

National Oceanography Centre, Southampton

Research and Consultancy Report No. XX

Report of the SNOMS Project 2006 to 2012 (Part 1 – Narrative Description)

SNOMS SWIRE NOCS Ocean Monitoring System

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NOC e-report Data Sheet

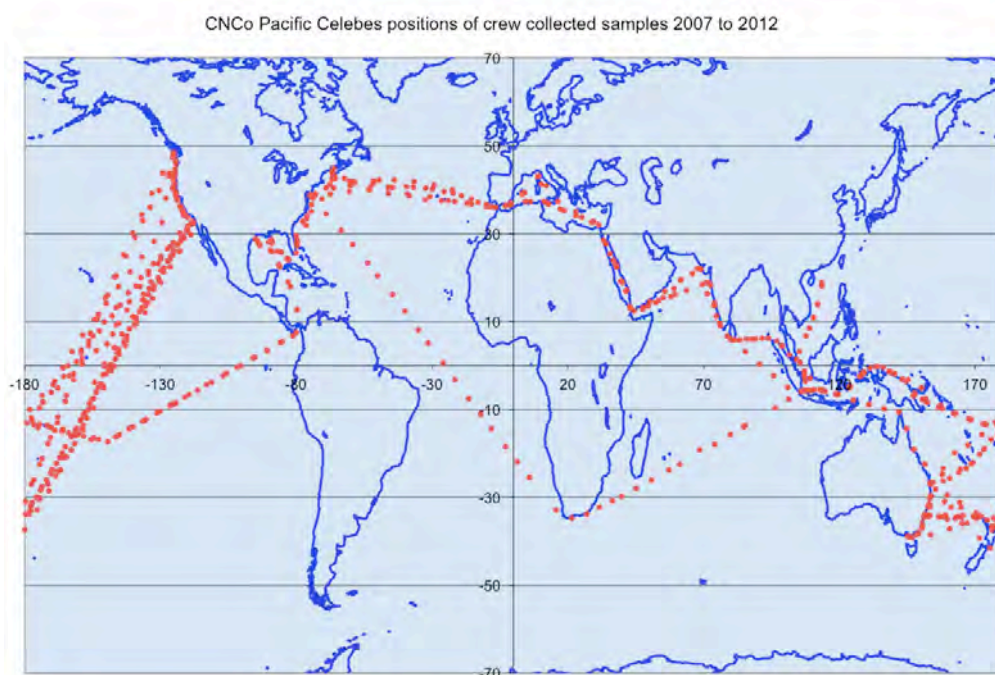
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ABSTRACT <p>The ocean plays a major role in controlling the concentration carbon dioxide (CO₂) in the atmosphere. Increasing concentrations of CO₂ in the atmosphere are a threat to the stability of the earth's climate. A better understanding of the controlling role of the ocean will improve predictions of likely future changes in climate and the impact of the uptake of CO₂ itself on marine eco-systems caused by the associated acidification of the ocean waters. The SNOMS Project (SWIRE NOCS Ocean Monitoring System) is a ground breaking joint research project supported by the Swire Group Trust, the Swire Educational Trust, the China Navigation Company (CNC) and the Natural Environment Research Council. It collects high quality data on concentrations of CO₂ in the surface layer of the ocean. It contributes to the international effort to better quantify (and understand the driving processes controlling) the exchanges of CO₂ between the ocean and the atmosphere.</p> <p>In 2006 and 2007 a system that could be used on a commercial ship to provide data over periods of several months with only limited maintenance by the ships crew was designed and assembled by NOCS. The system was fitted to the CNC ship the <i>MV Pacific Celebes</i> in May 2007. The onboard system was supported by web pages activities that monitored the progress of the ship and the functioning of the data collection system. To support the flow of data from the ship to the archiving of the data at the Carbon Dioxide Information Analysis Center (CDIAC in the USA) data processing procedures were developed for the quality control and systematic handling of the data. Data from samples of seawater collected by the ships crew and analysed in NOC (730 samples) have been used to confirm the consistency of the data from the automated measurement system on the ship.</p> <p>To examine the data collected between 2007 and 2012 the movements of the ship are divided into 16 voyages. Initially The <i>Celebes</i> traded on a route circum-navigating of the globe via the Panama and Suez Canals. In 2009 the route shifted to one between Australia and New Zealand to USA and Canada. Analysis of the data is an on going process. It has demonstrated that the system produces reliable data. Data are capable of improving existing estimates of seasonal variability. The work has improved knowledge of gas exchange processes. Data from the crew-collected-samples are helping improve our ability to estimate alkalinity in different areas. This helps with the study of ocean acidification. Data from the 9 round trips in the Pacific are currently being examined along with data made available by the NOAA-PMEL laboratory forming time series from 2004 to 2012. The data from the Pacific route are of considerable interest. One reason is that the data monitors variations in the fluxes of CO₂ associated with the current that flows westwards along the equator. This is one of the major natural sources of CO₂ from the ocean into the atmosphere.</p>	
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Frontpiece:

An important contribution to the success of the SNOMS project was made by the crews of Pacific Celebes who contributed enthusiastically to helping with installing and maintaining the system and collecting daily waters samples that were analysed back in NOC.



Picture above shows David Hydes training Celebes' engineers in how to collect and preserve the daily water samples. Below are shown the positions of the 730 measured crew-collected samples.



Executive summary

This report documents the activities undertaken in the SNOMS project (SWIRE NOCS Ocean Monitoring System) and the work that is on-going to exploit the scientific information in the data. It covers the period from 2006 to 2012. This report provides an overview of all the activities and progress of the SNOMS project - scientific, technical and outreach. A companion report brings together in one place a full history of the project to date (Hydes et al., 2013). It contains:- (i) maps of routes covered by the *Pacific Celebes*; (ii) documents and agreements between NOC and the Swire Group and Swire Educational Trusts; (iii) technical reports produced by the project; (iv) details of outreach activities; (v) graphical presentations of the data collected; (vi) listing of sensors and their performance.

In 2006 the Swire China Navigation Company (CNCo) made the groundbreaking step of instigating support for this activity. This work is essential if we are to understand the role of the ocean now and in the future in slowing the impact of anthropogenic releases of carbon dioxide (CO₂) on the earth's climate through the so called "green house gas effect". Each year the ocean absorbs a quarter to a third of the carbon dioxide released. To be able to predict how these processes are likely to behave in the future and what their impact on the earth's climate might be we need to better define the scale of this uptake and understand the processes controlling it. At the same time the work provides evidence on the rate at which the absorption of CO₂ is making the ocean more acidic. This increased acidity is a potential threat to the functioning of marine ecosystems.

The SNOMS project has carried out:-

- Design of a measurement system that would work reliably on a CNCo ship (that could only be visited by scientific maintenance staff at intervals of greater than four months - time determined by working route of the ship). Previous systems have required monthly maintenance and often scientists and technicians sailing with their equipment when fitted on commercial vessels.
- Development of that system so that it met the required specification including the development of appropriate maintenance and calibration procedures.
- Display of the project and its data on public access webpages, enabling rapid day to day assessment of the performance of the system.
- Development of systematic data processing procedures required for the quality assurance and quality control of the data generated by the system.
- Maintenance of the system by ship's crews and scientific personnel.
- Collection of water samples to provide calibration of the sensors and extra data on the carbonate chemistry of the water. Analysis of these samples in NOC laboratories.
- Outreach about the system to the scientific community, the public, policy-makers, potential funders (public and private) and to the shipping industry.
- Scientific interpretation of the data collected

The full definition of the physical system followed a visit to the CNCo *Pacific Celebes* in 2006 and the system was installed in Singapore in May 2007. From 2007 to 2009 the *Celebes* operated on a global trade circum-navigating the globe via the Panama and Suez canals. During this period the reliability of the system was progressively improved. A system evolved that was working very reliably by the time the route changed to the Pacific in 2009 and continued to work reliably until the withdrawal of the *Pacific Celebes* from service in March 2012.

Comparison of the data collected on board the ship, comparison with data collected by the NOAA-PMEL laboratory and shore based tests at Dalhousie University all show that data collected by the SNOMS system is reliable to within $\pm 6 \mu\text{atm}$ making it suitable for providing valuable data from large scale surveys and for assessing the scale of seasonal variations in the air-sea exchange of CO₂. An important contribution to this work came from the ships engineers who serviced the system and collected daily water samples. The samples both provide verification of the continuous records of pCO₂ but also information on the variation of alkalinity across the ocean: key information for connecting information on changes in concentrations of CO₂ in the ocean with changes in the acidity of ocean waters.

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Part 11. Technical Annexes published separately as NOC Report No. XX (Hydes et al., 2013)

- A1 Summary of the routes of the 16 SNOMS voyages (5 pp)*
- A2 Compiled NOC Swire Proposals and Contracts (54 pp)*
- A3 Assembled NOC SNOMS Technical Reports (123 pp)*
- A4 Graphical presentations of the SNOMS raw, intermediate and final data sets (143 pp)*
- A5 SNOMS related outreach and communications (81 pp)*
- A6 Instrument performance log*

1. Background

1.1 Introduction to the context of the SNOMS project

The ocean is important. It covers 70% of the Earth's surface; it contains 97% of the biosphere by volume and is a key component of the Earth's climate system. The ocean, the seafloor and the life within it provide food, energy and raw materials. Climate change is the most significant environmental challenge facing humankind. Ocean processes are vital in regulating the Earth's climate system. A significant threat to the stability of the climate is the large inputs to the atmosphere of "green house gasses" released by human activity. The most significant of these is carbon dioxide - CO₂. Each year the ocean absorbs about a quarter to a third of this extra CO₂. This uptake by the ocean is reducing the potential rate of global warming. To predict the future of the Earth's climate it is essential to know if the ocean will continue to act in the same way.

