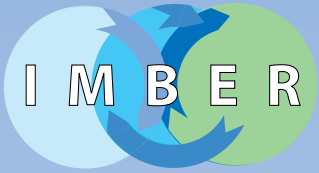




IMBER Report No.1 / SOLAS Report



Integrated Marine Biogeochemistry and Ecosystem Research

# Joint SOLAS-IMBER Ocean Carbon Research



## Implementation Plan



## TABLE OF CONTENTS

<b>PREFACE</b> .....	<b>4</b>
<b>ACTIVITY 3.1 – GEOGRAPHIC AND SUB-DECADAL VARIABILITY OF AIR-SEA CO<sub>2</sub> FLUXES</b> .....	<b>5</b>
3.1.1 – SUPPORT THE ESTABLISHMENT OF SURFACE OCEAN AND ATMOSPHERE CARBON OBSERVING SYSTEMS (INCLUDING ASSOCIATED DATA SCHEMES) SUITED TO CONSTRAINING NET ANNUAL OCEAN-ATMOSPHERE CO <sub>2</sub> FLUX AT THE SCALE OF AN OCEAN BASIN TO <0.2 PGC YR <sup>-1</sup> .....	5
3.1.1 a) <i>Measurement efforts</i> .....	5
3.1.1 c) <i>Data analysis and synthesis</i> .....	11
3.1.2 – CRITICALLY EVALUATE THE PERFORMANCE OF PROGNOSTIC CARBON CYCLE MODELS AGAINST FIELD OBSERVATIONS OF SEASONAL TO CENTENNIAL VARIABILITY, IN ORDER TO GUIDE MODEL DEVELOPMENT AND GAIN INSIGHT INTO THE IMPACT OF CHANGED FORCING ..	13
3.1.2 a) <i>Perform hindcast model simulations of seasonal to multi-decadal variability of the ocean carbon cycle during the 20<sup>th</sup> century and early 21<sup>st</sup> century</i> .....	13
3.1.2 b) <i>Reconstruct ocean carbon cycle variability for the last 250 years</i> .....	13
3.1.2 c) <i>Develop and perform model simulations of coastal biogeochemistry and its interaction with the open ocean and the adjacent land</i> .....	13
3.1.2 d) <i>Develop detection and attribution studies</i> .....	14
3.1.3 – USE OBSERVATION-BASED ESTIMATES OF AIR-SEA FLUXES AND ATMOSPHERIC INVERSION MODELS TO IMPROVE DETERMINATION OF THE MAGNITUDE AND LOCATION OF MARINE AND TERRESTRIAL CARBON SINKS.....	14
3.1.3 a) <i>Support the development of data assimilation and other inverse schemes that incorporate surface ocean measurements</i> .....	14
3.1.3 b) <i>Combine oceanic and atmospheric CO<sub>2</sub> constraints to estimate air-sea and air-land fluxes</i> .....	15
<b>IMBER THEME 3 ISSUE 1 - OCEANIC STORAGE AND TRANSPORT OF ANTHROPOGENIC CO<sub>2</sub></b> .....	<b>16</b>
3.1.4 – DETERMINE THE UPTAKE, TRANSPORT AND STORAGE OF ANTHROPOGENIC CO <sub>2</sub> ON DECADAL TIMESCALE TO WITHIN 10%.....	16
3.1.4 a) <i>Measurement efforts</i> .....	16
3.1.4 c) <i>Data analysis and synthesis</i> .....	19
3.1.5 – <i>Determine the sensitivity of the oceanic uptake of anthropogenic CO<sub>2</sub> to climate change</i> .....	19
3.1.6 – <i>Project future uptake of anthropogenic CO<sub>2</sub> for given atmospheric CO<sub>2</sub> scenarios, with and without climate change. Years 2025, 2050, 2100, 220020</i>	
<b>ACTIVITY 3.2 - CARBON TRANSFORMATIONS IN THE SURFACE OCEANS: SENSITIVITY TO GLOBAL CHANGE</b> .....	<b>21</b>
<b>IMBER THEME 1 ISSUE 1 - INTERACTIONS BETWEEN BIOGEOCHEMICAL CYCLES AND MARINE FOOD WEBS: TRANSFERS OF MATTER ACROSS OCEAN INTERFACES</b> .....	<b>21</b>
<b>IMBER THEME 2 ISSUE 1 - SENSITIVITY TO GLOBAL CHANGE: IMPACTS OF CLIMATE-INDUCED CHANGES THROUGH PHYSICAL FORCING AND VARIABILITY</b>	<b>21</b>
<b>IMBER THEME 2 ISSUE 2 - SENSITIVITY TO GLOBAL CHANGE: EFFECTS OF INCREASING ANTHROPOGENIC CO<sub>2</sub> AND CHANGING PH ON MARINE BIOGEOCHEMICAL CYCLES, ECOSYSTEMS, AND THEIR INTERACTIONS</b> .....	<b>21</b>
3.2.1 – INTRODUCTION.....	21
3.2.1 b) <i>System responses</i> .....	21
3.2.2 – PROCESS STUDIES AND OBSERVATIONS .....	25

3.2.1 a) Measurement of biogeochemical and ecosystem changes in the surface ocean from Voluntary Observing Ships (VOS).....	25
3.2.1 b) Co-located time-series and perturbation experiments .....	27
3.2.1 c) Observing natural perturbations.....	28
3.2.3 – Manipulative experiments .....	28
3.2.3 b) Manipulative experiments examining the interactions between multiple variables.....	30
3.2.3 c) Workshop on guidelines for comparability and quality standards for mesocosm experiments .....	30
3.2.3 d) Planning group for mesoscale open ocean CO <sub>2</sub> enrichment experiment .....	30
3.2.4 – DEVELOPMENT AND APPLICATION OF NOVEL BIOLOGICAL AND CHEMICAL METHODS.....	30
3.2.4 a) Autonomous measurement systems and observational approaches for time-series observations .....	31
3.2.4 b) Chemical and biological tools for non-manipulative interrogation of organisms, communities, and ecosystems.....	31
3.2.5 – COUPLED BIOGEOCHEMICAL-ECOSYSTEM MODELLING .....	32
3.2.5 a) Better representation of physical processes in global carbon models .....	32
3.2.5 b) Better representation of ecosystem dynamics including the mesopelagic in global carbon models .....	33
3.2.5 c) Representation of continental margins exchanges in global carbon models .....	33
3.2.5 d) Closer dialogue between observationalists and modellers for model evaluation and experiment design .....	34
3.2.5 e) Development of Earth System Models.....	34
<b>ACTIVITY 3.3 – AIR-SEA FLUX OF N<sub>2</sub>O AND CH<sub>4</sub>.....</b>	<b>35</b>
<b>IMBER THEME 3 ISSUE 3.2 – ECOSYSTEM FEEDBACK ON OCEAN PHYSICS AND CLIMATE .....</b>	<b>35</b>
3.3.1 – INTRODUCTION.....	35
3.3.2 – DETERMINE THE CONTRIBUTION OF MARINE EMISSIONS TO THE GLOBAL N <sub>2</sub> O AND CH <sub>4</sub> BUDGETS.....	35
3.3.2 a) Open ocean surface and air measurements of N <sub>2</sub> O and CH <sub>4</sub> .....	35
3.3.2 b) Enhanced measurement programmes of N <sub>2</sub> O and CH <sub>4</sub> in coastal areas, particularly as components of coastal observing systems .....	36
3.3.2 c) Validate N <sub>2</sub> O and CH <sub>4</sub> measurements by remote sensing.....	36
3.3.3 – IMPROVE UNDERSTANDING OF FACTORS REGULATING SURFACE CONCENTRATIONS OF N <sub>2</sub> O AND CH <sub>4</sub> , INCLUDING ASSESSMENT OF SENSITIVITY OF MARINE SOURCES OF THESE GASES TO CLIMATE CHANGE AND ANTHROPOGENIC RIVERINE INPUT .....	36
3.3.3 a) Determine the degree to which the globally extensive oxygen minimum zones are sources of N <sub>2</sub> O to the atmosphere .....	36
3.3.3 b) Measurements of N <sub>2</sub> O and CH <sub>4</sub> relevant biogeochemical variables controlling sources and sinks (oxygen, nutrients) in the water column near regions of production and consumption .....	37
3.3.3 c) Determination of impacts of changing inputs of nutrients and organics (e.g., rivers) on sources and sinks of N <sub>2</sub> O and CH <sub>4</sub> .....	37
3.3.3 d) Molecular techniques (e.g., probes, genomics, proteomics).....	37
3.3.3 e) Isotopic composition studies to provide insight on production pathways.....	37
3.3.3 f) Microbial kinetics of N <sub>2</sub> O and CH <sub>4</sub> production and consumption .....	38
<b>REFERENCES.....</b>	<b>39</b>
<b>ACRONYMS .....</b>	<b>40</b>

**Joint SOLAS/IMBER Carbon Implementation Group**

Kevin Arrigo (USA)  
Hermann Bange (Germany)  
Dick Feely (USA)  
Nicolas Gruber (Switzerland)  
Dennis Hansell (USA)  
Gerhard Herndl (Netherlands)  
Kitack Lee (Korea)  
Truls Johannessen (Norway)  
Ken Johnson (USA)  
Arne Körtzinger (Germany)Nicolas Metzl (France)  
Toshiro Saino (Japan)  
Britton Stephens (USA)

***With scientific contributions from:***

Javier Aristegui (Spain)  
Nick Bates (USA)  
Laura Farias (Chile)  
Julie Hall (NZ)  
Maria Hood (France)  
Dave Hutchins (USA)  
Rick Jahnke (USA)  
Alex Kozyr (USA)  
Corinne Le Quéré (UK)  
Bill Miller (USA)  
Peter Milne (USA)  
Wajih A. Naqvi (India)  
Yukihiro Nojiri (Japan)  
Ulf Riebesell (Germany)  
Casey Ryan (UK)  
Chris Sabine (USA)  
Helmuth Thomas (Canada)  
Daniela Turk (Canada)  
Carol Turley (UK)  
Rik Wanninkhof (USA)

## Preface

SOLAS and IMBER have direct interest in, and responsibilities, for observations and research on several aspects of the global ocean carbon cycle. Recognising the need for scientific discussion and coordination of marine carbon research, the two SCOR/IGBP projects established a joint carbon implementation group. The first task of the SOLAS/IMBER carbon group was to develop this joint implementation plan.

The Joint SOLAS-IMBER Ocean Carbon Research Implementation Plan sets out research priorities for ocean carbon research to be conducted over the next ten years. It is understood that these priorities will evolve as new knowledge and questions develop.

The document is structured around three main sections: carbon inventories and fluxes, sensitivity to global change, and the air-sea flux of N<sub>2</sub>O and CH<sub>4</sub>. These sections are mapped onto SOLAS *Activities* and IMBER *Themes and Issues* of similar intent. Within each section, specific objectives have been identified and implementation requirements described. The approaches recommended for meeting these objectives include: time-series, global pCO<sub>2</sub> fluxes, boundaries, fates, carbon transformations, experimental manipulations, VOS, pCO<sub>2</sub> systems in coastal regions, air-sea gas exchange, and process studies.

We encourage scientists from the international ocean carbon community to meet the challenges laid out in this implementation plan.

## Activity 3.1 – Geographic and Sub-Decadal Variability of Air-Sea CO<sub>2</sub> Fluxes

### IMBER Theme 3 issue 1 – Oceanic Storage of Anthropogenic CO<sub>2</sub>

**3.1.1 – Support the establishment of surface ocean and atmosphere carbon observing systems (including associated data schemes) suited to constraining net annual ocean-atmosphere CO<sub>2</sub> flux at the scale of an ocean basin to <0.2 PgC yr<sup>-1</sup>**

#### **3.1.1 a) Measurement efforts**

An analysis of existing partial pressure of carbon dioxide (pCO<sub>2</sub>) measurements suggests that constraining the air-sea CO<sub>2</sub> flux to <0.2 PgC yr<sup>-1</sup> per basin requires measurements on time and space scales of approximately monthly and 200-1000 km, respectively, with measurement accuracy of 3-10 µatm (Large Scale CO<sub>2</sub> Observing Plan; LSCOP, 2002, <http://www.carboncyclescience.gov>). Similar studies conducted for atmospheric sampling network design show that constraining basin-scale fluxes using atmospheric CO<sub>2</sub> data also requires significant advances in data coverage. Achieving the required accuracy of air measurements of ± 0.1 ppm will require dedicated instrumentation with special attention to air-drying, pressure and temperature control, and calibration gases traceable to the World Meteorological Organization (WMO) scale. Obtaining a mechanistic understanding of underlying processes requires both surface and near-surface observations with supporting measurements. The implementation issues associated with this effort have been discussed in several planning documents (IOC-SCOR and LSCOP, 2002).

