intermediate Water (26.8 σ_θ); while Watanabe *et al.* [Wata 97] estimated a production rate for NPIW. Tracers measured during WOCE in the South Pacific are used to estimate the northward transport of Antarctic Bottom Waters to the Samoan Passage on a time scale of 25 years [Bull 98].

Prior to WOCE, there were few CFC measurements in the Indian Ocean. In the Agulhas retroflection region, Fine *et al.* [Fine 88] found that the thermocline waters of the South Indian are generally "older" by a couple of years than those of the adjacent South Atlantic. Using CFC data for the South Indian Ocean, Fine [Fine 93] showed that the "youngest" Antarctic Intermediate Water enters the basin farther west than AAIW in the other two oceans within a compact anticyclonic gyre, and that "older" AAIW from the Pacific Ocean can thus enter into the southeastern Indian. Rhein *et al.* [Rhei 97] used CFCs to estimate the contributions of Indian Central Water and intermediate water masses to the Arabian Sea thermocline. Mecking and Warner [Meck 98] detailed the mixing processes which affect the CFC distributions of Red Sea Water within the Gulf of Aden.

Furthrmore, plumes of primordial ^{3}He in the deep ocean can trace the water mass pathways and spreading at very long time scales [Lupt 98]; [Rüet 99].

C. Rates of ventilation/subduction and mixing

Rates of ventilation/subduction and mixing can be estimated by using CFC-derived ages in the context of model formulations (e.g. [Thie 90]) which represent these processes. Note that the different processes (e.g., subduction, mixing) will have a different affect on the evolution of the tracer and CO_2 distributions. The work of Sarmiento [Sarm 83] and Jenkins [Jenk 87, 98] using tritium demonstrated that Ekman pumping only accounts for a fraction of thermocline ventilation rates, and that subduction is an important process. Jenkins [Jenk 87, 98] estimated subduction rates for the eastern North Atlantic subtropical gyre using tritium and helium-3. The long term evolution of the age fields for example has been used to conclude that the effects of mixing are an important part of the subduction process in the lower thermocline of the eastern North Atlantic [Robb 99]. Similarly the CFCs can provide useful constraints on subduction/ventilation models. As an example, O'Connor *et al.* [O’Co 98] calculated subduction rates for the Pacific Ocean thermocline using a combination of CFC, satellite and drifter data from WOCE.

Tracers have been used with a variety of simple models to estimate mixing rates. Jenkins [Jenk 87, 91, 98] has estimated the relative roles of isopycnal and diapycnal diffusivities on the distributions of tritium and helium-3 in the North Atlantic subtropical gyre. In the equatorial Atlantic, Reverdin *et al.* [Reve 93] used tracers in simple models to constrain their time evolution and their sensitivity to diapycnal processes. Within the Arctic halocline, diapycnal mixing processes are needed to model the measured CFC distributions [Wall 87]. In the eastern South Atlantic, Warner and Weiss [Warn 92] required a balance of about 6:1 between advection and isopycnal diffusion to explain the CFC distributions in AAIW. Olson *et al.* [Olso 92] constrained a mixing model of the modification of mode waters in Agulhas eddies using CFCs.

D. Freshwater residence time for Arctic Surface Waters

The freshwaters of the surface arctic ocean influence the pre-conditioning of the surface layers in the thermohaline source regions of the GIN and Labrador Seas. Oxygen-18 isotopes have been used (e.g., [Ostu 84]; [Bauc 95]) to measure the freshwater contribution to surface waters, and in concert with transient tracers to estimate freshwater residence times.

E. Constraints for rates of biogeochemical processes

Jenkins and Wallace [Jenk 92] and Jenkins [Jenk 95] have reviewed the applications of tracers to constrain rates of biogeochemical processes. Tracer ages were first used to estimate oxygen utilization rates (OUR) and nitrogen cycling rates by Jenkins [Jenk 77, 88]). These rates are a direct manifestation of the efficiency of the biological pump in sequestering carbon. Tracer-derived estimates of new production and suggestions of the pulse-like nature of nutrient injections into the photic zone (e.g. [Jenk 85]) have inspired a re-examination of traditional techniques for calculating these rates. CFC- and tritium/He-3 derived OUR have been used by Wallace *et al.* [Wall 87] and Zheng *et al.* [Zhen 97] to show that decomposition of organic matter produced by primary production over the continental shelf regions is a major component of the apparent oxygen utilization observed in the central Arctic Ocean. Similarly, Reverdin *et al.* [Reve 93], using CFCs and other tracers in simple models, found that a large portion of the influx of nutrients into the equatorial surface waters is likely to be supplied from the African coastal upwelling region. In the Arabian Sea, Olson *et al.* [Olso 93] calculated a residence time of about 10 years for waters in the low oxygen layer. They concluded that the low oxygen must be maintained by moderate oxygen consumption applied to waters with initially low oxygen concentrations. Howell *et al.* [Howe 97] used WOCE CFC data in a model to estimate the nitrate deficit resulting from denitrification in the Arabian Sea, and found no denitrification in the Bay of Bengal. Recently global inventories of anthropogenic CO_2 ocean storage have been published for different basins taking advantage of the high quality set of measurements of hydrographic properties, transient tracers and carbon system parameters made on WOCE, JGOFS and pre-WOCE sections [Grub 96]; [Holf 98]; [Sabi 99]; [Goye 99].