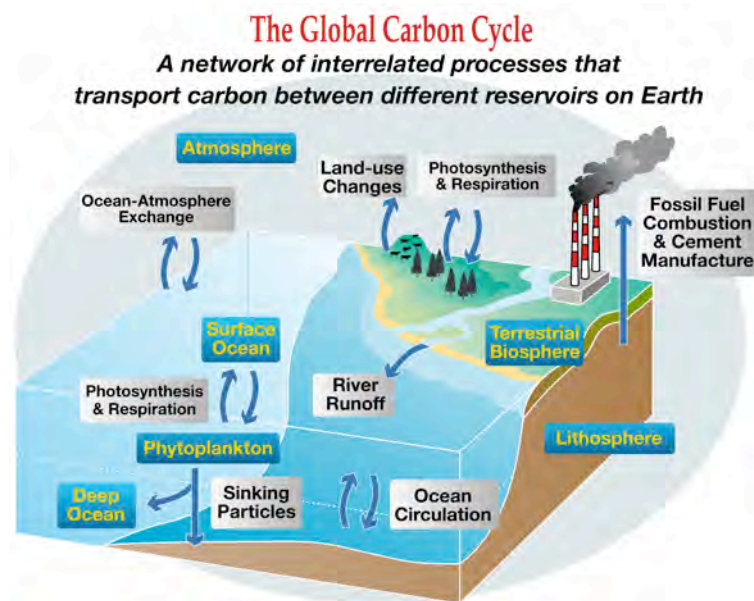


Figure 1.1. Diagram of carbon cycle and the routes of exchanges between the different reservoirs.

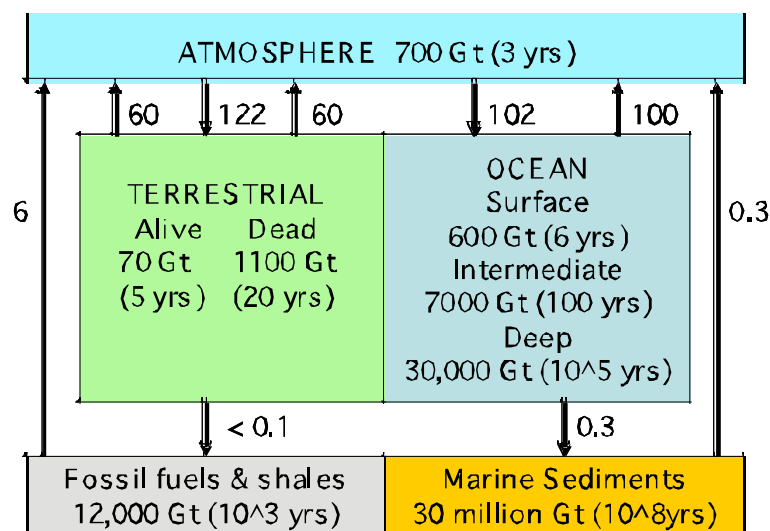


Figure 1.2. Quantified schematic of the carbon reservoirs and the scale and of exchanges between them. We add 6,000,000,000 tonnes (6 Gt) of extra anthropogenic "new" carbon to the atmosphere each year and of this about 2 Gt are "permanently" taken up by the ocean. This occurs as an addition to the natural cycle in which about 100 Gt move between the ocean and atmosphere each year. (Based on Royal Society, 2005 and Holman, 2000).

The interaction of processes that control the ocean's uptake of CO₂ is complex. The scale of processes ranges from those controlling global circulation of ocean water, which takes thousands of years, to biological processes that can halve the concentrations of CO₂ in surface water in a few days. We also know that progressive change in the ocean can be masked by cyclical changes in climate patterns that vary in their impact on scales of a few years to several decades. This presents marine scientists with the challenging task of determining what the important processes are and how they are evolving with time. In addition we need to know how the balance of processes changes from place to place over the globe. There is an additional problem. The annual uptake of CO₂, although it may benefit the climate by reducing the concentration of CO₂ in the atmosphere, it may have deleterious effects on marine ecosystems because the added CO₂ makes the ocean more acidic (Royal Society, 2005).

To meet these challenges we have to regularly visit many places across the ocean. Working with commercial shipping companies, who have a presence second to none spread across the globe, can provide scientists with platforms for collecting the data needed to see how the ocean is reacting with the increased concentrations of greenhouse gases in the atmosphere. This concept of so-called "ships of opportunity" (SOO) has the potential to open up "uncharted" - under-sampled regions in a highly cost-effective manner. Then by combining observations from these ships and from other tools such as satellites (measuring for example temperature and wind speeds) and Argo floats (measuring the depth of the ocean's surface layer) we can greatly extend our ability to quantify the size and the "where" and "how" of the uptake of CO₂ and other greenhouse gases by the ocean. This approach has already proven successful in the North Atlantic. The North Atlantic is the region of the ocean where most CO₂ is absorbed. Work linked through the EU funded CarboOcean project took data from the 9 SOO lines operating in the Atlantic to produce a budget for the CO₂ flux in the North Atlantic, which was reliable to within 10%. The information on pCO₂ being gathered by these ships also contributes to understanding of the acidification of the ocean, particularly where data are available on the alkalinity of the water. This enables the pH of the water to be calculated accurately.

Presently, to get a global picture, data have to be merged from observations made in different ways and in different years to give the balance sheet for an average year. This has been done in the "Takahashi Atlas" (Takahashi et al, 2009). This was a major effort, which took in the then 9 million data points that were available from observations of CO₂ in the surface ocean. Takahashi and his team worked with the data set to make best estimates covering the ocean, region by region, based on a 4 by 5 degree grid, for each month of the year. Coverage in many areas in the oceans is sparse to non-existent in some areas. As more data are accumulated, the effort goes on to improve the assessment. Each new data point adds to our knowledge and provides a test and insight into where the Takahashi team's extrapolations have worked and where they are less good, so that the next version will be more accurate.

The creation of the picture for an average year made by the Takahashi team is a necessary basis for initialising and testing global computer models of CO₂ uptake. These models provide quantitative assessments of the scales of processes and differences between different regions. They calculate how things may change in the future in the light of different emissions scenarios. The Takahashi Atlas itself does not allow us to see the present state of the ocean or to detect temporal change and then understand the causes of this change, similarly present day numerical models of the ocean fail to reproduce much of the variability we know to be present in the ocean. Work in the North Atlantic (a part of the ocean that is relatively rich in data) shows that an average year does not exist and fluxes change from year to year as the "weather" of the ocean changes. Understanding the causes of such change will only be possible through continued and increased in-situ observations of concentrations of CO₂ in the ocean alongside measurements that trace changes in related processes such as deep winter mixing (from Argo floats) and biological production (from satellites measuring ocean colour). Presently even adding one ship to the currently 20 or so commercial ships making continuous observations provides a significant increase in the flow of information. This is one of the reasons why the SNOMS project is important.

The absorption of anthropogenic CO₂ by the oceans has come to be recognised as a two-edged sword. The process is slowing down the rate of accumulation of CO₂ in the atmosphere so reducing the immediate impact of CO₂ on climate. On the other hand as the ocean takes up more CO₂ it is becoming more acidic (Figure 1.3). Recent reports have identified this process of ocean acidification

as a major concern because of its potential effects on marine biogeochemistry and ecosystems and the lack of appropriate information for assessing the risks (e.g. Gattuso & Hansson, 2011; Royal Society *et al.*, 2005). Progressive acidification could be measured directly as a reduction of the pH of a water. But, pH is presently difficult to measure with the accuracy and precision needed to monitor changes in the ocean and consequently an appropriate record of historical change does not exist. The acidity (pH) of water can be calculated if the $p\text{CO}_2$ and alkalinity of the water are known. The ongoing SOO measurements of $p\text{CO}_2$ are now providing an historical record and can be coupled with a knowledge of alkalinity to assess changes in acidity. However, much of the data collected for $p\text{CO}_2$ does not have associated data on alkalinity to go with it. Alkalinity can be estimated from salinity but the limits to which this can be done reliably need to be defined. The SNOMS project has measured alkalinity in the samples collected by the ship's crew. This is an additional reason why the SNOMS project is important - because this information on alkalinity helps to make data on $p\text{CO}_2$ collected by other groups useful for the assessment of ocean acidification.

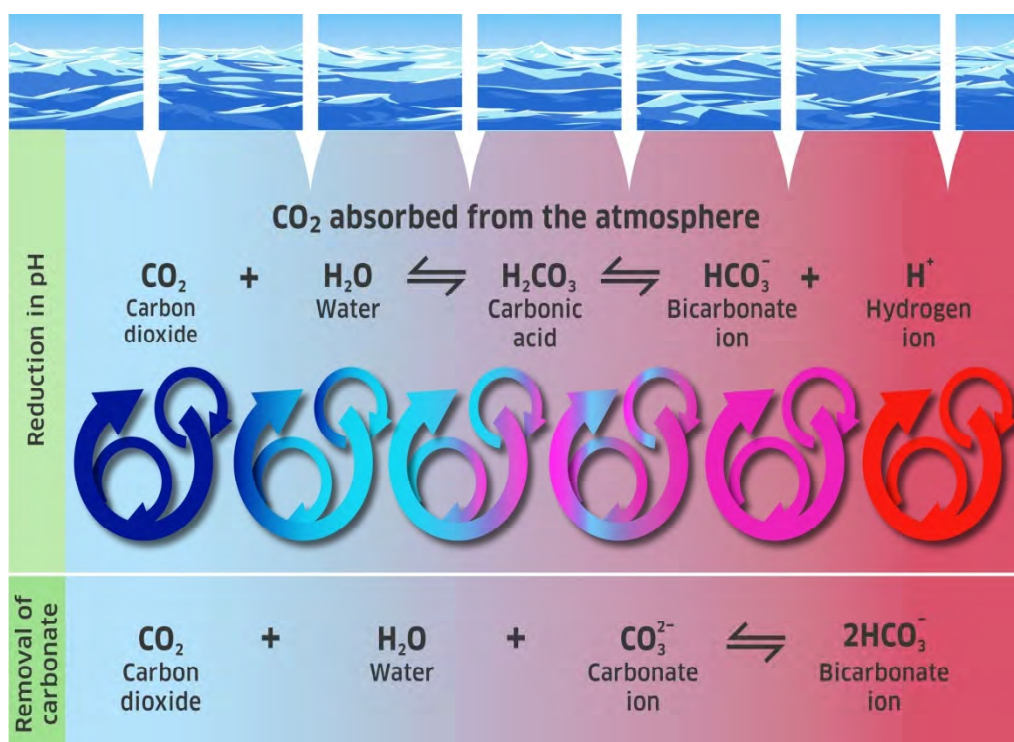


Figure 1.3. Illustration of the chemical equilibrium relationship between the different components of the carbonate system of seawater and the potential impact as a result of atmospheric absorption of CO_2 . This is a “litmus paper diagram” in which the colour changes from blue to red as more CO_2 is absorbed and the carbonate equilibria shift to release more hydrogen ions. (Source of diagram Baxter *et al.*, 2011).