- *Support the collection of oceanic and atmospheric boundary-layer measurements of CO<sub>2</sub> parameters and related biogeochemical properties*

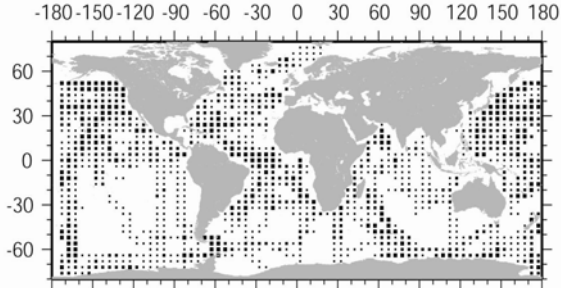
In general, quantitative network design studies in the ocean and atmosphere are critical in optimising observational efforts to achieve SOLAS/IMBER goals, in terms of temporal and spatial scales, accuracy, precision and existing data gaps. Although existing models may be limited relative to the tools that will eventually be used to interpret data in the future, they provide critical guidance on measurement accuracy as well as spatial and temporal coverage. A key issue where time-series stations are particularly helpful is their ability to help determine sub-surface gradients. Mixed layer deepening has been shown to be an important factor controlling pCO<sub>2</sub> temporal variability. This information is difficult to obtain from other approaches, particularly on Volunteer Observing Ship (VOS).

- *Focus additional sampling and time-series sustained observational efforts on currently undersampled regions*

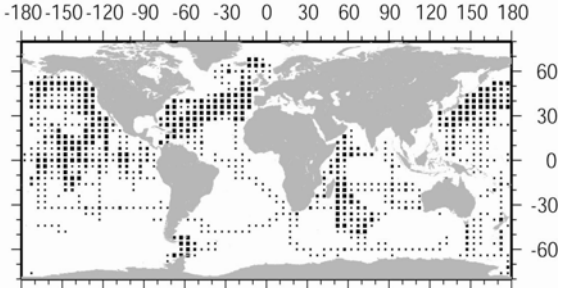
A number of ocean regions are grossly undersampled for oceanic pCO<sub>2</sub>, atmospheric CO<sub>2</sub>, and carbon-related time-series as evident in Figures 1-2.

## Number of Months of Observations of Seawater pCO<sub>2</sub>

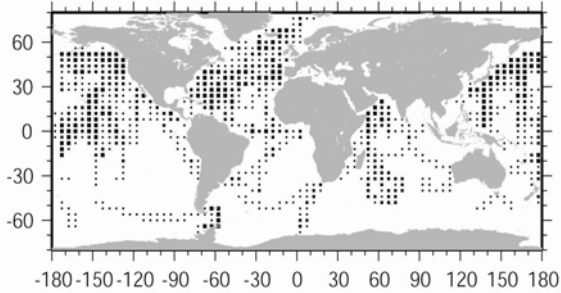
January, February, and March



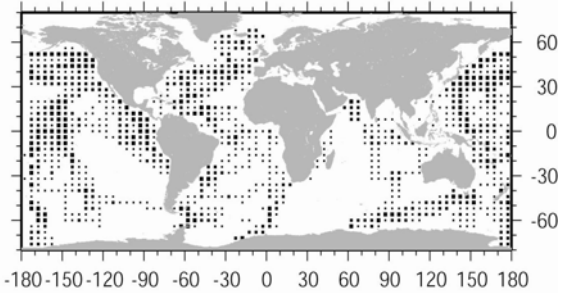
April, May, and June



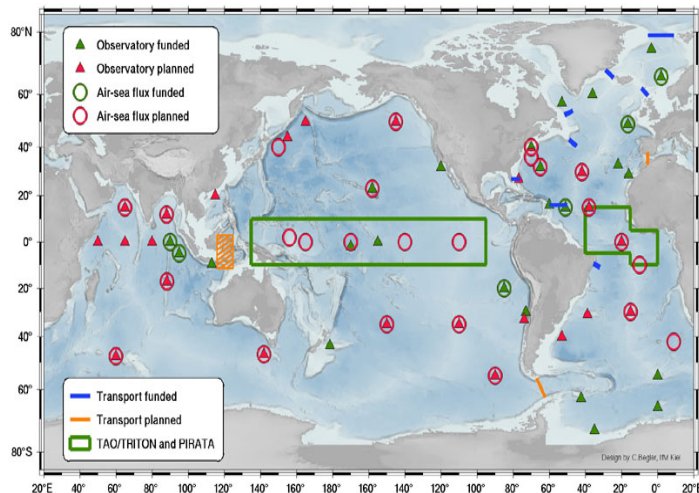
July, August, and September



October, November, and December



Source: Lamont-Doherty Earth Observatory, CO<sub>2</sub> Group.



**Figure 2. Map showing the current status of the global ocean time-series system, including planned sites. The colour code distinguishes implemented or funded sites (green, blue), and sites for which definite plans or a realistic chance of implementation in the near future exist (red, orange). The symbols differentiate air-sea flux reference sites (circles), transport sites (lines, hashed boxes), and generic observatory sites which could measure a mix of physical and/or biogeochemical variables in the water column (triangles). The tropical arrays in the Pacific and Atlantic are indicated summarily via boxes around their perimeter. *Source: OceanSITES project***

Undersampled regions include the Southern Ocean, the Southeast Pacific, areas of the high latitude oceans during winter, and most coastal regions. Measurements in these regions and at various times of year are challenging. A variety of autonomous platforms (e.g., moorings, drifters, gliders, etc.), are very promising for deployment in remote and harsh regions, but further technological development is required. Antarctic re-supply ships of several nations operate routinely in the Southern Ocean, several of which are outfitted with CO<sub>2</sub> sensors, but more of these vessels should be instrumented for underway measurements of pCO<sub>2</sub> and related parameters.

- *Maintain and enhance existing time-series stations*

Existing time-series stations (Table 1) cover at best the past 2.5 decades. It is imperative that these time-series be continued to allow identification of trends in ocean CO<sub>2</sub> levels from natural variability on the on all time-scales. These observatories are uniquely suited for fully sampling in depth and time, thus complementing other components of the observing system focused on spatial coverage (satellites, floats, ships). They resolve a wide range of temporal variability and potentially sample the water column from the surface to the bottom. Fixed-point stations will resolve multi-disciplinary variability and processes like CO<sub>2</sub> uptake, biological productivity, fluxes of heat, freshwater momentum and other properties between the ocean and atmosphere, and seismic and biological activity on the bottom. Furthermore, time-series allow us to identify processes underlying observed signals, a knowledge of which can be used to improve model parameterisations. The existing time-series stations should be enhanced with near-continuous measurement platforms, so that the full temporal spectrum of variability can be sampled.



**Table 1. Present times-series station for carbon cycle measurements in the global oceans**

Site	Dates	Surface	Deep	Frequency	Contact
Atlantic Ocean CO <sub>2</sub> Time-series Sites					
OWS Station M	1995-present	Yes	Yes	4	I.Skjelvan
Irminger Sea	1990-present	Yes	Yes	4	J. Olafsson
Bravo	1980's-present	Yes	Yes	1	P. Jones/H. Thomas?
ESTOC	1994-present	Yes	Yes	3	M. Gonzalez-Davila
BATS	1988-present	Yes	Yes	16	N.R. Bates
Hydrostation S	1983-present	Yes	No	12	C.D. Keeling
PIRATA	1997-2005	Planned	Planned	2	N. Lefèvre
DyFAMed	1991,1995,2001, 2003-	Yes	Yes	12	C. Goyet
Indian Ocean CO <sub>2</sub> Time-series Sites					
Arabian Sea		Yes	Yes		V. Sarma
Pacific Ocean CO <sub>2</sub> Time-series Sites					
OSP/line P	1970's to present	Yes	Yes	3	C.S. Wong
HOT	1988-present	Yes	Yes	12	D.A. Karl
New Zealand	1998 -present	Yes	no	6	K. Currie
KNOT	1998-2002	Yes	Yes	9	T. Saino
SEATS	1999,2003-present	no	no	12	K. K. Liu
TAO	1997-present	Yes	No	mooring	F. Chavez and C. Sabine
SMBO	2002 to present	Yes	Yes	Mooring, discreet measurements 24 per year	N. Gruber
Monterey Bay	1989-present	Yes	No	Mooring, underway pCO <sub>2</sub>	F. Chavez & G. Friederich

- *Encourage the establishment of new time-series sites, particularly at high latitudes*

Time-series observations that span several years are available in the northern mid-latitudes, and data analysis has been done that provides information in the equatorial Pacific. However, little information is available to assess the interannual to decadal variability of the upper ocean carbon cycle and the air-sea CO<sub>2</sub> flux, particularly at high latitudes and the southern hemisphere. Analysis of satellite observations of chlorophyll *a*, sea surface temperature and sea surface height suggest that the variability in biomass and in physical mixing is large at high latitudes, but models produce less variability compared with that seen in the equatorial Pacific. Time-series at high latitudes can provide strong constraints on model estimates. Fixed-point time-series are an essential component of the global observing system for climate under development by the Ocean Observation System Development Panel (OOSDP). The ocean components of the observing system were discussed and reviewed at the international Ocean Obs 99 workshop held in St. Raphaël, France in October 1999. Subsequent to the St. Raphaël meeting, international consensus confirmed the recommended framework for the integrated ocean observing system (Fine et al., 2001). The successor to the OOSDP, the Ocean Observations Panel for Climate (OOPC), together with the CLIVAR Ocean Observations Panel (COOP) recommended formation of an international science team to guide the development and implementation of Ocean Sustained Interdisciplinary Time series Environment Observation System (OceanSITES) which was formally known as Global Eulerian Observatories (GEO; Figure 2). Table 1 gives the locations of present oceanic times-series stations for the SOLAS/IMBER component of the global observing system.

- *Maintain and enhance past and present satellite observations of related parameters (e.g., chlorophyll a, SST, SSH and winds)*

Satellite observations (i.e., SST, SSS, Chl *a*, visible spectrum, winds, Sea surface height, sea-ice and CO<sub>2</sub>) that cover several years are extremely useful for providing information on the physical and biological processes driving the variability in carbon cycle models. These measurements are particularly important for developing algorithms of carbon distributions, particularly in high latitude remote regions where the total number of ship-based observations is low. These measurements should be maintained for as long as possible and efforts should be made to ensure long-term accuracy and precision. Examples of strategies to achieve this include overlapping of the instruments, comparison of different products, and generation of integrated databases that are made easily accessible to the scientific community.

- *Support atmospheric and oceanic measurements of O<sub>2</sub>, <sup>13</sup>C and <sup>14</sup>C*

Time-series measurements of oxygen and carbon isotopes in the air and in the ocean provide valuable alternative, complementary information concerning the ocean carbon cycle and the exchange of CO<sub>2</sub> between the ocean and atmosphere. Atmospheric and oceanic O<sub>2</sub>/N<sub>2</sub> and <sup>13</sup>C measurements are critical for partitioning global terrestrial and oceanic CO<sub>2</sub> fluxes. In addition, atmospheric O<sub>2</sub>/N<sub>2</sub> data can be used to constrain a number of important processes in the ocean. These include large-scale oceanic overturning, interannual variations in ventilation and heat fluxes, seasonal hemispheric productivity, and hemispheric gas-exchange rates. An increased network of atmospheric oxygen measurements is needed to provide additional information on regional variability, in particular of oceanic mixing, and would allow detection of changes in global ocean mixing and the capability of the models to reproduce them. Measurements of the carbon isotopes (<sup>13</sup>C and <sup>14</sup>C) provide a wealth of information about the processes controlling the upper ocean carbon cycle and air-sea fluxes. They are particularly attractive as they are influenced by the same processes as CO<sub>2</sub>, but are subject to fractionation effects, aging and bomb perturbations.

- *Enhance measurement programmes in coastal and marginal seas*

Net air-sea CO<sub>2</sub> fluxes in coastal and marginal seas are currently poorly constrained, primarily due to the lack of measurements in many critical regions. This represents a potential problem, as these regions may contribute significantly to basin totals (Dai et al., 2005; Thomas et al., 2004). Furthermore, coastal regions and marginal seas are currently not represented in the global-scale models of the oceanic carbon cycle used for the assessment of its future response to manmade and natural perturbations. As a result, these assessments may not accurately portray a substantial part of the response. An observational programme should be undertaken to enhance the few currently existing carbon-focused observational studies in coastal and marginal seas. However, given their high spatio-temporal variability for many biogeochemical properties and the limited resources available, we recommend that, as a first step, network design studies be undertaken to determine an optimal allocation of resources. A set of intensive studies should then be conducted, perhaps in conjunction with already existing networks, where the existing spatio-temporal variability is oversampled, permitting the determination of spatial and temporal decorrelation scales. Based on these studies and the experience gained from the existing observations, the observational programme would be scaled up. Tight integration with the coastal modelling programmes (such as those conducted by LOICZ and other organisations) should be encouraged, in order to foster synergies for the interpretation of the observations.

### **3.1.1 b) Technology development**

- *Develop robust, autonomous, low-maintenance and accurate instruments for the measurement of surface ocean and atmospheric pCO<sub>2</sub>. Work with the commercial shipping industry and other VOS stakeholders to improve access to VOS. Develop industry-science partnerships, possibly with political support*

In addition to supporting the immediate use of observation platforms based on existing technologies, SOLAS/IMBER should pursue technology developments in order to make observational approaches more efficient, and to address logistical limitations on improved data coverage through the use of autonomous instrumentation. Commercial ships will play a significant role in SOLAS/IMBER because they are excellent platforms for systematic and regular sampling of both the surface ocean and the lower atmosphere and are of lower cost compared with dedicated research vessels. Conducting science from commercial shipping vessels is not trivial, however, and requires that measurement systems can be rapidly installed, easily maintained, and not impact the ships' operations. Priority should also be given to working with the shipping industry on the design of standardised installations that will facilitate VOS measurements. However VOS are not the only avenue for surface pCO<sub>2</sub> observations and automated sensors on other platforms, including research ships and autonomous floats, buoys, and gliders, should be included in future technology developments.