F. An independent data set for model validation

Standard analysis techniques and numerical models, both in the forward and inverse senses, demonstrate a compelling need for on-going, long term tracer and carbon cycle measurements building on the WOCE/JGOFS data. The independent characteristic of the transient tracers is that their oceanic distributions inherently contain imprints of the past boundary conditions. For example, surface water CFC concentrations have increased quasi-exponentially in both hemispheres resulting in vast differences in horizontal and vertical gradients within the ocean. Model parameterizations of mixing will need to be correct to reproduce these distributions. It is crucial for long-term model integrations that water mass formation and transport occurs at the correct rates for predicting future atmospheric CO_2 levels and global heat and freshwater balances. Passive tracers, which do not effect the density field provide an ideal tool to evaluate a model's ability to reproduce these rates.

There have been several studies which use tracers in GCMs (e.g. [Sarm 83]; [Maie 87]; [Togg 89a, 89b]; [Engl 94, 95]; [Farl 93]; [Robi 95]; [Duff 95]; [Jia 96]; [Hu 97]; [Dixo 96]; [Hain 99]). In general, the results have pointed out the variety of natural processes which need to be better parameterized in models. Everything from air-sea gas exchange [Engl 94]; [Hain 97] to sub-grid-scale mixing schemes [Robi 95]; [Engl 97] affects the resulting tracer distributions in model integrations. Recently, Craig *et al.* [Crai 98] examined the distributions of CFCs in a one-degree resolution global GCM showing that the overall agreement between the model and the limited number of measurements was reasonable. Comparison of the time evolution of the model tracer fields with observations over time are a particularly strong constraint for models projecting future climate and CO_2 scenarios A major shortcoming of the model was the production of too little AAIW. Other notable differences appear in regions of deep water formation and within the subtropical gyre near the Kuroshio extension. They emphasized the need to improve model simulations of water masses in order to successfully simulate the oceanic uptake of CO_2. As a tracer ^{14}C has been used for model calibration of the invasion into the oceans of atmospheric CO_2 (e.g., [Togg 89]; [Grub 96]) and to check the exchange mechanisms of the models.

On the global scale, an intercomparison of different ocean carbon-cycle models has shown a quite different regional distribution of sources and sinks for atmospheric CO_2. Clearly, an observational strategy is urgently needed in order to understand the reasons for these differences. This has to be done before we get confidence in the scenario proposed by any of these models to predict interannual as well as long term variability of the role of the ocean to sequester atmospheric CO_2 [Orr 99].

3. SUGGESTED SAMPLING STRATEGIES

In order to obtain the full benefit of the tracer and carbon methodology outlined above, the following framework is advocated for future tracer and CO_2 observations. The strategy is to put in place a global observing network for tracers and CO_2 to document the continuing large scale evolution of these fields. Although hydrographic lines are advocated, a limitation is that of collecting sufficient realizations of the carbon and tracer fields to quantify the time averaged property fluxes. Thus there is the need to supplement these observations with time series and autonomous measurements to provide detail in the temporal evolution of the fields. In addition, a continuation of the multi-tracer approach is being advocated for several reasons. The differences between tracers (e.g., differences between tracer ages) yields valuable information on processes (e.g., water mass formation, mixing, exchange with the atmosphere, etc.). Additionally, multi-tracer data sets constrain models in cases where a single tracer yields ambiguous results. The multi-tracer approach provides a method for looking at the evolution of the tracer climatology for the purpose of contributing to understanding of interannual variability of processes (e.g., [Robb 99]).

The sampling priorities are: (1) global observations of the surface through intermediate layers and of the thermohaline circulation at and downstream of the source regions, and (2) documentation of the spreding of the tracer and anthropogenic CO_2 signal into those areas of the ocean that are as yet untouched by the transients. Those areas included under the first priority will have imbedded intensive arrays and autonomous samplers. Those areas included under the second priority can be considered as yet part of an initial realization of the climate state to be more closely monitored when the signals become more intensive. In addition to sampling for the transient tracers and carbon cycle, with little increased effort the stable isotopes such as $^{18}0$ and the noble gases in high latitudes should be included to provide a constraint for monitoring the variability in the high latitude freshwater flux. The program for tracer and carbon cycle observations relies heavily on that presented for Hydrographic observations. The program involves a grid of hydrographic lines (see Fig. 1 Hydrographic Report), and time series stations. In addition, we have embedded moorings to collect samples at key locations. The hydrographic lines will be used to document the large scale circulation, while the time series stations and moorings will be used to document the details of the temporal evolution of changes in the tracers and carbon properties. For the carbon cycle, there will also be autonomous samplers. Furthermore, the in situ measurement program will provide ground truth for estimations of air-sea gas fluxes using satellite data.