The SNOMS project brought together efforts in NOC and the Swire group. NOC is one of the world's leading centres of oceanographic research. It is at the forefront in developing sensor and communications packages, for installation on a wide range of ocean platforms - including research ships, SOOs, data buoys moored in deepwater, autonomous underwater vehicles and Argo Floats. These developments enable the measurement of key ocean properties to be made at the appropriate time and space scales needed to drive forward oceanographic research. The Swire Group are working globally to mitigate their own impact on the Earth's ecosystem and are supporting organisations working on environmental research. Swire has established itself as an international leader in the effort to protect and enhance the Earth's life support systems.

1.2 Aims of the SNOMS project

Initial aims:-

- Develop a robust system for use on a Swire ship:-
 - Design and build a system that can be operated reliably for periods greater than 3 months with minimal servicing to be provided by the ship's crew.
 - Train the ship's crew in operation of the system and its maintenance.
 - Establish the necessary operating procedures for use on the ship and on shore.
- Develop a system for transfer of the data from ship to shore, including:-
 - Automated data transfer.
 - Automatic display of the data on public web pages.
- Develop quality control and quality assurance procedures for the data based on:-
 - Validation by cross comparison of multiple sensors.
 - Validation of data from sensors running continuously against water samples collected by the crew and processed on shore.

Continuing aims:-

- Carryout sustained observations of the partial pressure of carbon dioxide in the surface of the ocean and:-
 - Use these data to assess the direction and magnitude of the exchange of carbon dioxide between the atmosphere and the ocean.
 - Relate the scale of these fluxes to the oceanographic characteristics of the different regions sampled.
 - Assess the variability of these fluxes over time.
- Provide to data to the international effort assembling such data.
- Help improve in regional and global estimates of exchange fluxes.

1.3 Introduction to this report

The SNOMS project is an innovative example of the impact partnerships between science and industry can have on global environmental research. Measurements from the SNOMS system are transmitted ashore in real-time, are quality-controlled and are made publicly and freely available.

In this first section of the report we describe briefly what and how things are done. We provide an overview of the different aspects of the SNOMS project over the period 2006 to 2012. The background and context of the project have been described in the preceding section. In the following sections we provide details on the developments that were needed to implement and sustain the project and the information that has been generated and assembled by the project. More specific information on the work and products of the project have been assembled in the Part 2 of this report (Hydes et al., 2013) so that a complete historical record of the project is available. The report provides an important “meta-data” resource for any future evaluation of the data as well as a how-to-do-it guide available for related follow-on projects.

In Section 2, we describe how the system was specified and the construction and installation of the system. This is followed by details of the work that was required on board the ship and on shore to keep the system running on a day-to-day basis. A major effort within the SNOMS project has been work to standardise and automate the procedures required for moving from the collection and assembly of the data streams recorded by the SNOMS equipment to the production of fully quality controlled and archived data sets.

In Section 3, we describe the outreach that has been carried out by the SNOMS project and its engagement in a wide range of areas. The SNOMS web pages were aimed at generating a wider knowledge of the project itself and at attracting the interest of others in the shipping industry. The SNOMS project worked to engage other shipping interests and foundations to support related scientific research. It has contributed to the development of a co-ordinated European programme for marine green house gas observations (ICOS) and the concept of an organised global approach (OceanScope) to scientific observations from commercial ships. One legacy of SNOMS will be the knowledge that has been accumulated by the Swire Educational Trust PhD student who will return to China at the end of 2013 to continue his research activities. The SNOMS project has been carried out with direct contributions from other laboratories (particularly the Institute of Ocean Sciences in Canada and NOAA-PMEL) and links to organisations such as the IOCCP (International Ocean Carbon Coordination Project) and UK and EU funded national and international activities.

In Section 4, we provide a brief look at the SNOMS project in a historical context before describing some of the results of the project. By intercomparison of the data collected on the *Pacific Celebes*, and comparison with data collected on SOO system operated by the NOAA-PMEL laboratory and in shore based tests of the SNOMS and other system at Dalhousie University we establish the limits of reliability of the SNOMS system. We consider how well the data compare to existing estimations of pCO₂ across the Pacific and show the new data from the SNOMS project will provide an improved basis for improving estimations across the Pacific Basin. We describe how the range of instruments collecting data in the SNOMS system has improved insight into air-sea gas exchange processes. Finally we relate how the data for alkalinity measured in the crew-collected samples can help with improved understanding of the rate of ocean acidification.

The annexes published in Part 2 of this report (Hydes et al., 2013) provide further and more detailed information in terms of the activities of the project and its background. Annex 1 shows the 16 routes of the *Pacific Celebes* between its major port calls (when samples were sent from the ships and either NOC or IOS project scientists visited the ship). In Annex 2 we have assembled the proposals for SNOMS project activities and the contracts drawn up between the Swire Trusts, NOC and the University of Southampton. In Annex 3, the technical reports produced by the project have been collected together. These provide detailed descriptions of the system, the work needed for running the system and how the data processing is carried out. Annex 4, provides graphical presentations of SNOMS raw and intermediate data sets. Annex 5, provides a listing of outreach products produced by the project and pdfs of some of the Powerpoint® presentations given by NOC staff that have described the project and its findings. Annex 6, is a simple log of the performance of the individual measuring devices used in the project.

2. System and operations

In this section we provide brief introduction to the physical aspects of the SNOMS hardware and its installation and operation on the *MV Pacific Celebes*. The complete detailed specification of the SNOMS system and the operations carried out on board are provided in the copies of four NOC technical reports in Annex 3 (of Hydes et al., 2013).

2.1 Specification

The shipboard part of the SNOMS system had to be self-contained.

It needed to record data for surface water values of temperature, salinity, dissolved oxygen, total dissolved gas pressure and partial pressure of dissolved CO₂; atmospheric data were needed for air temperature, pressure and humidity and atmospheric concentrations of CO₂; in addition the position of the ship had to be tracked and the data being recorded on the ship had to be transmitted to NOC. On shore a receiving system for the data was required that was linked directly to web pages to automatically display the data as it arrived.

The major challenge that working with a Swire ship set NOC was to develop a system that required only a minimum of maintenance that could be carried out by the ship's crew. This is an important novelty of SNOMS system. Other systems in operation round the world have to be serviced on regular basis by scientific staff either meeting the ship or in some cases sailing with it. This greatly increases the costs of operating a system. NOC was able to develop the required system because of the wealth of experience it has in the non-trivial task putting together equipment that works reliably at sea.

The core of the system is the device that measures pCO₂. This is the CO₂-Pro™ manufactured by ProOceanus, who based near Halifax in Canada. This unit was developed for long term unattended use on data buoys. This was the characteristic we needed. We then worked with ProOceanus on a modification that would be suitable for use in the SNOMS system. In use the sensor sits in a NOC designed flow through tank along side the ProOceanus GTD™ sensor. The GTD measures the actual total pressure of dissolved gasses in the water. The partial pressure of CO₂ (pCO₂) is calculated from the readings of the two instruments and is the true pCO₂. Other systems calculate pCO₂ from a measurement of the fraction of CO₂ in the dissolved gasses and a measurement of atmospheric pressure. This assumes the gasses in seawater at the time of measurement are close to equilibrium with the overlying air pressure. However this



Figure 2.1. The SNOMS flow through tank and data unit installed on the *MV Pacific Celebes*, in the ship's machinery space.



Figure 2.2. The SNOMS meteorological-data collection and satellite data transmission units installed on the *MV Pacific Celebes*.

calculation can have substantial errors when water becomes super saturated with oxygen and nitrogen for example in storm conditions or at times of year when water temperatures are changing rapidly.

On board the ship the ProOceanus sensors are suspended in purpose built 76 litre stainless steel tank through which seawater flows at 30 litres per minute. In the lid of the tank are triplicate sensors for water temperature and conductivity (salinity is calculated from these data) and a further three sensors for dissolved oxygen. Mounted next to the tank is the data-logging unit (Figure 2.1). This unit is also to atmospheric sensors and data communications system that are mounted on the ships “monkey island” the deck above the bridge top (Figure 2.2).

2.2 Construction and installation

Final specification of the system was arrived at after a visit to the *Pacific Celebes* when she was in dock in Singapore in June 2006. This visit also enabled suitable locations for the equipment to be found on board and a way of accessing a supply of clean seawater to be identified. Water was obtained by setting up a flow line in parallel to the water that is pumped to the ship’s fresh water generating system. All the works required for installation are detailed in Annex 3 (of Hydes et al., 2013). This includes details of the small modifications needed on the ship and the design plans for the flow through tank.