- *Develop and improve robust, autonomous sensors and sampling devices for other carbon relevant measurements*

Technology development should extend beyond surface pCO<sub>2</sub>, near-surface CO<sub>2</sub> species distributions, and atmospheric CO<sub>2</sub> measurement systems. For example, attention should also be given to, dissolved oxygen, pH, nutrients, biological sensors and various (trace-metal clean) water sampling devices. These developments could be coordinated with existing efforts for physical measurements with shared control circuitry and telemetry options. Infrastructure for delivering seawater to CO<sub>2</sub> instruments on VOS could also be

useful for measuring other species to help understand ocean surface biogeochemical processes. Dissolved O<sub>2</sub> saturation is sensitive to physical and biological changes in the ocean, and with recent improvements in sensor technology, O<sub>2</sub> concentrations should be measured in parallel with pCO<sub>2</sub> onboard VOS, research ships and other platforms. Measurement of <sup>13</sup>C in dissolved inorganic carbon in the surface ocean can also give important information on anthropogenic carbon sinks and new production. For this and other more complex measurements that can only be performed in a laboratory, development of autonomous samplers on moorings would provide valuable time-series information.

The development of improved technologies for use on fixed-point moored and profiling sensor platforms is needed. Sensors and measurement systems for the autonomous *in situ* measurement of near-surface pCO<sub>2</sub> are already commercially available but need to be improved, since problems exist with their deployment for long periods in the ocean surface. These problems include biofouling, as well as physical damage to near-surface sensors and moorings associated with wave action, ship traffic and ice. These are common problems which should be addressed by a CLIVAR-SOLAS-IMBER *in situ* technology working group. A common calibration facility with a high accuracy pCO<sub>2</sub> system for autonomous pCO<sub>2</sub> sensors is desirable. International collaboration of ship cruises deploying and recovering near-surface moorings and collaborative work with CLIVAR on the design and deployment will contribute to the extension of pCO<sub>2</sub> observations from moorings and provide ground-truthing for the autonomous sensors.

- *Perform inter-calibrations between atmospheric CO<sub>2</sub> measurements from VOS system with atmospheric flask samples*

Inversions of atmospheric CO<sub>2</sub>, one of the primary tools available to determine the spatial and temporal variations of the fluxes of CO<sub>2</sub> on a global scale, are currently severely data-limited. High-precision and accurate measurements of atmospheric CO<sub>2</sub> on the VOS lines would dramatically help to improve the data constraints, particularly in regions where there are no land-based sampling stations. There is some evidence that the VOS atmospheric CO<sub>2</sub> measurements may be under-measuring the real atmospheric concentration by about 0.5-0.8 ppm compared to flask samples. In order to achieve the required level of accuracy and precision, careful calibration routines need to be followed and implemented. One way to ensure the consistency of the different measurements is to collect concurrent flask samples which are then analysed at a single laboratory.

### **3.1.1 c) Data analysis and synthesis**

- *Develop and apply interpolation and extrapolation algorithms to estimate CO<sub>2</sub> fluxes from sparse data*

Even with the full surface observing system in place (as described above), the surface ocean pCO<sub>2</sub> measurements by themselves will often be insufficient in time and space to permit a sufficiently accurate calculation of the air-sea flux of CO<sub>2</sub>. Therefore, measurements need to be interpolated between observing locations and between measurement times. Regions with high spatio-temporal variability, such as the continental margins and/or lower sampling coverage, such as the Southern Ocean, are particularly challenging in this regard. Consequently, advanced algorithms for interpolating these sparse oceanographic data need to be developed.

Experimental studies are needed that will improve our ability to interpolate and extrapolate field results. Field observations that "oversample" the space-time variability in key regions will be used in statistical models that permit estimation of the mean from sparse data. Regression models should be developed with parameters that can be measured more readily and more frequently; i.e., either *in situ* or remotely. This requires that the planned *in situ* measurement programme includes key supporting variables, such as wind, temperature, salinity, mixed layer depth, nutrients, chlorophyll *a*, and particulate organic carbon, whenever possible.

These algorithms will be applied and continuously refined, using results from data assimilation studies that make use of the ancillary observations in a dynamically and biogeochemically consistent manner. The flux estimates will also be continuously improved and updated using insights about the environmental controls of the gas transfer velocity gained from SOLAS Focus 2.

- *Further develop and apply inverse (diagnostic) modelling approaches that make use of the surface ocean pCO<sub>2</sub> distributions and/or ocean interior carbon distributions to estimate air-sea CO<sub>2</sub> fluxes*

The ocean interior inorganic carbon distribution reflects the time and space integrated flux of CO<sub>2</sub> across the air-sea interface. Over the last few years, inverse techniques have been developed that permit use of such ocean interior observations and allow identification of what is the optimal distribution of air-sea fluxes at the surface of the ocean in order to explain the ocean interior observations (see e.g., Gloor et al., 2003, Mikaloff Fletcher et al., in press). These approaches are attractive as they also permit the separation of the total flux estimate into its natural and anthropogenic components. A second major development is the advent of major oceanographic reanalysis projects (e.g., Global Ocean Data Assimilation Experiment; GODAE), wherein observations from a large number of platforms (satellite, Argo, etc) are used to arrive at an optimal estimation of the oceanic state. At present, these programmes are focused primarily on physical aspects, but efforts are underway to expand them to include biogeochemical properties (e.g., chlorophyll *a*, etc). SOLAS/IMBER recommends the further development of such data-model fusion techniques, ranging from relatively simple steady-state approaches to time-varying data assimilation schemes. Results from such activities have many additional benefits, such as improved estimates of the gas transfer velocity and improved parameterisation for surface ocean inter- and extrapolation methods.

- *Develop tools to understand drivers for mean CO<sub>2</sub> flux and its variability*

Determination of the factors controlling the observed air-sea CO<sub>2</sub> flux variability is necessary to develop the capability to predict how the fluxes will respond to future climate change. A range of methods should be developed to diagnose these drivers, and modelling is an important tool to understand the drivers. A crucial requirement is the availability of concurrent measurements of carbon and related parameters on underway programmes and at time-series sites, such as dissolved inorganic carbon (DIC), total alkalinity (TA<sub>ik</sub>), nutrients, chlorophyll *a*, dissolved organic carbon (DOC), particulate organic carbon (POC), etc. Approaches envisioned include simple thermodynamic separation of pCO<sub>2</sub> variability into its thermodynamic (SST) and biological (DIC/TA<sub>ik</sub>) driven variability and analyses of the results from global-scale data assimilation (reanalysis) efforts. Of particular importance is the separation of the total flux into its natural and anthropogenic CO<sub>2</sub> components, as their sensitivity to climate change is very different. Strong linkages to activities implemented under recommendation Focus 2.2 will need to be exploited. Results from this activity will also benefit the integration of flux

estimates with transport and storage change estimates. This effort will also be conducted in conjunction with SOLAS Focus 2 in order to improve the parameterisation of gas transfer.

### **3.1.2 – Critically evaluate the performance of prognostic carbon cycle models against field observations of seasonal to centennial variability, in order to guide model development and gain insight into the impact of changed forcing**

#### ***3.1.2 a) Perform hindcast model simulations of seasonal to multi-decadal variability of the ocean carbon cycle during the 20<sup>th</sup> century and early 21<sup>st</sup> century***

Hindcast simulations provide one of the most powerful means to evaluate ocean biogeochemistry models against observations with regard to their sensitivity to physical and chemical forcing. The successful representation of this sensitivity is a critical test for models used for making projections about the future response of the ocean carbon cycle. Implementation of this goal requires close collaborative work with the data synthesis studies in Activity 1 SOLAS and Issue 1 of IMBER Theme 3, so that data can be made available to modellers in a synthetic form. The best observations for model evaluation are those that cover a similar time-scale to that of climate change; i.e., a few years to several decades. Critical parameters in addition to physical measurements (Salinity (S), Temperature (T), CFCs) are surface ocean pCO<sub>2</sub>, nutrients, oxygen, chlorophyll *a*, DIC, TAik, <sup>13</sup>C of DIC, DOC and POC.

#### ***3.1.2 b) Reconstruct ocean carbon cycle variability for the last 250 years***

Evaluations of past ocean carbon cycle variability by direct observations are strongly limited by the amount of available observations, particularly on the decadal to centennial time-scales which are critical for assessing the sensitivity of the ocean carbon cycle to future climate change. Proxy observations that extract variability over the past 250 years have already been developed for physical processes (i.e., <sup>14</sup>C in corals, <sup>14</sup>C in high-resolution ice cores; IMBER Theme 1 Issue 1.3), but no such methods exist at present to constrain the ocean carbon cycle on this time scale.

Innovative ideas are encouraged to address theoretical and technological limitations that prevent us from acquiring information on this time-scale. Examples include very high-resolution laminated sediments from high accumulation regions (e.g., anoxic basins on margins) or proxies developed from organisms that grow annual layers (corals, mussels, etc).

#### ***3.1.2 c) Develop and perform model simulations of coastal biogeochemistry and its interaction with the open ocean and the adjacent land***

The last few years have seen a rapid development and application of regional models focusing on coastal biogeochemical processes. They provide a natural way to address the very large spatio-temporal variability present in these systems and to study the very dynamic physical-biological interactions that determine this variability. They are also very powerful in providing a context for the interpretation of the observations, which are generally sparse in these regions. Continuing development and application of high-resolution regional coupled physical-biogeochemical-ecological models are necessary. Ideally these models should be run in a configuration where the sub-domain models are embedded into basin- or even global-scale models in order to investigate the coupling

between the regional scale processes and those occurring at the large-scale. Another aim of these model simulations and their analyses is to develop parameterisations for the impact of the coastal regions on large-scale processes, so that coarser-resolution models can include the net effect of these regions without the need to explicitly resolve them.

### **3.1.2 d) Develop detection and attribution studies**

In the last decade, substantial advances have been made in order to separate the increase in DIC that is due to the uptake of anthropogenic CO<sub>2</sub> from the natural variability in DIC. These separation methods hinge critically on the assumption of steady-state in ocean circulation and biogeochemistry. This is an imperfect assumption, whose impact on the results is not well known. Recent observations indicate clearly that substantial changes in DIC occur on sub-decadal to decadal timescales that are unrelated to the uptake of anthropogenic CO<sub>2</sub>, but are due to climate variability. Some of this climate variability may be part of the natural variability of the climate system, but some of it may be caused by the human influence on climate through changes in greenhouse gas concentrations, for example. While research in the detection and attribution of the human influence has a long history in the atmosphere in connection with temperature changes, little research has been done so far in the biogeochemical community and very little in the oceanic realm.

Detection (the identification of an anthropogenically forced change in the climate system) and attribution (the determination of the forcing factor responsible for that anthropogenic change) have been hindered primarily because of the limited length of our observational records in the ocean and the generally sparse sampling. This lack of data and of a clear understanding of oceanic variability, make it extremely difficult to determine how much of a given observed signal in oxygen, for example, is due to natural variability and how much is due to anthropogenic climate change. This is, of course, difficult as the anthropogenic forcing, with the exception of CO<sub>2</sub> levels, is not yet above the noise of natural variability.

In the future, the need to distinguish between natural variability and a physical climate change signal will increase. Society's need for such information will also increase as a result of international agreements to limit CO<sub>2</sub> in the atmosphere. Without the clear ability to make this separation, one of the major goals of the planned repeat hydrographic studies, i.e., detecting the oceanic accumulation of anthropogenic CO<sub>2</sub>, will be in peril, since we will not be able to assume that long-term changes in dissolved inorganic carbon concentrations are primarily due to the oceanic uptake of anthropogenic CO<sub>2</sub>. Studies of the marine oxygen cycle are of particular importance in this regard, as oxygen tends to react very sensitively to climate variability and is not affected by the oceanic uptake of anthropogenic CO<sub>2</sub>. A better determination of the ocean atmosphere balance of oxygen has also direct benefit for the use of the atmospheric O<sub>2</sub> method to separate land from ocean sinks for anthropogenic CO<sub>2</sub>.

### **3.1.3 – Use observation-based estimates of air-sea fluxes and atmospheric inversion models to improve determination of the magnitude and location of marine and terrestrial carbon sinks**

#### **3.1.3 a) Support the development of data assimilation and other inverse schemes that incorporate surface ocean measurements**

Direct estimates of basin-scale air-sea CO<sub>2</sub> fluxes will have considerable independent value for understanding and predicting ocean carbon cycle behaviour. In addition, much can be learned about the whole earth system by comparing and integrating these estimates with information from other techniques, such as atmospheric <sup>13</sup>C and O<sub>2</sub>/N<sub>2</sub> constraints, atmospheric CO<sub>2</sub> inversions, and global mass balances incorporating terrestrial flux estimates. This should be accomplished through both direct comparisons of independent methods and by using oceanic measurements and flux estimates as input to data-assimilation and inverse models. Surface ocean measurements capture information on time and space scales not accessible through atmospheric or terrestrial measurements, and can help to identify inconsistencies in estimates from other domains (Link to Global Carbon Project (GCP), Analysis Integration and Modelling of the Earth System (AIMES)).