A. Hydrographic Sampling

The strategy recommended in the Hydrographic Report of doing repeats of selected WOCE sections on a 5-7 year time scale is adopted for tracer and carbon sampling. Several key short sections should be continued. Those nearer to the high latitude deep water source regions should be repeated annually, including: the section across the Labrador Sea AR7W, a section across the center of the Greenland Sea at 75ºN, and sections across the Fram and Bering Straits. The detailed time history of the tracers in the deep water source regions is needed to maximize interpretation of the measurements made throughout the oceans. The 55°W [Pick 98], 26.5°N [Moli 98], 35°W [Rhei 95] boundary current sections in the North Atlantic are needed to monitor the export of NADW from the subpolar and Gulf Stream recirculations.

Measuring oceanic fluxes of CO_2

The coupling and reconcilation of ocean carbon inventory changes with increases in the atmosphere must occur by measuring the interfacial fluxes. It is proposed that a quantitative estimate of the CO_2 uptake by the ocean be made from measurements of pCO_2 at the surface of the ocean combined with SST and wind data. Such studies can be made at a regional scale, on a monthly, annual or interannual basis, taking advantage of repeat sections on research vessels [Metz 99]; [Feel 99] as well as measurements made by new automated systems designed to measure pCO_2, mounted either on voluntary observing ships or on moored or drift buoys. Space and time extrapolation of the in situ measurements is then made using satellite estimation of SST, wind and ocean colour [Hood 99]. This last quantity would be used to identify the limits of a biogeochemical province within an oceanic basin.

B. Time Series stations and Autonomous sampling

Given the long time between hydrographic surveys, they need to be supplemented with more frequent sampling in several ways including time series stations, autonomous sensors, and aircraft or submarine sampling (e.g., Arctic). The operational time series stations that do not already include transient tracer measurements and carbon cycle components must be expanded to include them on a seasonal basis. While many of the stations are near the high latitude source regions, others are needed to quantify how rapidly climate anomalies reach different interior regions. This will have an effect on uptake and storage.

Operational Time Series Stations

			Tracers	CO_2
S/BATS	Bermuda	Bermuda/US	no	yes
Station Papa	NE Pacific	Canada	?	yes
Mike	Norwegian Sea	Norway	?	no
HOTS	Hawaii	US	no	yes
ESTOC	Canary Islands	Spain/Germany	yes	?yes
Bravo	Labrador Sea	Canada	?	?
Pacific	0: 165°E, 140°W, 110°W	US	no	no

Time Series Stations Suggested in Hydrography Report

Station W	40°N, 70°W	US?
NE Atlantic	Poss 55°N, 20°W	UK/EU?
Weddell Sea	63°S, 50°W	US?
N. Pacific	Poss 30°N, 135°E	?
SE Pacific	Poss 50°S, 90°W	?

There is advancing development of moored systems now being tested, which have the potential to collect and analyze samples for some transient tracers and components of the carbon system. These moorings will greatly enhance and expand the global observing network. They are likely to lessen the need for samples from time series stations. As an example, the Bermuda Testbed Mooring (BTM) located close to the BATS station in the Sargasso Sea. It provides the oceanographic community with a deep-water platform for developing, testing, calibrating, and inter comparing instruments which can obtain long-term data sets. This platform has recently be used to validate a novel automated instrument to measure pCO_2 at the ocean surface [Bate 99]. The MBARI pCO_2 and optical sensors in the equatorial Pacific have shown the effect of the El Niño on carbon and biological parameters [Chav 99]. Deployment of the NOPP/OSCOPE, mooring at Station P (50°N, 145°W) will provide a critical test of deploying autonomous chemical and physical sensors at high latitude.

An array of moorings should be designed to supplement the hydrographic surveys and time series stations for the purpose of monitoring the thermohaline circulation. It will be necessary to document how the tracer and carbon parameters vary with time at the deep water source regions in order to maximize interpret their distributions downstream and to develop realistic boundary conditions for models. It is proposed that the moorings be placed as follows: one south of the Denmark Straits Overflow, one south of the Grand Banks to monitor the water exiting the subpolar gyre. One at 26.5°N to monitor that water making it south of the Gulf Stream recirculation, one in the Guiana Basin to monitor the water before exiting the North Atlantic, one along 35°W south of the equator, one north of the South Sandwich Trench to monitor the AABW flowing equatorward.

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