The complete system was assembled at NOC in early 2007. It was then installed on the P&O Ferry Pride of Bilbao in March 2007 for shipboard tests. In April it was shipped to Singapore. In May Jon Campbell and David Hydes joined the ship to work with the ship’s crew to install the system. They sailed with the ship to Jakarta for a trial of the system. The system functioned well during this trial, but a high level of vibration around the tank was experienced. Welding a frame with rigid lateral supports to the tank cured this. The ship’s own engineers built the frame. The vibration lead to one of the few major failures of the system as it broke the very sensitive pressure sensor in the ProOceanus GTD unit.

An important part of the second stage of Swire’s support for the SNOMS system was that we were able to purchase a complete second set of sensors. This allowed the sensors to be swapped out on a regular basis for servicing and calibration without the need to close down the system, as we had to do between June and October in 2008. Change over of the sensors has been done both by NOC personnel and by the ship’s crew. This was a good test of the system and has proven that the system met the requirement for remote operations for which little or no scientifically trained support were available.



Figure 2.3. Lid of the SNOMS flow through tank being refurbished off by Mark Squires in the NOC workshop.



Figure 2.4. Lid of the SNOMS flow through tank loaded with the nine Aanderaa sensors ready for operation.

2.3 Ship based operations

A detailed report on all shipboard operations carried out by the ship's engineers is provided in Annex 3 (of Hydes et al., 2013). This covers details of the procedures themselves and the necessary safety documentation.

Each day the ship was at sea two water samples were collected. These were analysed on shore - one for salinity and second for Total Alkalinity (TA) and Total Dissolved Inorganic Carbon (DIC). The Chief Engineer e-mailed a list of the samples collected to NOC at the end of each month.

Each time the ship went into port the tank was opened, the sensors in the lid of the tank were wiped gently with a soapy sponge and then all the surfaces of the tank and sensors were washed down with fresh water spray. At regular intervals photographs were taken of the sensor surfaces before and after cleaning and these photographs were then emailed to NOC.

Initially when the ship arrived in the service port the ship was met by personal from NOC. Later when the service port became Vancouver, on alternate occasions, the visit was made by staff from the Institute of Ocean Science, Sidney on Vancouver Island. During these visits the system was checked, changes of instruments were made as necessary and the crew were consulted on the systems performance. The visitors then worked with the crew to bring aboard empty sample bottles and get the full samples prepared for shipping back to the UK. IOS also analysed some duplicate sets of DIC/TA samples.

2.4 Shore based operations

2.4.1 Daily checks

Each day the system was in operation the SNOMS web page was checked to see that data were being successfully received from the ship and that all the sensors were functioning. Each day's new data were inspected as a time series plot to check that they were within likely data limits. When errors were noted a control signal were sent to the logging system on the ship via the Iridium satellite communication system to interrogate the logger unit. If the logger unit was operating correctly but the fault still persisted the Chief Engineer was e-mailed and asked to do a visual inspection. On two occasions the Chief Engineer was able to assist by replacing a sensor with a spare units kept on board the ship.



Figure 2.5. Chief Engineer Valeri Didenko opening the SNOMS tank for cleaning.



Figure 2.6 Mark Hartman from NOC and crew-members Ren and Gao checking the sampling procedure.



Figure 2.7 Kyle Davidson (left) and Marty Davelaar from IOS Canada picking up samples in Vancouver.

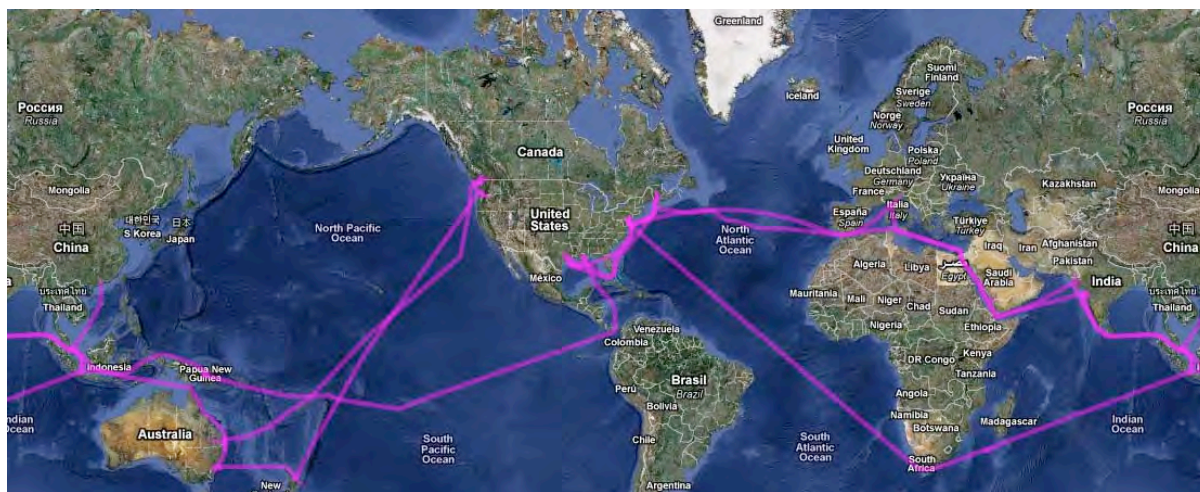


Figure 2.8 Map of the routes taken by the MV Pacific Celebes during 2009. The map was generated by the Google Earth related software developed at NOC to display the daily position of the ship on the SNOMS webpages

2.4.2 Sample analysis

Three sets of analyses were carried out on the samples returned to NOC. The salinity samples were sent to the “Calibration Lab” at NOC where the salinity was measured using a high precision salinometer Guildline Autosol™ in a temperature controlled laboratory.

The more complex measurements were those of TA and DIC. These were made using a Marianda VINDTA-3C™ instrument. On average 8 to 10 samples a day can be measured with this machine. The measurements are standardised by measuring certificated reference solutions alongside the samples from the *MV Pacific Celebes*. The residual sample was then used for the analysis of the nutrients elements nitrate, phosphate and silicate. This information is needed along with the data from the VINDTA and the salinity of the sample to calculate the actual DIC and TA content of each sample and after that to calculate the pCO_2 and pH of the samples. The information from the samples is used to calibrate the information recorded from the continuously recording instruments.

The final quality controlled data set (Hydes et al., 2012) was then reported to the Carbon Dioxide Information and Analysis Centre at the Oak Ridge National Laboratory in the USA CDIC is the centre for collection of all such data agreed by the IOCCP (International Ocean Carbon Coordination Project).

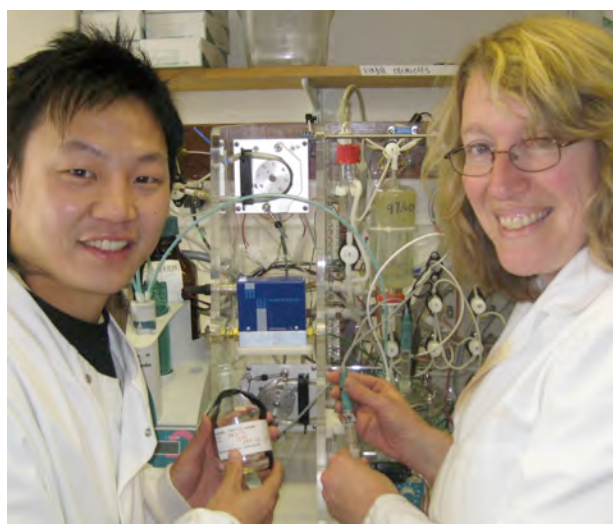


Figure 2.9 Sue Hartman and Swire pH student Zongpei Jiang working with the VINDTA instrument at NOC.



Figure 2.10. Dave Childs determining the salinity of a SNOMS water sample on the Guildline Autosal at NOC.

2.5 Data management

The data from the SNOMS project are being archived at the Carbon Dioxide Information and Advisory Center (CDIAC; Oak Ridge, USA; <http://cdiac.ornl.gov/>). The NOC report Hartman et al. (2012; In Annex 3, Hydes et al., 2013) provides a complete description of the processing used to move from the raw data collected on the ship to the final archived data set. The report forms part of the meta-data set produced by the SNOMS project, and it is be available with the main data set and will be made available to users of the data by CDIAC.

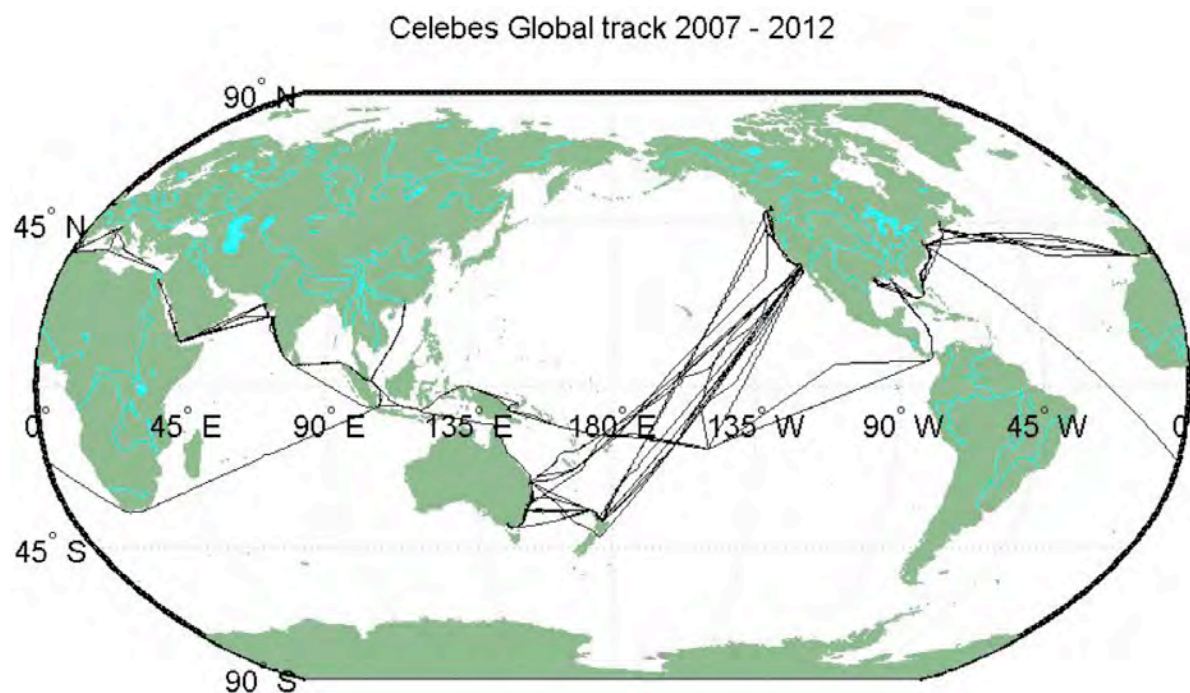


Figure 2.11 Map of positions of all the data recorded by the SNOMS system the MV Pacific Celebes from 2007 to 2012. Taken from Hartman et al. (2012) Data processing procedures for SNOMS project 2007 to 2012. Version-1; NOC Report, Internal Document 05. (see Annex 3, Hydes et al., 2013).