Data assimilation offers the possibility of incorporating multiple data types from the surface and interior ocean, atmosphere, land, and satellites with information derived from models. In principle, this should provide a more comprehensive picture of the air-sea carbon flux distribution. Basic experimental, statistical, and theoretical work is required to develop and verify such approaches. Links to operational oceanography and modelling programmes should be encouraged and model-data inter-comparison studies supported. Links are seen here with GCP and AIMES.

### ***3.1.3 b) Combine oceanic and atmospheric CO<sub>2</sub> constraints to estimate air-sea and air-land fluxes***

Inverse modelling of atmospheric observations will continue to play a major role in improving our estimates of the contribution of the ocean to variability of atmospheric CO<sub>2</sub>. Such modelling should also explore the sensitivity of inversions of atmospheric concentration data to constraints imposed by observation-based estimates of the air-sea flux. Of particular interest is the recent development of a joint atmospheric-oceanic inversion approach (Jacobson, 2005) that combines ocean interior data of both natural and anthropogenic inorganic carbon with atmospheric CO<sub>2</sub> data to estimate fluxes at the Earth's surface. This initial attempt can be extended by also incorporating surface ocean observations and other data constraints. Due to the strong constraint imposed by the global mean content of CO<sub>2</sub> in air, a better estimation of the air-sea flux has large and direct benefits in the ability of inverse models to estimate exchange fluxes with the terrestrial biosphere.



## IMBER Theme 3 Issue 1 - Oceanic Storage and Transport of Anthropogenic CO<sub>2</sub>

### 3.1.4 – Determine the uptake, transport and storage of anthropogenic CO<sub>2</sub> on decadal timescale to within 10%

#### 3.1.4 a) Measurement efforts

- *Collection of water-column CO<sub>2</sub> species and related parameter distributions on Repeat Hydrography*

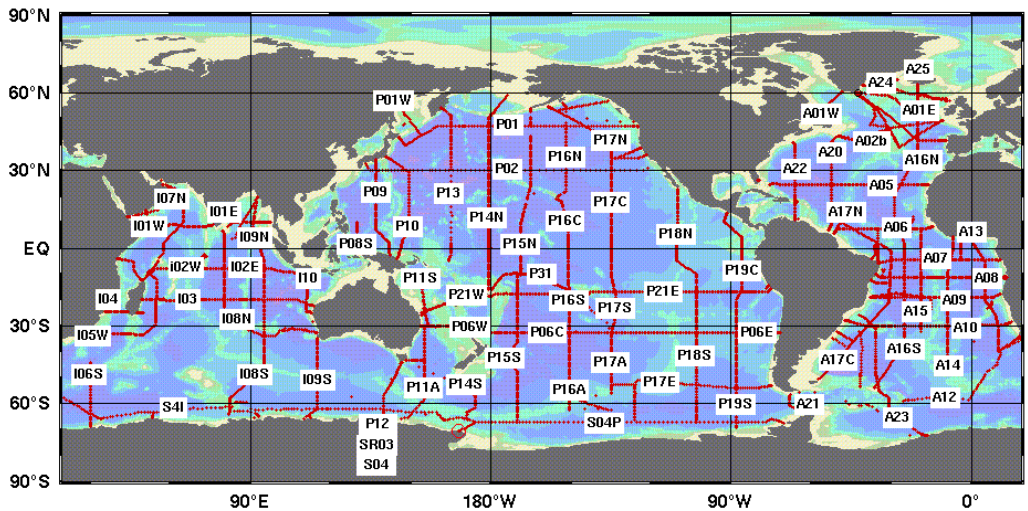
Predictions of how changes in climate will affect marine ecosystems and biogeochemical cycles will require an understanding of: 1) how climate change will affect the physical environment in the oceans and 2) how specific changes in these physical conditions will affect biogeochemical processes including carbon exchange, transport and storage. A series of repeat ocean transects, involving reoccupation of selected meridional and zonal WOCE lines (Figure 3) is required for observing directly the temporal evolution of the fields of inorganic and organic carbon and other biogeochemically relevant species (e.g., carbon isotopes, nutrients, oxygen, trace metals, dissolved organic matter, tracers, microorganism biomass, pigments, community structure, etc.). Measurements will be obtained on the response of those fields to increased warming, stratification, and slowed thermohaline circulation and reconciling net carbon uptake estimates and spatial patterns derived from different methods (e.g., atmospheric CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> constraints; <sup>13</sup>C isotopic composition; existing and new transient tracer proxies and forward and inverse models). The current major challenges are improving the understanding of the biological and physical processes controlling the interannual to decadal variability and potential secular trends, assessing the significant regional differences (e.g., Southern Ocean) between *in situ* and atmospheric inverse derived transport fluxes, and estimating time averaged air-sea fluxes and determining changes in water mass formation rates.

- *Collection of water-column CO<sub>2</sub> species and related parameter distributions on time-series and sustained observatories*

Comprehensive collection of water-column CO<sub>2</sub> species and biogeochemically-related parameters at time-series (Figure 2) sustained observatories and repeat sections will contribute directly to observing the seasonal to decadal evolution of air-sea CO<sub>2</sub> exchange and CO<sub>2</sub> storage in the ocean interior over time. A variety of observing strategies will be employed from shipboard-related water-column observations to autonomous observing sensors. We encourage the continued development and ground-truthing of *in situ* water-column sensors for CO<sub>2</sub> species and biogeochemically-related parameters to improve efficiency and accuracy of measurements at time-series sites.

- *Collection of novel and related parameters (e.g., Fe, transient tracers, nitrogen isotopes), distributions on repeat hydrography, time-series and sustained observatories*

We encourage the development of novel analytical methods and conceptual insights for new tracers that are important for understanding biogeochemical properties and for new tracers that are important for understanding biogeochemical properties and their interaction with ocean circulation. For example, changes in  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of NO<sub>3</sub><sup>-</sup> can be used to estimate sources of nutrients, remineralisation and mixing processes as well as N<sub>2</sub>-fixation and denitrification. The  $\delta^{18}\text{O}$  of O<sub>2</sub> is a tracer that



**Figure 3 Map showing the existing WOCE lines. Source: CDIAC**

interpretation of these unique signals is in its infancy. The triple isotope composition of dissolved  $O_2$  reflects the fraction of dissolved  $O_2$  derived from photosynthesis. This property constrains rates of primary production and provides a tracer of water mixed from the euphotic zone into subtropical mode waters and the thermocline provided ventilation processes are properly accounted for. In addition, development and use of new transient tracers (i.e.,  $SF_6$ , HCFCs,  $CCl_4$ ) that can constrain ventilation timescales and pathways should be encouraged. Trace metals play an important role in controlling biological productivity in the ocean, yet the large-scale distribution of many metals is poorly known. This is in part due to the special care that needs to be taken in order to ensure trace-metal clean sampling, but also due to the analytical challenges associated with the measurement of some of these metals. The development of new and simplified sampling and analysis methods is encouraged. Synergies with GEOTRACES and other trace metal programmes should be exploited to reach this goal.

### **3.1.4 b) Technology development**

The successful implementation of the above goals requires a substantial investment in technology development, as the currently available platforms and instruments are aging, too expensive and/or not easily scalable to the envisioned observing networks. This programme has the opportunity to develop the instruments and platforms of the next generation, enabling SOLAS/IMBER to conduct critical measurements and leave a legacy for the future.

- *Develop novel technologies for water-column profiling of  $CO_2$  species*

The development of improved technologies for measurement of  $CO_2$  species on profiling sensor platforms is supported. Sensors and measurement systems for the autonomous *in situ* measurement of near-surface  $pCO_2$  are already commercially available and may be modified for profiling floats. However, deployment of autonomous observing systems remains a considerable challenge. Long development times are required to bring sensor systems from the laboratory to a robust status where they are capable of operating in large arrays at sea. An observing system that is based on chemical sensors could serve as the core framework for the next generation of global carbon flux studies. Sensors for at least two of the inorganic carbon properties (i.e., DIC,  $pCO_2$ , pH and TAlk) would provide a complete description of the inorganic carbon system, giving important

constraints on the processes that control the spatio-temporal variability of inorganic carbon in the ocean. Although there is utility in limited deployment of these sensors, a means should be developed to deploy them in large numbers throughout the ocean. Nearly 1500 vertical profiling floats that are equipped with temperature, salinity and pressure sensors are operating over large ocean areas in the Argo array. The Argo system provides a global assessment of heat storage in the ocean, a key component of the Earth's climate system. This array could serve as the backbone for a global biogeochemical observing system by outfitting the floats with pertinent biogeochemical sensors.

- *Improve other moored and profiling sensors including O<sub>2</sub> and nutrients*

Development of improved technologies for use on moored, drifting and profiling sensor platforms will increase our ability to increase sample density. Long development times are required to bring sensor systems from the laboratory to a robust status where they are capable of operating in large arrays. Oxygen sensors, optical particulate matter sensors and optical nitrate sensors are recent innovations that are of particular interest. The sensors installed on profiling floats have been shown to be robust in recent field trials (Friis et al., 2004). The measurements can be used for regional biogeochemical state estimates of the ocean as related to carbon cycling. An observing system that is based on chemical sensors could serve as the core framework for the next generation of global biogeochemical studies. This is particularly pertinent with recent evidence of significant changes in water column apparent oxygen utilisation (AOU) and nutrient levels in the thermocline, suggesting a non-steady state environment. The sensors for oxygen, particulate matter and nitrate would provide key constraints on productivity and export.

- *Improve the existing shipboard water-column CO<sub>2</sub> analytical techniques*

Improved instrumentation and certified reference materials have been the cornerstones of the high quality inorganic carbon measurements that now permit scientists to quantify the anthropogenic CO<sub>2</sub> burden in the ocean during the WOCE/JGOFS study (Sabine et al., 2004). The precision and accuracy of current shipboard instrumentation for the measurement of DIC, TAlk, discrete pCO<sub>2</sub> and/or pH are adequate for addressing the objectives in the SOLAS/IMBER joint implementation plan. Necessary is an increased efficiency and sample throughput and an update of decade old electronic technology. Personnel requirements for carbon measurements are high, requiring dedicated qualified analysts for each carbon system measurement. DIC coulometric analysers should be equipped with inlet systems to handle multiple samples, and the instrument interface should be enhanced for unattended operation for batches of samples. Robust instruments should be built to handle multiple analyses on single water aliquots. Steps are underway to build such instruments but resources should be made available to accelerate these improvements. A system to measure TAlk and DIC on the same sample is in prototype phase. Systems to measure all four inorganic carbon system parameters *in situ* are in design phase and it should be investigated if this technology can meet the exacting accuracy requirements for shipboard work, where traceable accuracy over several decades is imperative. Most instrumentation for carbon analyses used to date has been custom built and designed by scientific investigators. Commercialisation of this technology, with appropriate product support, is the next step to increase the user base and so accomplish the increased sampling requirements of the SOLAS or SOLAS/IMBER programme. A longer-term objective is to infuse new technology into the measurement of the parameters. For instance, spectrophotometric measurements can replace electrode based approaches for TAlk measurements, and coulometric measurement might be able to replace by faster infrared analysis.

### **3.1.4 c) Data analysis and synthesis**

- *Develop and apply methodology to separate the anthropogenic CO<sub>2</sub> signal from natural climate variability*

Fundamentally, changes in the inorganic carbon concentration in the interior ocean over time can arise from any combination of the following: uptake of anthropogenic CO<sub>2</sub> from the atmosphere, changes in the natural pool of inorganic carbon in the ocean due to intrinsic variability, and changes in the natural pool of inorganic carbon in the ocean due to anthropogenically induced climate change. Since the drivers for the above changes have fundamentally different sensitivities to changes in physical forcing, it is imperative that observationally based methods are developed that attempt to separate them. These methods are likely to require the combination of many biogeochemically important tracers, such as nutrients, oxygen, carbon isotopes etc., as well as a number of transient tracers, such as CFCs. This requires that these tracers are given high priority in the measurement programmes.

- *Further develop and apply diagnostic approaches to estimate ocean uptake, transport and storage of anthropogenic CO<sub>2</sub>*

During the last decade, several methods have been developed to estimate the uptake, transport and storage of anthropogenic CO<sub>2</sub> by the ocean. These methods need to be refined and their robustness extensively tested (Matsumoto and Gruber, 2005). Methods used so far include direct transport estimates using high-resolution sections (Holfort et al., 1998), as well as ocean transport model based inversions of the reconstructed anthropogenic CO<sub>2</sub> (Gloor et al., 2003; Mikaloff-Fletcher et al., in press). The simultaneous determination of the uptake flux, transport and storage of anthropogenic CO<sub>2</sub> permits scientists to fully account for the oceanic uptake of anthropogenic CO<sub>2</sub> from the atmosphere and determine its fate in the interior of the ocean. These new approaches should undergo further development and testing employing the newer, high-precision oceanographic data.

- *Study drivers for the uptake, transport and storage of anthropogenic CO<sub>2</sub>*

Determination of the factors governing the uptake, transport and storage of anthropogenic CO<sub>2</sub> is crucial to carefully evaluate the models that will be used for making projections for the future uptake of anthropogenic CO<sub>2</sub>. Critical processes of relevance for the uptake of anthropogenic CO<sub>2</sub> are the formation of mode and intermediate waters in both hemispheres. For example, the formation of subantarctic mode waters and Antarctic intermediate waters in the Southern hemisphere is currently the single most important pathway for the uptake of anthropogenic CO<sub>2</sub> from the atmosphere and for transporting it into the ocean interior. We encourage studies that focus on these critical regions. We envisage that these studies will be done in close collaboration with the CLIVAR programme. In this context, it is also critical to study the role, drivers and variability of the biological pump.