To monitor the operation of all the sensors used in the system (listed in Table 2.1) a subset of the data (spot values at intervals of 5 minutes) were telemetered every six hours via the Iridium satellite link to NOC and displayed immediately on a public webpage at <http://www.noc.soton.ac.uk/snoms/>. On board the ship the full data sets from each of the sensors were logged in binary format onto compact flashcards in the two data logger units. These were firstly in the engine room collecting data from the hydrographic instrumentation and secondly mounted on the monkey island collecting data from the meteorological instruments.

Hartman et al. (2012) describe the processing of the data that were written to these flashcards. Two methods were used to provide quality control (QC) of the data sets:-

(1) In the case of the sensors providing data on tank temperature, conductivity and concentration of dissolved oxygen the measurements were replicated by using three of each type of sensor. The use of triplicate readings enabled the identification of less a well functioning sensor. Following comparison of the match of the output from the three sensors a single output measurement based on the choice of the “best” most closely functioning instruments was generated. In addition a fourth a hull mounted temperature sensor provided a further cross check on the stability of the temperature measurements made in the tank and visa versa.

(2) Water samples (that are able to be stored without deteriorating for extended periods) were also collected, these provided quality control of the measurements of conductivity and the measurements of $p\text{CO}_2$ (by calculation of $p\text{CO}_2$ from measurements of Total Alkalinity - TA and Total Dissolved Inorganic Carbon - DIC made on the water sample). The ship’s crew collected these seawater samples on a daily basis while the ship was underway. These consisted of a 200 ml salinity sample and a 250 ml sample for TA/DIC. The samples were shipped back to NOC for analysis from the break point

ports in the operation, listed in Table 2.2. Hartman et al. (2012) describe the steps taken to achieve a “best” data set on a 5-minute time step. These were then adjusted as necessary on the basis of the water sample data. All adjustments made to the data and the precise scale of the adjustments are recorded in the meta-data set. A pictorial overview of the processing procedure is given in Figures 2.12 and 2.13 these should be used in conjunction with the written descriptions in Hartman et al (2012) to follow of the procedures involved. The linked originating documents are publicly available from NOC.

For the Pro-CO₂ sensor, Table 2.2 provides an indication of the percentage of time data were considered of good enough quality to have the full set of quality control procedures applied. A spreadsheet is presented in Annex 6 of Hydes et al., (2013) that provides details the times data from each of the sensors used passed the initial visual inspection stage.

The basic steps described in detail in Hartman et al. (2012) are:-

(1) After the data had been transferred from the flashcards they were processed using bespoke NOC software coded in the C-language-code using Lab VIEW™ software. This software concatenates, averages and merges the parameters from all of the instruments and converts the binary files into ASCII files for further processing.

(2) Further processing of the data was performed using procedures that were coded using MathWorks Inc’s Matlab™ software to inspect, quality control, adjust and write the archive-able data files.

Table 2.1 Sensor list of the individual sensors used on in the SNOMS system

Maker	Measurement	Model	Method	Serial numbers
Aanderaa	Sea water Temperature	4050	Thermistor	11; 13; 15; 25; 34; 55; 90
Aanderaa	Sea water O ₂ concentration	Optode3835	Fluorescence Quenching	338; 339; 340; 641; 34; 1008; 1009; 1014; 1357
Aanderaa	Sea water Conductivity	3919	Inductive	136; 138; 139; 674; 952; 1061
Pro-Oceanus	Sea water CO ₂ concentration	CO ₂ -Pro	Infra Red absorption	47; 48; 94
Pro-Oceanus	Sea water dissolved gas pressure	GTD-Pro	Gas tension	49; 98
SeaBird	Ship’s Hull Temperature	SBE48	Contact thermistor	23; 25
Vaisala	Atmospheric CO ₂	GMP343	Infra Red absorption	B2840006; D4150004
Vaisala	Atmospheric pressure temperature humidity	PTU-200	Press; Humidity/capacitive; Temperature -PRT	
Vaisala	Atmospheric pressure temperature humidity	PTU-300	Press; Humidity –capacitive; Temperature -PRT	
Vector	Wind Direction	W200G	Vane	2118
Vector	Wind speed	A100R3	Cup anemometer	1894

Table 2.2 Break point ports for division of the data sets. If all equipment on board, (On – Yes or No). An indication to 10 % of the %age of time the main CO₂ sensor was collecting data to which quality controls could be applied.

Voyage	Start Port	End Port	Start date	On	CO ₂ % good
1	Singapore	Livorno	02/06/07	Y	10 %
2	Livorno	Livorno	12/09/07	Y	20 %
3	Livorno	Livorno	29/01/08	Y	60 %
4	Livorno	St John	13/06/08	N	N
5	St John	St John	25/10/08	Y	100 %
6	St John	Livorno	21/03/09	Y	100 %
7	Livorno	Vancouver	18/08/09	Y	100 %
8	Vancouver	Vancouver	27/11/09	Y	50 %
9	Vancouver	Vancouver	21/03/10	Y	100 %
10	Vancouver	Vancouver	23/06/10	Y	40 %
11	Vancouver	Vancouver	28/09/10	Y	100 %
12	Vancouver	Vancouver	14/01/11	N	N
13	Vancouver	Vancouver	29/04/11	Y	90 %
14	Vancouver	Vancouver	26/07/11	Y	100 %
15	Vancouver	Vancouver	29/10/11	Y	100 %
16	Vancouver	Melbourne	05/02/12	Y	100 %

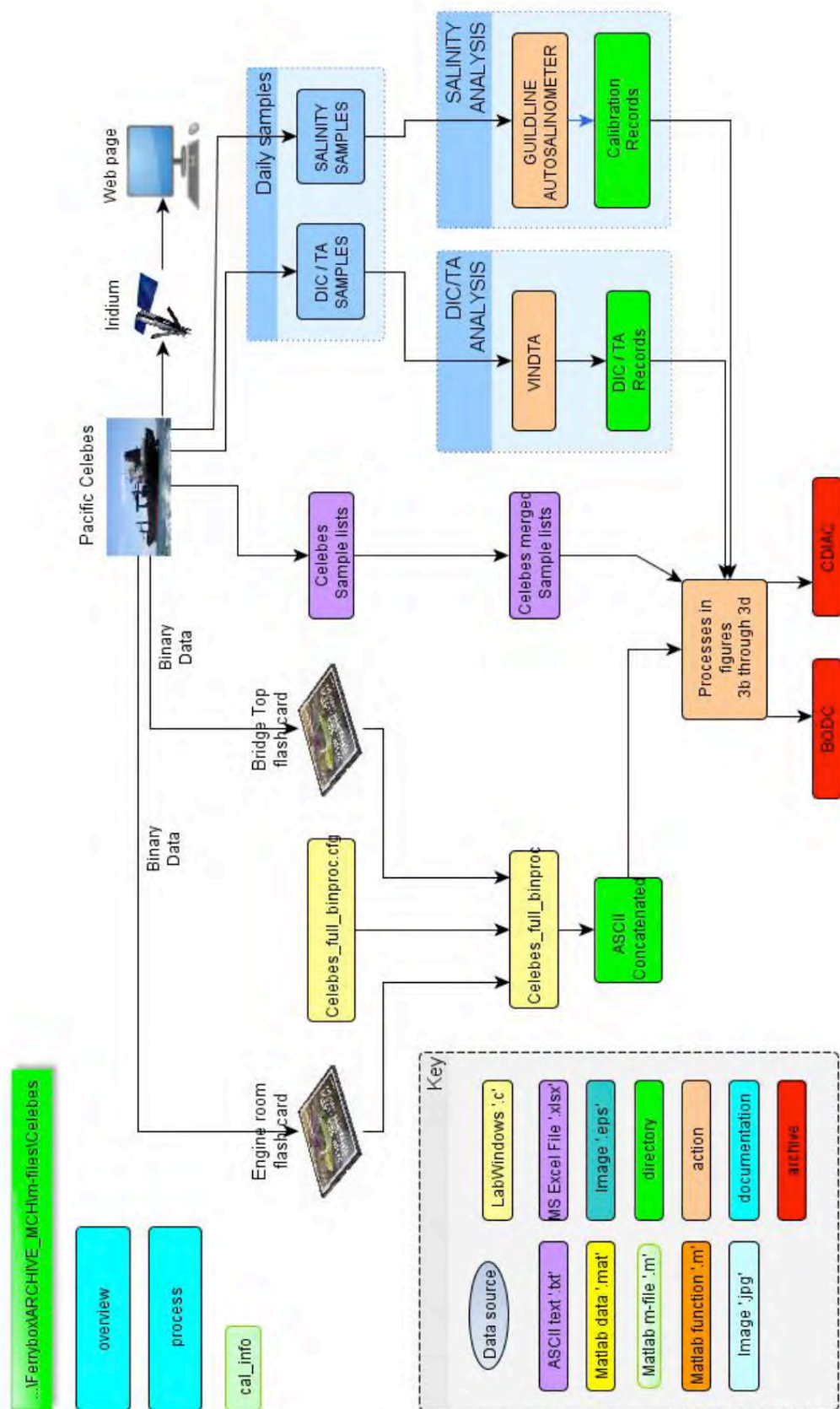


Figure 2.12 Diagram of the relationship between the different SNOMS data streams.

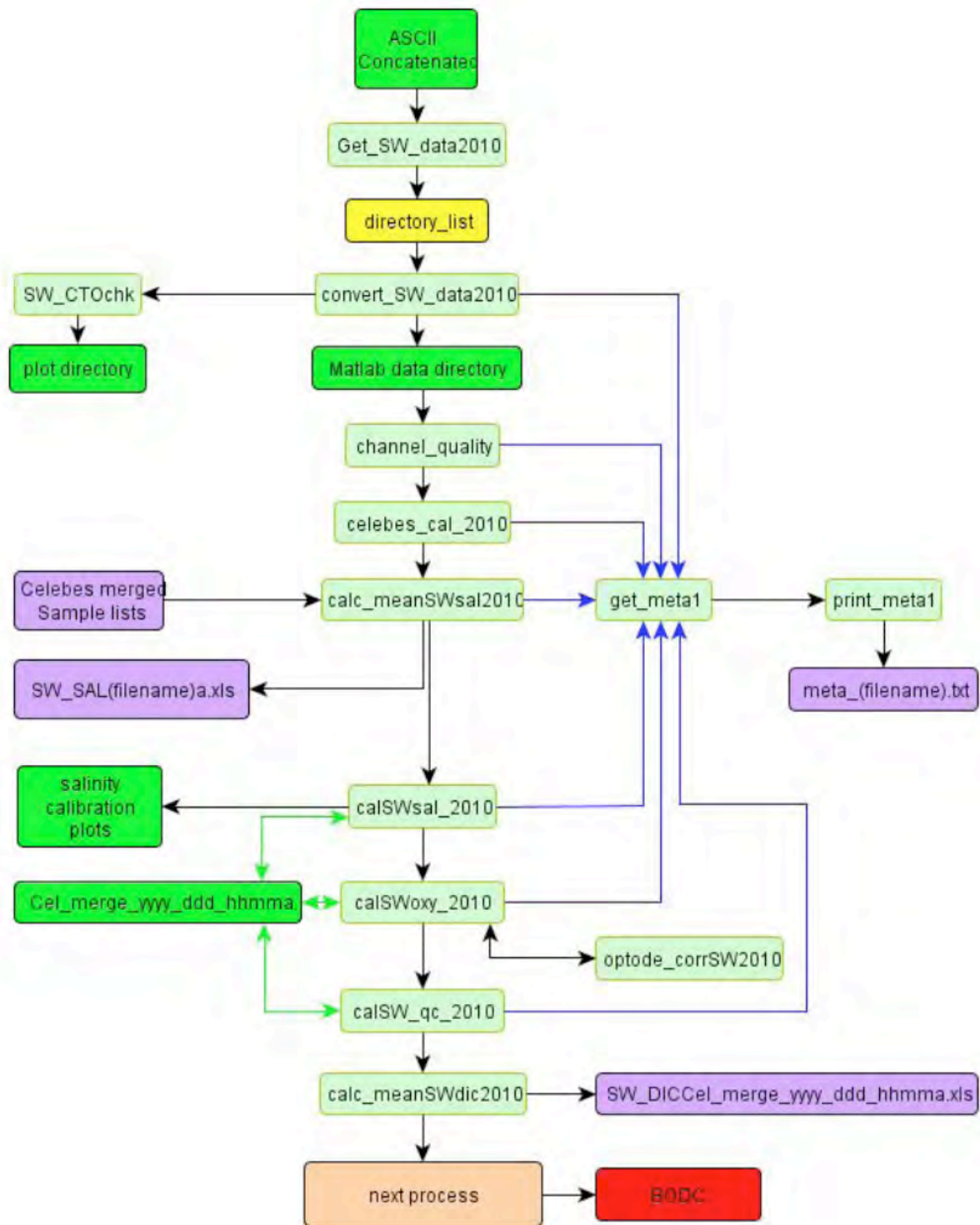


Figure 2.13. Flow chart describing the steps in processing the SNOMS underway data.

3. Outreach and wider activities related to the SNOMS project

The SNOMS project sits within the global community of scientists gathering data on the accumulation of anthropogenic CO₂ in the ocean and the resulting process of Ocean Acidification. Secondly it is part of the community exploiting the huge potential that working with the global merchant shipping fleet has for expanding marine scientific observations both at the surface and into the depths of the ocean.

In this section we review the specific outreach activities of the SNOMS project starting with the SNOMS webpages and then looking at other relevant surrounding activities such as ICOS and OceanScope. SNOMS outreach actions have ranged from publications in scientific journals and other media to direct approaches to foundations and shipping companies for support and the organisation of meetings which have showcased the effort and helped link the global community carrying out this work.

3.1 Webpages (<http://www.noc.soton.ac.uk/snoms/>)



Figure 3.1. SNOMS webpages - Home Page.

An important part of the SNOMS activity is the web pages. These have a dual function. They display the activity to the world-wide-web audience and provided the NOC team and others with instant access to information on how well the system is operating at any time. This has enabled remedial action to start being organised as soon as glitches have occurred. The pages also provide a historical record of how well the system has functioned at any one time, beginning with the *MV Pacific Celebes* sailing from Singapore in May, 2007 to its final working port call in Melbourne in March, 2012. This immediate access to the raw information on system functioning is a key feature of the approach NOC has taken to providing unfiltered information on the functioning of its remote data collection operations, in the SNOMS, other Ferrybox - SOO type projects and in the leadership of the EuroSites collective of fixed observation platforms e.g. <http://www.eurosites.info/pap/data.php>.

On the SNOMS web pages, the home page introduces the system and provides the link to pages that show (i) the position of the ship - this was automatically deactivated when the ships was passing though pirate-waters off the Horn of Africa (ii) the blog gives an introduction to the various activities needed in the project and an introduction to some the many people involved (iii) the routes taken by the *Pacific Celebes* are described and linked to CNCo schedules (iv) all the instrumentation used is described and web-linked to more detailed information that can be down loaded from the University of Southampton "e-prints" site (v) "Data Access" is an important page as it shows all the data that has been produced by the project (vi) the remaining pages support the out reach activities of the project.

3.2 Project Partners and International Activities related to SNOMS

3.2.1 IOCCP The International Ocean Carbon Coordination Project (<http://www.ioccp.org/>).

IOCCP is the body supported by International Oceanographic Commission that provides communication and coordination services for the ocean carbon community. It has been instrumental in developing global co-operation. Key achievements have been establishing a single data centre for collection of data from observing activities round the globe. The linkages set up by the IOCCP were instrumental in the success of the development of the Takahashi CO₂ Flux Atlas discussed in sections 1. This has led on the development of the SOCAT activity (<http://www.socat.info/>) - The Surface Ocean CO₂ Atlas Project, is an international effort to establish a standardised global dataset of surface ocean data. All publicly available data on pCO₂ which are being cross-checked and then made available in a common format with agreed quality control flags. Volunteers round the world do the checking and flagging of the data. It is also supported by NOAA, who host the SOCAT database working closely with CDIAC. IOCCP is the principal link of the ocean carbon community in to the development of systems for continuous routine “operational” observations of ocean conditions. The observations link into external users of the data particularly the Global Carbon Project (<http://www.globalcarbonproject.org/>).

The Global Carbon Project (GCP) requires *in situ* marine data from field observations and numerical models to deliver its core objectives which are to:- (1) compile, analyse, report and archive statistics and information on the global and regional balance of CO₂ fluxes, (2) identify and monitor important CO₂ sinks and natural reservoirs of carbon, and (3) facilitate the development of accounting methods that can help fill the gaps in current assessments. It therefore plays a vital role in the development of IPCC (Intergovernmental Panel on Climate Change) assessments and potentially the development of agreements limiting the emission of green house gasses and the required monitoring procedures.

3.2.2 ICOS - Integrated Carbon Observing System - a European Research Infrastructure Consortium (ERIC)

The European Union is supporting the development of ICOS (Integrated Carbon Observation System).

Marine observations using ships of opportunity are seen as providing a major contribution to this programme. The EU vision for the implementation stage is that national and private funding will support it. This will build on the highly successful efforts of the IOCCP and the EU CarboOcean project that have so far coordinated international observation in the North Atlantic.