### **3.1.5 – Determine the sensitivity of the oceanic uptake of anthropogenic CO<sub>2</sub> to climate change**

- *Determine climate change impacts on uptake, transport and storage of anthropogenic CO<sub>2</sub>*

A variety of methods and approaches will need to be employed to determine the sensitivity of the oceanic uptake of anthropogenic CO<sub>2</sub> to atmospheric and climate variability. Approaches envisaged here will be varied but include: 1) model approaches, and 2) collaborative and integrative studies with CLIVAR scientists. For example, variability in the uptake of CO<sub>2</sub> is particularly sensitive to variability in the rates of water mass formation and transformations, which in turn are sensitive to atmospheric and climate modes (e.g., El Niño- Southern oscillation, ENSO; Pacific decadal oscillation, PDO; North Atlantic (or Arctic) oscillation, NAO/AO; Antarctic annular mode). There is a critical need to understand carbon dynamics during mode and intermediate water formation and transformation, particularly in the Southern Ocean. Strong linkages to research pursued under in Activity 1 will need to be exploited. Results from this activity will lead to better mechanistic understanding of the physical processes controlling the oceanic uptake, transport and storage of anthropogenic CO<sub>2</sub> as well as improved quantification of the associated errors. Again, the biological pump is important here as part of the system of uptake, transport, and storage of carbon.

### **3.1.6 – Project future uptake of anthropogenic CO<sub>2</sub> for given atmospheric CO<sub>2</sub> scenarios, with and without climate change. Years 2025, 2050, 2100, 2200**

- *Conduct model simulations of future uptake, transport and storage of anthropogenic CO<sub>2</sub>*

Model simulations should be performed to determine the oceanic uptake of anthropogenic CO<sub>2</sub> in the future, given a set of CO<sub>2</sub> emission scenarios, such as those developed by IPCC. These model simulations will need to differentiate between the uptake under constant climate and the uptake under a changing climate. The difference between the two represents the anthropogenic CO<sub>2</sub> component of the oceanic carbon-climate feedback. Such simulations can be done with fully coupled climate models or also with ocean only models that are forced with output from coupled models. Detailed prior evaluations of these models with the available observational constraints for the uptake of anthropogenic CO<sub>2</sub> by the ocean are a necessity. Model diversity is encouraged, in order to determine the robustness of the results. Interactions between inverse and prognostic approaches should be promoted, in order to achieve projections with well quantified uncertainties.

## Activity 3.2 - Carbon Transformations in the Surface Oceans: Sensitivity to Global Change

IMBER Theme 1 Issue 1 - Interactions between Biogeochemical Cycles and Marine Food Webs: Transfers of Matter across Ocean Interfaces

IMBER Theme 2 Issue 1 - Sensitivity to Global Change: Impacts of Climate-Induced Changes through Physical Forcing and Variability

IMBER Theme 2 Issue 2 - Sensitivity to Global Change: Effects of Increasing Anthropogenic CO<sub>2</sub> and Changing pH on Marine Biogeochemical Cycles, Ecosystems, and their Interactions

### 3.2.1 – Introduction

#### 3.2.1 a) *Global Change Driven Perturbations*

There is significant potential for future alteration of the large natural component of the oceanic carbon cycle to a wide range of known and anticipated global change driven (GCD) perturbations. However, it is hard to predict the overall effects with our current level of understanding of the relevant processes or from comparisons with the past. The focus of this activity therefore is to examine the integral effect of GCD perturbations on carbon transfers/transformations and marine ecosystems. Global change will encompass a whole suite of changes in the physical, chemical and ecological environment of the ocean. These include:

- *Changes in physical forcing*

Temperature (T); freshwater fluxes and salinity (S); stratification and change in large scale circulation (as a result of changes in T and S); wind forcing; seasonality and extent of sea ice formation and coverage; solar radiative flux quantity and quality

- *Changes in chemical forcing*

CO<sub>2</sub> system speciation and saturation state; seawater acidity (pH); oxygen concentrations; boundary fluxes (atmosphere, rivers, mesopelagial, sediments) of macro- and micronutrients and their speciation

- *Changes in ecological forcing*

Human impact on top level of food web (fisheries) and subsequent impact on ecosystems and biogeochemistry

#### 3.2.1 b) *System responses*

Given the multitude of possible responses and the likelihood of synergistic/antagonistic effects between them, a major task will be to evaluate these feedback mechanisms of carbon transformations based on the following criteria:

- Vulnerability to perturbation;
- Feedback magnitude;
- Longevity of the feedback

Among the processes vulnerable to GCD perturbations, research priorities should be given to those that bear the highest feedback potential on a decadal to centennial timescale. Potentially vulnerable feedback loops comprise the processes and resulting biogeochemical impacts listed in Table 2.

*Explanation of feedbacks listed in Table 2:*

1. Global warming propagates into the ocean, and via changes in the hydrological cycle, causes a decrease in surface ocean salinity. Since the resulting change in CO<sub>2</sub> solubility will be dominated by the temperature change, the overall effect will be reduced solubility of CO<sub>2</sub> in the surface ocean.
2. An increase in storm frequency will cause deeper mixing, eroding into sub-surface waters with elevated CO<sub>2</sub> levels, with more CO<sub>2</sub> being released to the atmosphere.
3. In general, lower sea ice cover will result in better ventilation and a release of CO<sub>2</sub> to the atmosphere, thus determining the sign given in Table 2. However, changed ecosystems, alterations in circulation, etc. will complicate the prediction of the overall sign.
4. Because of global warming and the enhancement of the hydrological cycle, global cloudiness may increase and as a result less biological production, less fixation of surface ocean CO<sub>2</sub>, and increased atmospheric CO<sub>2</sub> concentrations may result.
5. Lower seawater buffer capacity caused by CO<sub>2</sub>-driven shifts in the marine CO<sub>2</sub> system will decrease the ocean's capacity to further absorb atmospheric CO<sub>2</sub>.
6. Enhanced upper ocean stratification and decreased ocean ventilation, as predicted in many models, will reduce the transfer of anthropogenic CO<sub>2</sub> from the ocean surface to the intermediate and deep ocean. As a result, a larger fraction of the oceanic carbon sink would remain at the surface and reduce the rate of uptake of atmospheric CO<sub>2</sub>.
7. Enhanced upper ocean stratification and decreased ocean ventilation will reduce the vertical flux of nutrients, alkalinity and DIC into the surface layer. Although this would most likely lead to a decrease in global ocean new production there would be no net effect on atmospheric CO<sub>2</sub> (in a "Redfieldian Ocean"). However, reduced ocean ventilation increases surface layer residence times, which could increase nutrient utilisation efficiency in areas with excess nutrients (e.g., High- Nutrient, Low- Chlorophyll (HNLC) areas). This could enhance the CO<sub>2</sub> draw-down via the soft tissue pump. Changes in surface ocean productivity may also result from climate-related shifts in surface ocean divergence and convergence. Enhanced surface layer stratification directly affects primary producers by increasing mixed layer light availability, with possible consequences for phytoplankton distribution and succession.
8. Changes in micro- and macronutrient fluxes across air-sea and land-ocean boundaries have the potential to affect the ocean's biological carbon pump. Changes in the atmospheric and fluvial influx of macronutrients into the surface ocean can modify nutrient inventories. Changes in air-sea fluxes of micronutrients (such as Fe and Zn) can influence the efficiency of nutrient utilisation, particularly in HNLC areas, and may also alter oceanic N<sub>2</sub> fixation. These responses each affect the strength of export production with possible consequences for CO<sub>2</sub> sequestration in the ocean.

**Table 2. Examples of major perturbations in the marine realm and their potential effects on ocean carbon transformations and storage (GHG = greenhouse gases).**

<i>Perturbation → impact on</i>	<i>Direction of</i>	<i>Magnitude on</i>	<i>Magnitude on</i>	<i>Level of under-</i>
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	<i>change wrt atm. GHGs</i>	<i>century time-scale</i>	<i>glacial-interglacial time-scale</i>	<i>standing</i>
Increased temperature and changes in salinity → CO <sub>2</sub> solubility	+	high	moderate	high to moderate
Increased storm frequency → upper thermocline ventilation	+	low to moderate	low to moderate	moderate
Decreased sea ice cover → gas exchange, light conditions, etc.	+	moderate	high	moderate
Changed light conditions	+	moderate to high	moderate to high	low
Decreased buffer capacity → oceanic uptake capacity for anthropogenic CO <sub>2</sub>	+	high	high	moderate
Increased stratification → vertical penetration of anthropogenic CO <sub>2</sub>	+	high	nil	moderate
Increased stratification → decreased vertical nutrient supply, stronger utilisation efficiency	-	moderate	moderate	low
Increased (atmospheric, coastal) boundary nutrient fluxes → strength of export production	-	low to moderate	high	low
Carbon over-consumption/DOM-POM conversion → stoichiometry of exported matter	-	unknown, potentially high	high	low
Changed mesopelagic remineralisation stoichiometry → efficiency of the biological pump	unknown	low to moderate	unknown	low
Decreased oxygen saturation → N/P-cycling (e.g., denitrification, anammox)	Unknown	low	high	low
Increased temperature → T-dependency of carbon fixation/respiration balance	+	unknown	unknown	Moderate
Increased seawater acidity → calcification, CaCO <sub>3</sub> dissolution, PIC export	-	low to moderate	high	Moderate
Decreased PIC export → mineral ballast effect on export	+	unknown	unknown	Moderate
Increased harvest of top predators → food web carbon transfer	Unknown	low	unknown	low



9. Changes in the Si:C:N:P stoichiometry of exported matter have a particularly high potential for modifying the carbon cycle in the ocean. These can be brought about by changes both in the stoichiometry of primary production and in subsequent transformations of primary produced organic matter. Related processes that may be sensitive to GCD perturbations are carbon over-consumption, particularly during nutrient-limited phytoplankton growth, the conversion between dissolved and particulate carbon pools (e.g., via aggregation or dissolution), as well as shifts in the composition and productivity of plankton functional groups.
10. The remineralisation stoichiometry of particulate material by the mesopelagic community controls the dissolved macro- and micronutrient ratios in deep-ocean and upwelled waters. Changes in nutrient stoichiometry impact the distribution and productivity of plankton functional types, with possible cascading effects on the pelagic food web. In addition, differential nutrient recycling may act as a feedback on primary producers. The related changes in ecosystem structure and carbon transformations can modify the efficiency of the biological pump.
11. Decreasing oxygen levels in the ocean will directly impact on nutrient-related biogeochemical processes such as denitrification and anammox. This has the potential to drive long-term changes in the oceanic reservoir of bio-available nitrogen. Furthermore, increasing suboxia/anoxia will also impact on the supply of phosphorus and iron from sediments as well as on remineralisation length and time-scales mainly within the mesopelagic zone. Oxygen-driven changes in ecosystem structure and ecological stoichiometry may thereby alter the efficiency of the biological pump, with direct consequences for oceanic carbon sequestration.
12. The temperature dependence of biological activities, commonly expressed by the  $Q_{10}$  factor – the factorial increase in the rate for a 10°C increase in temperature – differs between biological processes. While bacterial heterotrophic activities typically have a  $Q_{10}$  factor between 2 and 3, phytoplankton growth and photosynthesis show only a moderate temperature sensitivity ( $1 < Q_{10} < 2$ ). Based on this simple scheme, global warming may shift the balance between organic matter source and sink terms in the surface ocean, with possible consequences for the balance between new and regenerated production ( $f$ -ratio). On the ecosystem level, however, these processes are influenced by a variety of other factors, including light and substrate availability, as well as interfering biological and biophysical processes with a wide range of temperature sensitivities. Thus, the relative importance of these interacting processes and their individual temperature-sensitivities will determine the overall temperature effect at the ecosystem level.
- 13 and 14. Bio-calcification by marine calcifying organisms is sensitive to CO<sub>2</sub>-related changes in seawater carbonate chemistry (pH, carbonate saturation state). Changes in calcium carbonate precipitation in the plankton are likely to influence the ratio of particulate organic carbon versus inorganic carbon in export matter (rain ratio), with likely consequences for air-sea exchange of CO<sub>2</sub>. Since CaCO<sub>3</sub> is also of primary importance as a ballast mineral accelerating organic carbon flux to the deep ocean, changes in PIC export have the potential to alter the depths of organic matter remineralisation and, hence, the efficiency of the organic carbon pump.
15. Biologically mediated feedbacks based on changes in ecosystem structure and involving trophic interactions are a primary focus of IMBER. Anthropogenic perturbations of food chain carbon transfer mechanisms potentially include the effects of upper trophic level harvesting. Trophic cascade effects could be important in determining the way marine food webs process carbon, and could even determine the ultimate fate of organic materials in the surface ocean.

The broad goals are:

1. Examine the existence, and then direction, of feedbacks between projected changes in forcing and processes transforming carbon in the ocean.
2. Quantify the feedback to the atmospheric CO<sub>2</sub> reservoir (improve estimates of magnitude in Pg C yr<sup>-1</sup>) on decadal and centennial timescale.