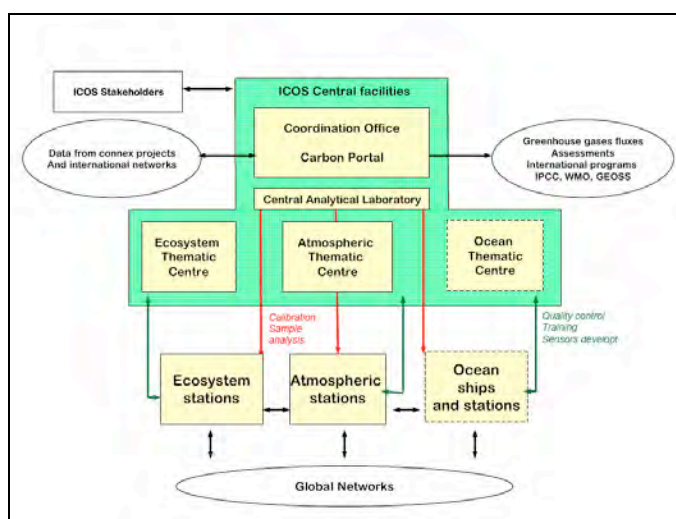


Figure 3.2. Relationship of the component activities of ICOS

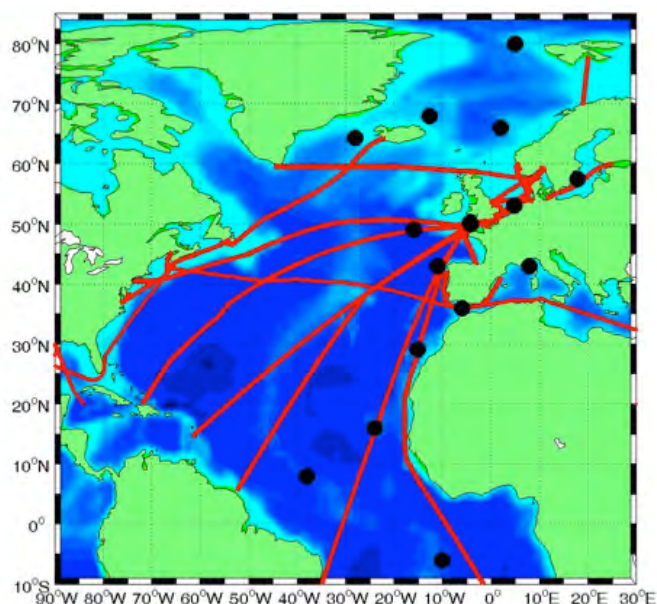


Figure 3.3 Locations of the initial contributions to the ICOS marine network

ICOS is a major European scientific infrastructure project, being developed in a European partnership. (See http://www.icos-infrastructure.eu/proj_doc and follow link to latest stakeholder handbook). It will be governed by a legally binding agreement to provide a sound long-term basis for its activities. ICOS infrastructures will supply the *in situ* observations of greenhouse-gas fluxes and dynamics required to provide the process understanding and quantification of carbon sources and sinks on a regional scale. Its data will be used to produce statistically robust estimates of green house gas sources and sinks resolved at appropriate time and space scales. Coordinated, long-term, high-quality observations from across Europe and the Atlantic Ocean will provide the field data needed to validate and constrain climate models and enable improved prediction of future variability of carbon sources and sinks. This information will inform policy and underpin future mitigation strategies. The pillars of ICOS are its thematic centres. These will develop and support marine, atmospheric and terrestrial observation (Fig. 3.2). The international coordination should maximise the return on individual observing programmes and minimise the duplication of resources in the different nations involved.

An ICOS Ocean Thematic Centre - OTC will manage a potential network of European marine observations similar to that shown in Fig. 3.3. The network will build up from existing SOO operations and fixed-point time-series platforms. A key concept of ICOS is the move from discrete science and process based academic studies to the development of a sustained observing system with a lifetime of several decades. ICOS will not directly fund new observational programmes but will instead use existing observational programmes and it will foster new programmes specifically focussed on key gaps. The OTC will bring together existing and developing activities in: marine observations, data management, system development, training and knowledge transfer. The OTC will establish consistent methodologies to allow comparable observations of the ocean atmosphere exchange of green house gasses through the sea surface to be made. Obtaining time and space resolved estimates of this sink are critical to the whole project because:- (i) the marine data provides “top-down” constraint on adjacent land sinks, which are more heterogeneous and thus more difficult to observe directly, and (ii) much of the variability seen in the ocean sink is not yet reproduced in ocean models.



Figure 3.4 The ICOS network in the N. Atlantic will develop out of existing operations. The trade in bananas has provided a stable route for CO₂ observation made by UEA since 2002 working with Geest Lines and Seatrade. MV Santa Maria in unloading in Portsmouth.

3.2.3 Ocean Acidification - OA

Observation of CO₂ fluxes and ocean acidification are closely crossed linked. The work of ICOS and other efforts will link into a global OA observation programme currently being developed under an initiative lead by NOAA. A first globally-international planning meeting was held at the University of Washington in June 2012. A plan based on the discussions there is to be published in January 2013. For the studies of OA in the North Atlantic OSPAR (The commission overseeing the “Convention for the Protection of the Marine Environment of the North-East Atlantic” (the ‘OSPAR Convention’) and ICES (International Council for the Exploration of the Seas) have set up a Study Group to advise OSPAR signatories on best practice for monitoring of processes related to OA and CO₂ uptake by the ocean. This group met for the first time 12 -14 December 2012. David Hydes of the SNOMS project represented the ICES Marine Chemistry Working Group at the meeting.

3.2.4 EU Projects FerryBox, CAVASOO and CarboOcean

The EU Science Framework-5 funded the project “FerryBox” from 2002 to 2005. The project enabled the cooperation of 11 organisations and established the coordinated use of commercial ferry-ships for the collection of scientific data. This has been an important step towards achieving the cost-effective

extension of the European marine observing and reporting network envisioned in the EuroGOOS concept. The 11 partners operated on 9 shipping routes around Europe, from the eastern Mediterranean to the Baltic. Four core parameters were measured on all the routes, alongside other route-specific measurements. Common data quality control and archiving procedures were adopted, and the data from the project period are available from BODC (British Oceanographic Data Centre). The scientific value of the detailed near-continuous observations made possible with FerryBox systems was proved in studies, which for example validated the benefits of regular FerryBox measurements in improving numerical models through data assimilation and demonstrated the mutual benefit of linking remote sensing (satellite) observations with more direct FerryBox measurements. The EuroGOOS report on the EU project is available at:- <http://www.eurogoos.org>. Following on from the EU-Project, FerryBox continues to operate as an informal group that now has a global reach (see <http://www.ferrybox.com>). Meetings are held every 18 months for the exchange of reports on scientific and engineering progress. These meetings provide an important cross over point for the sharing of information between the more shelf sea oriented FerryBox community and the groups working on ocean going routes. It is this sharing of experience that helped several developments in the SNOMS project on their way both in terms of the equipment used and handling of the data produced. EuroGOOS is the European division of GOOS (Global Ocean Observing system) this is now becoming more of a global reality through US funding of IOOS (Integrated Ocean Observing System <http://www.ioos.gov/global.html>).

In parallel to the FerryBox project the EU funded the CAVASOO project. It also ran in 2002 to 2005. The CAVASOO project showed that the measurement of CO₂ concentrations in the surface ocean could be done reliably using ships of opportunity. The subsequent CarboOcean (2005-2009) project developed methods for the synthesis of data from different SOO routes (which is one dimensional along each fixed route) with data on temperature and biological production collected by satellites (which is two dimensional across the surface of the globe). Using these methods a precise estimate of CO₂ fluxes across the surface of the North Atlantic based on data collected in 2005 was achieved. The results were published by Watson et al., (2009). Unfortunately observations and data synthesis have been more poorly funded in the subsequent CarboChange project (2011-2015) as it was assumed that ICOS would have developed more quickly than it has done. Consequently in 2013 the peak years of operations in the N. Atlantic remains 2005.

3.3 Engagement

3.3.1 SCOR - Ocean Scope

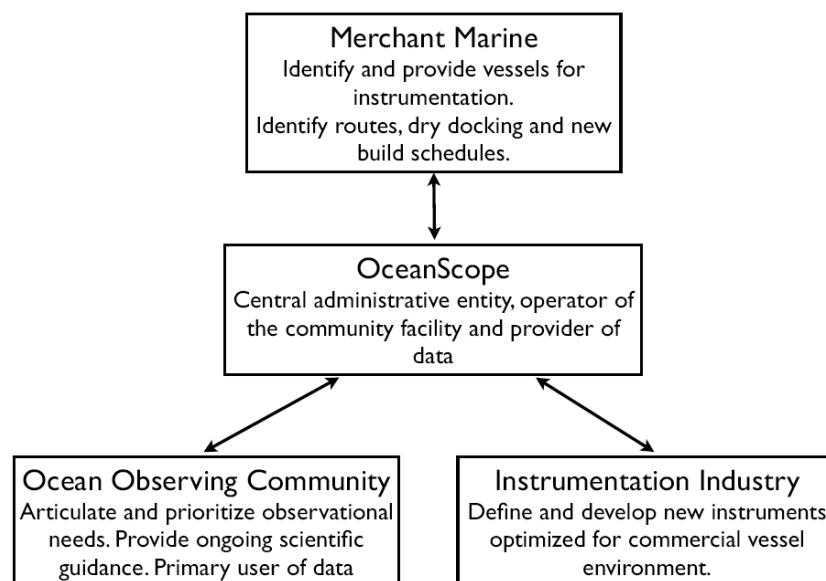


Figure 3.5. Schematic diagram illustrating the potential linkages between an OceanScope organisation and the maritime industries, the ocean observing community and instrumentation companies

SCOR (Scientific Committee on Oceanic Research) in 2008 convened an international working group “OceanScope” which reported in 2011. David Hydes was one of the working group. It was lead by Tom Rossby (University of Rhode Island, USA). The group included representatives from the International Chamber of Shipping, ship’s architects and engineers as well as expertise in marine science and international law. The group has provided a road map for the extension of ship of opportunity scientific observations over the next 20 years. The vision is a much-expanded partnership with the merchant marine. The aim is to build on existing activities particularly the work of groups such as FerryBox, IOCCP and ICOS. These have focussed on measurements of the surface layer. A key concept promoted by OceanScope is the greater use of acoustic methods which can monitor subsurface structure and currents. These methods will allow the surface and the depths of the ocean to surveyed regularly almost in the way that satellites now report on the atmosphere and the earth’s surface. Important product of the acoustic work will be information on the both true subsurface structure of the ocean and much improved data on the magnitude and location of ocean currents. The Final Report is available at http://www.scor-int.org/Working_Groups/wg133.htm.