In order to address these issues, SOLAS/IMBER suggests natural and purposeful experimentation, including observation of system responses to contemporary (e.g., seasonal, geographic, climate modal) variations in forcing, as well as deliberate perturbations to simulate global change forcings. Modelling lies at the heart of the strategy, not only because improved understanding of processes should be incorporated into models, but also because models can inform the design and interpretation of the experimental and observational studies.

The emphasis of here on experimentation implies a difference in strategy from previous programmes. JGOFS, for example, pioneered the use of ocean time-series sites and process studies as its research tools. These approaches were, however, often applied separately in different regions. We foresee process studies (Approach 1-see below) to be conducted in the geographic and temporal context of longer-term observations. Further, the experimental orientation of this plan includes the use of large-scale, whole-ecosystem manipulation experiments. The design and utility of such experiments is likely to be maximised if relevant data from longer-term observations and process studies of responses to contemporary forcing are available. Therefore, we will consider and promote the coordination and co-location of applications of Approaches 1 (process studies) and 2 (manipulative experiments).

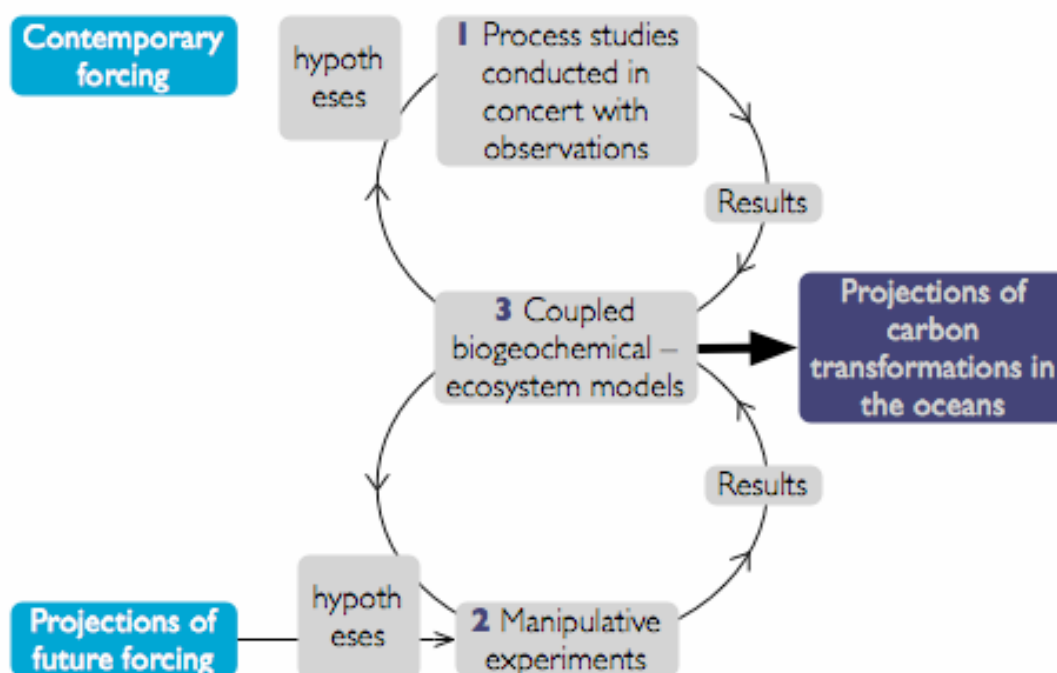
Implementing these goals requires three lines of approach, numbered 1-3 in the Figure 4.

### **3.2.2 – Process studies and observations**

#### **3.2.1 a) *Measurement of biogeochemical and ecosystem changes in the surface ocean from Voluntary Observing Ships (VOS)***

- *Support the collection of surface water biological variables and CO<sub>2</sub> parameters and the development of technology needed to identify plankton functional groups on VOS lines*

VOS lines (Figure 5) offer the opportunity to acquire data on the biological systems that are responsible for the seasonal changes in seawater chemistry. The measurement of such additional biological variables should be added to VOS lines where a comprehensive suite of carbon and nutrient parameters including dissolved and particulate, inorganic and organics phases is being measured. Significant value could be added by equipping selected VOS lines with sensors and/or auto samplers to allow the measurement of additional biological variables and the identification of plankton functional types. The development of such sensors is in its infancy, but some exist and should be installed on selected lines as soon as possible. Among these, fluorometric measurements, including Pulse Amplitude Modulated (PAM) and

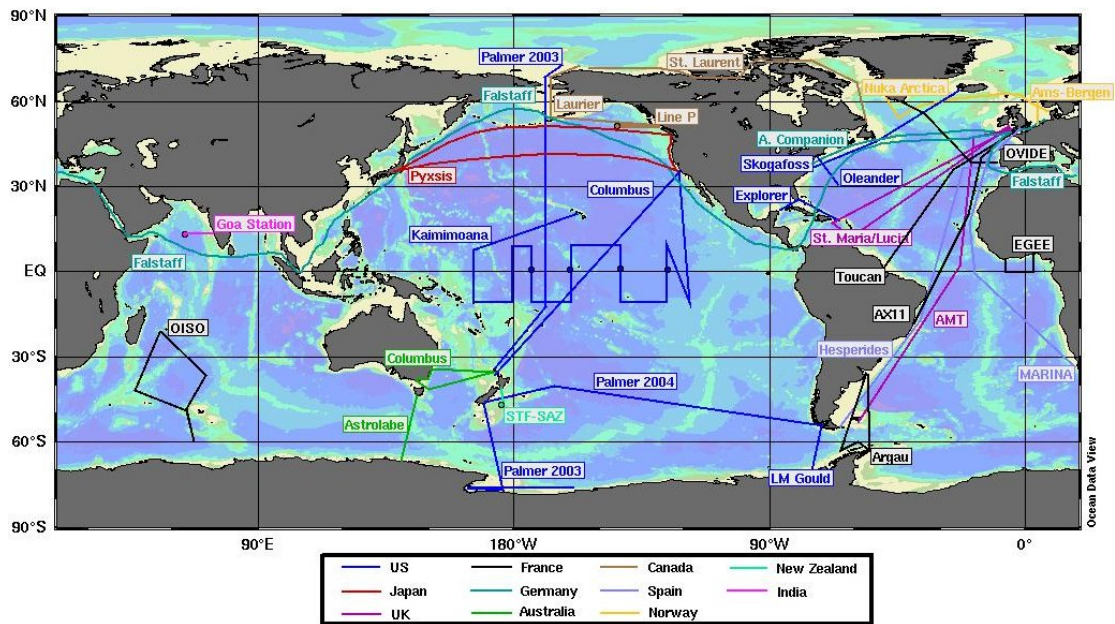


**Figure 4. Diagram showing the implementation approaches required to examine the feedbacks between projected change in forcing and processes transforming the carbon in the ocean.**

Fast Repetition Rate (FRR) fluorometry are ready for use and should be combined with ocean colour remote sensing. Recent progress in automated flow cytometry also offers exciting possibilities. Until the technology for a range of automated bio-sensors becomes available, discrete samples should be taken and analysed in laboratories or stored for future work. Some VOS lines are XBT-lines and some provide ADCP measurements, which can give information on changes in the mixed layer depth over time. This approach should add value in terms of providing a comparison to the output of coupled biogeochemistry-ecosystem models and in validating biological information gained from remote sensing.

- *Develop the use of back trajectory analysis hindcast model simulations reanalysis, etc. and incorporate it into the timing and location of process-oriented measurement campaigns*

The ability to perform back trajectory analysis of water masses would allow the utilisation of the 'natural laboratory' of surface waters with different histories. It would also allow investigation into the effects of water preconditioning on the development and succession of pelagic systems. Combined with biogeochemical and biological measurements on VOS lines, this would form the basis for integrated field campaigns allowing extended temporal coverage and a direct comparison of water masses of different preconditioning.



**Figure 5 Global map of existing and planned near-surface pCO<sub>2</sub> measurements. Labels indicate ship name or project title. Source: IOCCP**

### 3.2.1 b) Co-located time-series and perturbation experiments

- *Presently operational time-series should be maintained/improved and extended by conducting perturbation experiments at nearby locations*

vast data sets obtained include highly resolved seasonal cycles and their interannual Open ocean and continental margin time-series/process studies extend observations beyond ship surveys. The few long-term time-series sites (e.g., BATS, HOT) have provided an incredible wealth of information. Products and insights gained from the

variability for a whole suite of biogeochemical parameters. Time-series are best suited for providing detailed system and process understanding in a one-dimensional picture. Spatial extrapolation of this information remains a major challenge and needs to be informed by other types of data. Therefore time-series sites should be nested in a spatial observing network that comprises the following components:

- A series of repeated ocean transects such as reoccupation of selected meridional and/or zonal WOCE lines;
  - Occasional intense process studies are required to supply relevant biological and chemical information and to ground-truth sensor data.
  - A network of 'Voluntary Observing Ships' (see 3.2.1.a);
  - Surveys of selected biogeochemical properties (e.g., oxygen, PIC, DIC, POC/DOC, PON/DON) from profiling floats ;
  - Remote sensing support to place sites in a larger spatial context (circulation patterns, bio-optical domains, proximal drivers).
- *Sustained observations should be extended to biogeochemical provinces that are predicted to be most sensitive to global change and these locations should also be used to perform manipulative experiments*

The extremely successful long-term time-series approach needs to be expanded to other biogeochemical provinces, and in the context of this activity, to those that play a large role in carbon export (e.g., temperate regions) or are expected to be highly susceptible to global change (e.g., eastern tropical oceans with oxygen minimum zones) or ocean acidification (e.g., polar and sub-polar surface waters). We plan to take this a step further by using the context provided by sustained observations to conduct manipulative experiments. The scientific strategy will be:

- Identify sites sensitive to global change using prognostic climate models and historical data.
- Establish background measurement systems that can resolve seasonal cycles of basic physical and biogeochemical parameters for at least a few years (using VOS lines and autonomous measurements systems).
- Conduct manipulative experiments (see below) at these locations and in the context of the ongoing data collection.

Ecosystem and hydrologic conditions in the overlying surface zone will control rates of processes in the underlying mesopelagic. Conversely, if there is a change in remineralisation in the mesopelagic, this will impact surface water nutrient concentrations and comparative analysis of systems is necessary to understand the differences in the systems. Emphasis should be on incorporating new technologies for understanding ecological and biogeochemical processes. Work at the selected sites should be expended to include co-located perturbation experiments and should also be linked to basin-wide hydrographic transects, in collaboration with CLIVAR and GEOTRACES.

### **3.2.1 c) Observing natural perturbations**

We encourage the creative use of natural perturbations to examine carbon transformations in the ocean and atmosphere. Natural variability throughout the ocean-atmosphere system provides unique opportunities to observe the effect of physical, chemical and ecological forcing on carbon transformations and feedback to atmospheric CO<sub>2</sub>. Island effects, in particular, provide variable physical and chemical drivers that establish downstream conditions with distinct deep-ocean and atmospheric exchange dynamics, supporting variable ecosystems:

- Cyclonic and anticyclonic eddies develop as the western boundary current interacts with islands in the North Atlantic. These create stable and distinct chemical/physical oceanic environments in potential high dust deposition areas.
- Iron fuelled productivity/CO<sub>2</sub> fixation downstream, e.g., from the Galapagos Islands, Crozet, South Georgia, varies with ENSO strength.
- Ice melt in high latitude spring provides a pulse of freshwater and nutrients that can drive unique and transient ecosystems and biogeochemical processes.
- Seasonal upwelling and terrestrial runoff during high and low-flow regimes can provide natural drivers for examination of carbon transformations.

### **3.2.3 – Manipulative experiments**

Effects of future forcing can be studied in manipulative experiments ranging from:

- Laboratory-based single-species experiments in batch or chemostat cultures;
- Mesocosm experiments with natural communities under laboratory-controlled or field conditions;
- *In situ* experiments in the open ocean or in enclosed water masses.

Manipulative experiments are well suited to examine species, population, and ecosystem responses to:

- Rising CO<sub>2</sub> (changing pH, CO<sub>2</sub>(aq), carbonate saturation state);
- Increasing surface water temperature;
- Changes in nutrient concentrations/ratios;
- Changes in mixed layer light availability.

Effects of CO<sub>2</sub>-related changes in carbonate chemistry can be addressed in all of the manipulative experiments listed above. For an integrated understanding of the ecosystem response there is a particular need for manipulative experiments on the community level, which can be achieved in both mesocosm and open ocean *in situ* experiments. Regardless of the size and location of a manipulative experiment a high quality standard including control experiments and replication should be maintained (see 3.2.2.c),

### **3.2.3 a) Technological improvements for open ocean manipulative experiments including open ocean mesocosms**

The scale and design of traditional laboratory-culture and mesocosm experiments do not allow full representation of whole plankton communities and have restricted their use to coastal applications. In order to conduct manipulative experiments with whole pelagic communities in various oceanographic settings, new mesocosm facilities are needed. The design not only needs to survive the physical conditions encountered in the open ocean but should also allow replication as well as easy deployment and recovery. Furthermore the design should provide opportunities for installation of sensors. Important questions that need to be considered:

What is the optimal size of the facility for the plankton community considered?

Should enclosures cover full mixed layer depths?

Should enclosures allow vertical in/out-migration of zooplankton?

Possible applications of such new facilities include

- pH/CO<sub>2</sub> perturbations,
- Macronutrient and/or trace element enrichments,
- Nutrient stoichiometry experiments,
- Dust additions,
- Temperature perturbations,
- Zooplankton exclusions.

Manipulative experiments related to increasing surface ocean temperatures can be done under laboratory-controlled conditions and in small to medium scale mesocosm experiments. While temperature effects have been studied extensively on individual marine organisms, information on the effect of global warming on mixed populations comprising both auto- and heterotrophic components and natural communities is still scarce. Community level experiments should therefore be the focus of future experiments.

Manipulating the degree of stratification and mixed layer depth at realistic scales is difficult with existing technology. Therefore, the development of new mesocosm facilities should also aim at including manipulation of these properties.

### ***3.2.3 b) Manipulative experiments examining the interactions between multiple variables***

Understanding the effects of individual variables like CO<sub>2</sub>, temperature, nutrients, trace metals and top-down controls on the ocean carbon cycle should be a first priority. However, it is important to realise that, multiple variables may interact synergistically or antagonistically to drive food webs and biogeochemical cycles in directions which are hard to predict. For instance, sea surface warming could increase the growth rates of calcifying algae, while rising pCO<sub>2</sub> could simultaneously reduce calcification rates. Predicting the net outcome of these types of multiple variable interactions is presently difficult, if not impossible, and will require the design of realistic multivariate manipulative experiments. For purely logistical reasons, such experiments are best performed on enclosed meso- or microcosm scales.

### ***3.2.3 c) Workshop on guidelines for comparability and quality standards for mesocosm experiments***

A set of guidelines analogous to the terrestrial FACE (Free-Air-CO<sub>2</sub>-Enrichment Study) experiments should be established which should provide recommendations on mesocosm design and manipulation and should define minimum requirements in terms of replication, controls, core parameters and measurement precision. We support the development of a workshop for the SOLAS/IMBER community to discuss these guidelines.

### ***3.2.3 d) Planning group for mesoscale open ocean CO<sub>2</sub> enrichment experiment***

We will explore the options for mesoscale open ocean CO<sub>2</sub> enrichment experiments to allow whole-ecosystem manipulations on adequate space and times scales. Such ambitious experiments should build on the information to be gained from open ocean mesocosm experiments. They will be planned jointly by IMBER and SOLAS to make sure that the necessary expertise to trace the propagation of signals into the deeper ocean and the atmosphere is provided.

Results from manipulative experiments should directly feed into integrated ecosystem biogeochemical models (3.2.4) which, in turn, will help to guide open ocean experiments.

## **3.2.4 – Development and application of novel biological and chemical methods**

### **3.2.4 a) Autonomous measurement systems and observational approaches for time-series observations**

We will encourage the technical development of sensors and autonomous measurement systems as well as the improvement of observational approaches (e.g., mooring technology) suitable for establishing time-series in the ocean. Where possible, the sustained observations at these sites should rely on sensors and automated equipment that can be installed on long-term moorings. Presently, this approach is limited by two factors that require technological improvements:

**Sensors and autonomous measurement systems:** The lack of biogeochemical sensors and autonomous measurement systems that meet the extremely demanding requirements of reliable long-term deployment in the marine environment is striking. While new approaches are in sight and encouraging developments have been made with regard for example to CO<sub>2</sub> (pCO<sub>2</sub> sensor), O<sub>2</sub> (oxygen optode), nitrate (UV-based optical system), and PIC/POC sensors, major technological improvements are still required and should be given high priority.

**Mooring technology:** Present mooring technology does not allow deployment of sensors and measurement systems at very shallow mixed layer depths, where most of the GCD changes will take place. In high latitude oceans this is due to extreme dynamic forces which prohibit the use of large surface buoys. In such environments measurements are made from sub-surface floats which typically sit at a few tens of meters depth and also submerge to great depths for several days (e.g., >1000 m in Labrador Sea) during wintertime baroclinic events. At low latitudes, where dynamic forces do not pose major obstacles, biofouling and sometimes vandalism complicate the use of surface buoys and instruments at shallow depths. New approaches in mooring technology are therefore urgently needed. The profiling surface element will serve as a versatile sensor platform and provide a bi-directional satellite telemetry link. Its design is not trivial and needs to take into account the following aspects: a) permit reliable data transmission even in rough seas and/or in strong surface currents, b) allow easy exchange of sensors and measurement systems in a payload bay with well-defined standards for interfaces, power supply, data formats, etc., c) develop intelligent algorithms or devices to avoid profiling during adverse situations (storms, ice cover, etc.) and hence prevent damage and loss of instruments.

### **3.2.4 b) Chemical and biological tools for non-manipulative interrogation of organisms, communities, and ecosystems**

New biological and chemical approaches that can be applied in both approaches – process studies and observations as well as manipulative experiments – are now becoming available that allow non-manipulative interrogation of individual organisms, mixed communities, and whole ecosystems. For example, sensitive molecular biological methods can detect the presence and expression of genes that are regulated by the availability of nutrients or trace metals, or by ambient conditions of temperature and pCO<sub>2</sub>. Another example that offers a synoptic view of important biological parameters is the combination of cell-level taxonomic and functional group probes with shipboard flow cytometry.

Many new chemical methods are also becoming available. For instance, membrane inlet mass spectrometry opens the possibility of near real-time shipboard measurements of critical biogeochemical species such as CO<sub>2</sub>, O<sub>2</sub>, and DMS. These new biological and



chemical methods will be applied in both observational and manipulative studies, and promise novel insights into the processes that control ocean carbon cycling.

Quantifying metabolic rates of microbes and biogeochemical fluxes in the dark ocean is still a challenge; technological developments designed to more accurately determine these rates are required. Particular effort must be placed on addressing direct respiration measurements in the deep ocean by using different biological and biogeochemical approaches. Since respiration integrates many aspects of the functioning of the marine ecosystem, long-term shifts in respiration may provide an early warning system for global change. Time-series observations developed for investigation of the mesopelagic zone will need to employ emerging biological, chemical, optical/video and acoustic sensors. Analytical techniques must be developed to advance our ability to determine the changing composition of DOM. Sensors are needed to determine bulk DOM concentrations, and/or its components.

There is a large uncertainty in the activity levels of deep water microbes. Commonly, deep water microbial activity is measured under sea surface pressure conditions. Based on these measurements, microbial activity in deep waters (and their remineralisation rates) is higher than might be expected. This apparent imbalance points to the fact that metabolic rate measurements are stimulated upon decompression, or that lateral inputs of organic matter can contribute. The general scarcity of biogeochemical and biological rate measurements under *in situ* pressure indicates the urgent need for reliable methods to determine these rates under realistic conditions. A combination of molecular approaches should be used to elucidate the phylogeny and the metabolic potential of deep-water microbes. These approaches should be combined with single cell analysis to establish phylogenetic-functional relationships of specific deep-water microbes. Compound-specific stable isotope analyses combined with cell-sorting approaches might reveal new insights into the metabolic capacity of specific prokaryotes. The role of planktonic Archaea in deep water biogeochemical cycles needs to be elucidated since their functional role remains enigmatic, despite the fact that they dominate the prokaryotic biomass in the deep ocean.

### **3.2.5 – Coupled biogeochemical-ecosystem modelling**

- *Process models*

Process models represent tools for interpretation and critical evaluation of experimental results such as from mesocosm and open ocean manipulation experiments. They should be developed in close consultation with experimentalists.

- *Global ocean biogeochemistry models*

Global carbon models of the type used to project future ocean transformations include full carbon chemistry, physical transport and validated parameterisations of marine ecosystem fluxes. Current models represent few of the important feedback processes highlighted in this section.

#### **3.2.5 a) Better representation of physical processes in global carbon models**

Changes in physical transport need to be better quantified, especially at high latitudes where large-scale oceanic stratification and reduction in the overturning circulation are projected to occur. Climate models indicate that changes in both of these processes will reduce the vertical exchange between surface and intermediate/deep waters in the

future. A reduction in vertical exchange would reduce the out-gassing of deep waters rich in carbon, but it would slow down the penetration of anthropogenic carbon from the surface to the deep ocean. The net effect is not well quantified, and depends on the intensity and location of the physical changes, and on their additional impacts (i.e., associated changes in ice extent or light and nutrient supply).

Models currently tie changes in marine ecosystems very closely to changes in ocean physics. The tight link between physics and ecosystems needs to be relaxed by including a better representation of ecosystem dynamics and related processes. Efforts should be made to parameterise as independently as possible the different processes leading to export of organic matter, in particular primary production by phytoplankton, grazing, particle aggregation and sinking, and remineralisation. Furthermore, results from process studies, observations and manipulative experiments should be used to identify the conditions that can cause shifts in ecosystems, potentially leading to changes in surface fluxes.

### ***3.2.5 b) Better representation of ecosystem dynamics including the mesopelagic in global carbon models***

Most ecosystem models used in the coupled physical-ocean carbon cycle simulations to date are relatively simplistic and often include only one limiting nutrient element (generally nitrogen), one phytoplankton class, and one zooplankton class. In addition, the cycles of the different elements are tightly coupled to each other through fixed stoichiometric ratios. Finally, processes in the mesopelagic are nearly always parameterised. That is remineralisation of organic matter, and dissolution of  $\text{CaCO}_3$  and opal are often modeled using fixed remineralisation curves that are independent of the environmental conditions. Models that include multiple nutrient element limitation, multiple phytoplankton functional groups, and explicit modeling of mesopelagic processes have been developed in the last 5 to 10 years, but their implementation into three-dimensional ocean physical models has been relatively slow. This process needs to be accelerated, permitting the study of the coupling of ocean physical and biogeochemical/ecological processes and how they respond to perturbation in much greater detail. A diversity of approaches and models is imperative, as it is currently not clear what level of complexity and detail are needed to capture the leading order ecosystem processes of relevance for the long-term ocean-atmosphere carbon balance. Active, two-way exchange between the process studies, laboratory experiments and other observationally based studies and the model development and application programmes need to be insured, so that the insights from both approaches can be shared and inform the respective research directions. Current research on the role of iron is a good example, as our understanding of iron chemistry and the formulation of questions is currently driven by models of marine iron chemistry as well as by experimental and observational data.

### ***3.2.5 c) Representation of continental margins exchanges in global carbon models***


Global carbon models should strive to include a realistic representation of the coastal ocean fluxes. Processes in the coastal ocean are difficult to parameterise because of the high resolution required and because of the difficulty of representing physical processes accurately. However, coastal areas are very active and sensitive to anthropogenic changes, in particular to changes in nutrient supply by rivers and atmospheric deposition and to warming. Possible approaches include, but are not limited to, embedded grids, super-parameterisations (i.e., reduced-order grids inside normal grids), and explicit resolution of the relevant processes.

### **3.2.5 d) Closer dialogue between observationalists and modellers for model evaluation and experiment design**

Global carbon models can be used to quantify the potential impact of changes in physical and biological processes on air-sea fluxes. However, models need to be evaluated for their capacity to reproduce observations and experiments that test the response of the models to changes in the underlying processes. Iron fertilisation and mesocosm experiments provide such evaluation data. In a complementary way models are needed for optimising the design of laboratory, mesocosm and full field experiments.

### **3.2.5 e) Development of Earth System Models**

The quantitative determination of the sign and magnitude of the potential feedbacks between the physical climate system and the global carbon cycle requires fully coupled models; i.e., physical climate models that include a fully prognostic description of the carbon cycle on land and in the ocean. The current generation of carbon cycle models in such whole earth models is rather crude, since they include only a limited subset of feedbacks. As a result, these model results need to be viewed cautiously. The ultimate goal should be a transfer of information gained on global change driven reactions of the natural marine carbon reservoir into the whole earth models. Only at this level of full coupling of all rapidly exchanging reservoirs and their feedback characteristics are robust and reliable future predictions possible. Again, the validation of models against data and knowledge acquired within IGBP projects is of central interest.



## Activity 3.3 – Air-Sea Flux of N<sub>2</sub>O and CH<sub>4</sub>

### IMBER Theme 3 Issue 3.2 – Ecosystem Feedback on Ocean Physics and Climate

#### 3.3.1 – Introduction

One molecule of N<sub>2</sub>O has up to 300 times the greenhouse warming potential of CO<sub>2</sub> on a 100 years time horizon. Globally and annually, the oceans add around 3 million tons of N<sub>2</sub>O-nitrogen to the atmosphere, or one third of the total flux. However, this estimate does not take into account N<sub>2</sub>O emissions from coastal areas. Global estimates, explicitly including N<sub>2</sub>O coastal emissions such as those from estuaries, suggest that the oceanic emissions have to be revised upwards by at least a factor of 2 (Bange, in press). Much of the N<sub>2</sub>O in the ocean arises from microbial activity in low oxygen environments (i.e., suboxic conditions) and in sinking particles. In oxygenated waters, nitrification is the main source of N<sub>2</sub>O, but the yield of N<sub>2</sub>O during nitrification increases markedly as oxygen concentrations approach zero. Under suboxic conditions, denitrification is enhanced and produces and consumes N<sub>2</sub>O. During the “spin-up” of denitrification there is net production and in the core of oceanic suboxic zones there is net N<sub>2</sub>O consumption. These factors can combine to produce very strong gradients at the temporal and spatial boundaries of suboxic regions where production can be enhanced by both nitrification at low oxygen concentrations and the early stages of denitrification. Oceanic N<sub>2</sub>O production arises from denitrification in marine sediments as well, particularly in nutrient rich areas such as estuaries and hemipelagic regions, and in the growing regions of suboxia in the water column, although net production (or release from sediments) may be low.

Methane (CH<sub>4</sub>) is the second most important anthropogenic greenhouse gas, after the primary greenhouse gas CO<sub>2</sub> (excluding H<sub>2</sub>O vapour). Estuaries and coastal waters are responsible for about 75% of the total oceanic CH<sub>4</sub> emissions. CH<sub>4</sub> release from gas seeps and through mud volcanoes (i.e., geological CH<sub>4</sub> sources) in shallow coastal environments have been recently identified as potentially significant global sources of atmospheric CH<sub>4</sub> (e.g., Etiope and Milkov, 2004). However, due to inadequate data coverage, the contribution from geological sources is highly uncertain. Moreover, the significance of CH<sub>4</sub> release to the atmosphere by the decomposition of CH<sub>4</sub> hydrates due to the ongoing global warming is essentially unknown.

#### 3.3.2 – Determine the contribution of marine emissions to the global N<sub>2</sub>O and CH<sub>4</sub> budgets

##### 3.3.2 a) *Open ocean surface and air measurements of N<sub>2</sub>O and CH<sub>4</sub>*

To achieve this first goal measurements of surface N<sub>2</sub>O and CH<sub>4</sub> and marine boundary layer N<sub>2</sub>O and CH<sub>4</sub> have to be made with adequate spatial and temporal coverage. This requires development of robust, autonomous, low maintenance and accurate surface and atmospheric measurement approaches of these gases.

In order to constrain the emissions of N<sub>2</sub>O from the oceans it is essential to make repeated underway measurements along fixed lines. This can be done along selected lines being occupied for the pCO<sub>2</sub> measurements (see Activity 3.1), though specific lines through regions of elevated N<sub>2</sub>O production (eastern South Pacific, Arabian Sea including the West Indian Shelf) must be added. Measurements should be performed on

a monthly time-scale. The required accuracy should be better than  $\pm 1$  ppb. Calibration gases, traceable to Scripps Institution of Oceanography (SIO) or NOAA standards, have to be utilised to ensure comparability of the measurements. In order to improve the existing technology for underway surface measurements, SOLAS/IMBER should support the development of autonomous  $N_2O$  and  $CH_4$  instruments, which can be used as measurement platforms on commercial ships (see Activity 3.1).

### **3.3.2 b) Enhanced measurement programmes of $N_2O$ and $CH_4$ in coastal areas, particularly as components of coastal observing systems**

$N_2O$  and  $CH_4$  emissions from coastal areas contribute significantly to the overall oceanic emissions (e.g., Pacyna et al., 2004). However, the release of  $N_2O$  from coastal areas such as upwelling regions (e.g., Arabian Sea, eastern tropical Pacific, West African coasts) and continental shelf areas with seasonally occurring suboxic/anoxic conditions (e.g., Gulf of Mexico, West Indian Shelf, Southwest Africa) are poorly constrained due to lack of measurements. Underway surface measurement surveys, preferably along representative coast-perpendicular transects, should be repeated on a seasonal basis.

$CH_4$  and  $N_2O$  emissions from coastal wetlands (e.g., tropical mangrove ecosystems) are probably important but hitherto poorly quantified terms in the oceanic  $CH_4$  and  $N_2O$  budgets. There is increasing evidence that anthropogenic-induced changes such as enhanced eutrophication in coastal wetlands will lead to an increase of  $CH_4$  and  $N_2O$  production and subsequent release to the atmosphere (Kreuzwieser et al., 2003; Purvaja and Ramesh, 2001). Direct measurements of  $CH_4$  and  $N_2O$  fluxes are possible in the wetland systems, and should be made in adequate numbers and in different areas so as to get reliable estimates of the flux from these ecosystems.

### **3.3.2 c) Validate $N_2O$ and $CH_4$ measurements by remote sensing**

It is now possible to determine the  $N_2O$  and  $CH_4$  mixing ratios in the troposphere with the SCIAMACHY (SCanning Imaging Absorption SpectroMeter for Atmospheric CHartography) instrument on the European Research Satellite ENVISAT (Frankenberg et al., 2005). However, SCIAMACHY has a low signal-to-noise ratio over the oceans. Validation of the satellite data is required through high precision ( $< \pm 0.5\%$ ) and accurate measurements of  $N_2O$  and  $CH_4$  in the marine boundary layer during ship campaigns in areas which coincide/overlap with the satellite measurements.

### **3.3.3 – Improve understanding of factors regulating surface concentrations of $N_2O$ and $CH_4$ , including assessment of sensitivity of marine sources of these gases to climate change and anthropogenic riverine input**

The surface concentrations of both gases depends on: a) the relative rates of production and loss processes in the water column and sediments as well as b) transport processes that connect sites of production with the surface ocean and the air-sea interface.

#### **3.3.3 a) Determine the degree to which the globally extensive oxygen minimum zones are sources of $N_2O$ to the atmosphere**

The production and loss rates for  $N_2O$  are non-linearly dependent on oxygen concentrations. This oxygen sensitivity depends on the nature of the processes, and the abundance and activity of the microorganisms and enzymes involved. Hence, climate variation and altered riverine inputs are likely to affect  $N_2O$  production and loss in the

future via alteration of oceanic and coastal oxygen levels as well as alteration of the input or production rate of 'precursor' nitrogen species (Codispoti et al., 2001). With decreasing oxygen concentrations, N<sub>2</sub>O yield can increase dramatically; however, an uncertain threshold exists where net production rapidly switches over to net metabolism. Because the oxygen sensitivity is strongly non-linear, the mean surface saturation is sensitive to transient changes and variability of oxygen as well as the mean state.

### **3.3.3 b) Measurements of N<sub>2</sub>O and CH<sub>4</sub> relevant biogeochemical variables controlling sources and sinks (oxygen, nutrients) in the water column near regions of production and consumption**

The role of benthic nitrogen and carbon transformations in N<sub>2</sub>O and CH<sub>4</sub> cycling is still not fully understood as the sediments may variably serve either as net source (for N<sub>2</sub>O and CH<sub>4</sub>) or a net sink of N<sub>2</sub>O for the overlying water column. The sediment-water exchange is most important in shallow waters where the mixed layer extends to the seafloor and where sedimentary N<sub>2</sub>O and CH<sub>4</sub> production is linked directly to the sea-to-air flux. Presently, it is not known how ongoing anthropogenic nitrogen loading in coastal waters is affecting benthic transformations involving N<sub>2</sub>O and CH<sub>4</sub>. Field and experimental studies including the deployment of benthic chambers should be carried out, in various environments, for addressing this important issue.

### **3.3.3 c) Determination of impacts of changing inputs of nutrients and organics (e.g., rivers) on sources and sinks of N<sub>2</sub>O and CH<sub>4</sub>**

Prediction of future N<sub>2</sub>O and CH<sub>4</sub> saturation changes requires further research into production processes and metabolism, including experimental and field studies of N<sub>2</sub>O and CH<sub>4</sub> yields as a function of dissolved oxygen concentration. This research should be combined with a detailed characterisation of the microbial communities involved.

### **3.3.3 d) Molecular techniques (e.g., probes, genomics, proteomics)**

Use of molecular probes will help in identifying the role of specific organisms in the cycling of N<sub>2</sub>O (Jayakumar et al., 2004). The possible regulatory effects of trace metals (such as copper) in the activity of the enzymes involved in the production and consumption (such as N<sub>2</sub>O reductase) should also be investigated (Granger and Ward, 2003). In addition to the field-based process studies, controlled laboratory and mesocosm experiments should be used to evaluate the influence of specific environmental factors (e.g., dissolved oxygen levels) on rates of N<sub>2</sub>O and CH<sub>4</sub> production and degradation.

### **3.3.3 e) Isotopic composition studies to provide insight on production pathways**

Isotopic data (<sup>15</sup>N, <sup>18</sup>O and <sup>13</sup>C) can provide insight into production pathways of N<sub>2</sub>O and CH<sub>4</sub>. Both natural isotope abundance studies as well as experimental work using stable isotopes should be undertaken for this purpose, though fractionation factors need to be well characterised. The position of <sup>15</sup>N in the linear N<sub>2</sub>O molecule can provide additional information on production mechanisms and this approach should be used whenever possible. The measurement and interpretation of natural isotopic composition is non-trivial however, and there is a need for additional basic experimental characterisation of fractionation factors and for internationally agreed-upon reference materials and inter-calibration of stable isotope measurement techniques.

Oceanic CH<sub>4</sub> is formed by methanogens operating within ocean and coastal sediments. However, in contrast to N<sub>2</sub>O, oceanic pathways of CH<sub>4</sub> are strongly modulated by consumption processes such as aerobic and anaerobic oxidation, which occur in the water column as well as in the sediments.

### **3.3.3 f) Microbial kinetics of N<sub>2</sub>O and CH<sub>4</sub> production and consumption**

Vast quantities of CH<sub>4</sub> are produced in oceanic sediments. It is therefore important to determine the microbial consumption kinetics for CH<sub>4</sub> in order to be able to evaluate how much of the gas released from the sediments at various depths in the oceans and coastal systems is able to escape to the atmosphere and hence affect climate. Recent studies have shown that the sediment and water column act as an effective 'biological filter' in which released CH<sub>4</sub> is partially or totally consumed by oxidising bacteria prior to reaching the air-sea interface. Even very large sub-surface releases (such as found in the Black Sea) appear to be effectively oxidised prior to reaching the mixed-layer and hence the atmosphere (Schmale et al., 2005). However, in shallow coastal environments, such as estuaries, the 'biological filter' for CH<sub>4</sub> seems to be weak, resulting in a comparable high flux of CH<sub>4</sub> from the sediments to the atmosphere (Pacyna et al., 2004).

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## ACRONYMS

ADCP	Acoustic Doppler Current Profiler
AIMES	Analysis Integration and Modelling of the Earth System
AOU	Apparent Oxygen Utilisation
Argo	drifting profiling floats that will measure the temperature and salinity of the upper 2000 m of the ocean.
BATS	Bermuda Atlantic Time-series Study
CCL <sub>4</sub>	Carbon Chloride
CFC	ChloroFluoroCarbone
CLIVAR	Climate variability and predictability research programme
COOP	CLIVAR Ocean Observations Panel
DIC	Dissolved Inorganic Carbon
DMS	Dimethylsulphide
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DON	Dissolved Organic Nitrogen
DyFAMed	Dynamique des flux de matière en Méditerranée
ENSO	El Niño- Southern Oscillation
ENVISAT	ENVironmental SATellite
ESTOC	European Station for Time-series in the Ocean, Canary Islands
FACE	Free-Air-CO <sub>2</sub> -Enrichment study
FRR	Fast Repetition Rate
GCD	Global Change Driven
GCP	Global Carbon Project
GEO	Global Eulerian Observatories
GEOTRACES	Global marine biogeochemical cycles of trace elements and their isotopes
GHG	Greenhouse Gases
GODAE	Global Ocean Data Assimilation Experiment
HCFC	Hydrochlorofluorocarbon
HNLC	High- Nutrient, Low- Chlorophyll
HOT	Hawaii Ocean Time-series
IGBP	International Geosphere-Biosphere Programme
IOC	Intergovernmental Oceanographic Commission
IPCC	Intergovernmental panel on climate change
IMBER	Integrated Marine Biogeochemistry and Ecosystems Research
JGOFS	Joint Global Ocean Flux Study

KNOT	Kyodo North Pacific Ocean time-series
LOICZ	Land-Ocean Interactions in the Coastal Zone project
LSCOP	Large Scale CO <sub>2</sub> Observing Plan
NAO/AO	North Atlantic (or Arctic) Oscillation
NOAA	National Oceanic and Atmospheric Administration
OceanSITES	Ocean sustained interdisciplinary time-series environment observation system
OOPC	Ocean Observations Panel for Climate
OOSDP	Ocean Observation System Development Panel
OSP/lineP	Ocean station PAPA
OWS	Ocean Weather Ship
PAM	Pulse Amplitude Modulated
PDO	Pacific Decadal Oscillation
PIC	Particulate Inorganic Carbon
PIRATA	Pilot Research moored Array in the Tropical Atlantic
POC	Particulate Organic Carbon
POM	Particulate Organic Matter
PON	Particulate Organic Nitrogen
SCIAMACHY	Scanning imaging absorption spectrometer for atmospheric chartography
SCOR	Scientific Committee for Oceanic Research
SEATS	South East Asia time series station
SF6	Sulfur Hexafluoride
SIO	Scripps Institution of Oceanography
SMBO	Santa Monica Bay observatory
SOLAS	Surface Ocean Lower Atmosphere Studies
SSH	Sea Surface Height
SST	Sea Surface Temperature
SSS	Sea Surface Salinity
TAlk	Total Alkalinity
TAO	Tropical Atmosphere Ocean project
VOS	Volunteer Observing Ship
WMO	World Meteorological Organization
WOCE	World Ocean Circulation Experiment
XBT	Expendable BathyThermograph