3.3.2 Engagement efforts at NOC

The support from the Swire Trust allowed NOC to set up and carry out the SNOMS project. Work around the project was also supported by funding of staff time within NOC by the NERC core science “Oceans 2025” project (2007 to 2012) and NERC-National Capability (In Ocean Carbon Science) from 2012 onwards. The EU projects CarboOcean (2005-2010) CarboChange (2011-2015) and JERICO (2011-2015) have also contributed to running costs, costs of staff time for sample processing, data quality control development and scientific interpretation.

In addition to these standard academic sources of funding a quest for other sources of funds was lead by Joanne Donahoe of the University of Southampton’s Office for Development and Alumni. Throughout most of the project Joanne worked with the SNOMS team at NOC principally Boris Kelly-Gerreyn seeking support for extending the project from a wide range of organisations ranging from Royal Caribbean Cruises, the UK Passenger shipping organisation, to White Link Ferries and BP shipping. In Annex 5 (of Hydes et al., 2013) we provide a more detailed report on these activities. There we also provide examples of the advertising-flyers and the recruiting brochure that were prepared by Jo and Boris. Other flyers were produced including one distributed by David Watkins from CNCo at the “Green Ships” meeting in Singapore in 2011.

A copy of the presentation made by David Hydes to the World Ocean Council (WOC) organised “Smart Ocean Industries” meeting held at UNESCO in Paris in December 2011 is included in Annex 5 (of Hydes et al., 2013) along with other examples of outreach produced by the SNOMS project. The



Figure 3.5. Cover of recruiting brochure produced by Joanne Donahoe and Boris Kelly-Gerreyn to set up a consortium of shipping companies to support a more widely based SNOMS project.

WOC presentation was co-authored with Maciej Telszewski the IOCCP Project Officer. It is an example of the presentations made at a range of meetings that demonstrated what already has been

achieved and that what more would be possible with closer cooperation with shipping companies.

In general following the economic slump of 2008 it has been easier to convince the scientific community of the value of the work than it has been garner financial support outside the normal government related sources.

Other highlights of these activities included:- The major (US) science journal “Science” published a substantial news article on our work following the international FerryBox’08 meeting held at NOCS in September 2008. The work on the *MV Pacific Celebes* was featured on a stand at the prestigious annual Royal Society’s Summer Exhibition. David Hydes was invited to give a keynote presentation in Concepcion, Chile to POGO (Partnership for Observation of the Global Oceans), which is the annual meeting of the heads of the world’s major marine institutions. This was followed by IMarEST (The Institute of Marine Engineering, Science & Technology) arranging a meeting on the topic of ship of opportunity work and the concept of OceanScope. The outcome from these activities has been a general recognition among the science and commercial communities about the value of a potential partnership to better understand our oceans. However the example set by the Swire Trust and their early leadership has not yet been followed.

3.4. Swire Educational Trust Student

A SNOMS PhD student is supported by the Swire Educational Trust for four years. His studies started in Southampton in October 2009. The student, Zongpei Jiang joined NOC after completing his MSc at the University of Xiamen. He is co-supervised by David Hydes and Toby Tyrrell in NOC and Prof Minhan Dai, who is Director of the Marine Environmental Laboratory of the University of Xiamen. Jiang has spent time in Xiamen during his studentship and this helps link two of the world’s important centres for marine research. Jiang’s work focuses on two themes:-

(1) Assessing the relative importance of marginal seas to the global CO₂ budget. Sampling in these areas complements the work in Xiamen on the major Chinese project Choice-C (China Ocean Carbon). Choice-C is looking at the complexity of the carbon cycling in South China Sea and East China Sea, which span a wide range of latitudinal zones with distinct ecosystem structures. Jiang has published one paper on his work while in NOC based on the data from his MSc project and he has a second paper in press. This paper examines changes in the CO₂ system in the north Atlantic. The data used is from the NOC SOO system on the P&O ferry *MV Pride of Bilbao*. He has presented papers on his work at two major science meetings, these were at the American Geophysical Union meeting in San Francisco in December, 2011 and at the “Oceans in High CO₂ World” meeting in Monterey,



Figure 3.7. “Winners” of the CO₂-Quiz at the “Breathing Ocean” exhibit at the 2008 summer hands on science exhibition at the Royal Society’s Carlton Terrace Head Quarters



Figure 3.8 The engineering team on the *MV Pacific Celebes* seen in the slide show about the *Celebes*’ work at the Royal Society.

California in September, 2012. Jiang has had hands on experience with the SNOMS system. He made one maintenance visit to the MV Pacific Celebes at the break point in Vancouver where he worked on the PSI-CO₂ measurement devices. Prior to that he had carried out lab tests of the SNOMS

instruments at NOC. His work identified improvements that could be made in the ProCO₂ devices and these have now been incorporated in the instruments by their manufacturer, ProOceanus.

(2) The work that Jiang is pursuing now is the interpretation of data collected by the *MV Pacific Celebes* during its Pacific crossing from 2009 to 2012. During his visits to the USA and Canada in 2011 he arranged with the NOAA and IOS groups to also get access to their data. He will assess the scale of variability along the route and the variation of the air-sea flux of CO₂ with the seasons. A key point of interest along the route the *MV Pacific Celebes* worked between Australia and the US and Canada was that it crossed the equatorial current. This region is the largest single marine source of CO₂ to the atmosphere. The current transports a plume of cold CO₂ enriched deep water that rises off the coast of Peru and then moves west along the equator releasing CO₂ to the atmosphere as the water warms. The use of the NOAA data along with the SNOMS data will enable us to see if identifiable changes have taken place in concentrations of CO₂ in surface waters across the Pacific between 2004 and 2012.



Figure 3.9. Swire Student Zongpei Jiang servicing the PSI-CO₂ instrument onboard the *MV Pacific Celebes* in Vancouver in July 2011.

4. SNOMS Science and engineering

4.1 Introduction and historical context

The SNOMS project set out to develop and deploy a robust system to determine the concentration of CO₂ in ocean waters round the globe. It followed in the traditions of the modern science of oceanography that were laid by the HMS Challenger Expedition 1872-76. That expedition carried out the first global scientific ocean survey sounding the depths and collecting water and biological samples for systematic analysis. The scientific side of the expedition was organised and lead by Charles Wyville Thomson and John Murray. The Royal Naval crew included Herbert Swire as a navigating sub lieutenant.

II. CHEMICAL OBSERVATIONS.

1. Samples of sea water should be collected for chemical analysis at the surface and at various depths, and in various conditions. Each sample should be placed in a Winchester quart glass-stoppered bottle, the stopper being tied down with tape and sealed in such a manner that the contents cannot be tampered with.

2. Portions of the same samples should be, immediately after their collection, boiled *in vacuo*, the gases collected, their volume determined as accurately as may be, and a portion, not less than one cubic inch, hermetically sealed in a glass tube, to be sent home at any time for complete analysis.

3. Frequent samples of sea water taken at the surface, and others taken beneath as opportunity offers, should have determinations of chlorine made upon them at once, or as soon as convenient.

This operation could easily be carried on in any but very heavy weather. On the other hand, it is not thought that any trustworthy analyses of gases could be made on board ship, unless in harbour or in the calmest weather.

4. Such samples of the sea bottom as are brought up should be carefully dried and preserved for examination and analysis.

5. The gas contained in the swimming-bladders of fishes caught near the surface and at different depths should be preserved for analysis. In each case the species, sex, and size, and especially the depth at which the fish was caught, should be stated.

Figures 4.1 above: Objectives of the chemical sampling on board HMS Challenger reproduced from the first volume of the Challenger Expedition Reports edited by John Murray. Figure 4.2 below: Officers and scientists aboard HMS Challenger 1872.



Officers and scientists aboard H.M.S. Challenger, 1873. Courtesy British Museum (Natural History).
1. Capt. G.S. Nares, 2. Prof. C. Wyville Thomson, 3. J.J. Wild, Artist, 4. J. Murray, Naturalist, 5. H.N. Moseley, Naturalist, 6. R. von Willemoes-Suhm, Naturalist, 7. J.Y. Buchanan, Chemist, 8. Cdr. J.F.L.P. Maclear, 9. Lieut. P. Aldrich, 10. Lieut. A.C. Bromley, 11. Lieut. G.R. Bethel, 12. Sub-Lieut. A.F. Balfour, 13. Sub-Lieut. A. Channer, 14. Sub-Lieut. H.E. Harston, 15. Nav. Sub-Lieut. A. Havergal, 16. Nav. Sub-Lieut. H. Swire, 17. Staff Surgeon A. Crosby, 18. Surgeon G. Maclean, 19. Paymaster R.R.A. Richards, 20. Ass. Paymaster J. Hynes, 21. Engineer W.J.J. Spry, 22. Ass. Engineer W.A. Howlett. The dog is probably "Boss", belonging to Channer, which was lost in a penguin colony on Nightingale Island.

Many of the samples collected are achieved and can still be accessed through the Natural History Museum in London. The chemical work included the intention to measure the gasses dissolved in all the water samples taken - a similar task as that of the SNOMS project.

When it comes to water sampling from research vessels the scenes aboard HMS Challenger (1874) and RRS Discovery (2012) are reminiscent of one another - the major difference being our ability to sample up to 24 bottles held on a “rosette” in 2012 as opposed to the single bottle sampled on Challenger. Sampling of multiple bottles attached to single wire did not become a successful operation until the development of the “NIO-bottle” by the UK’s National Institute of Oceanography (now NOC) in the 1950s.

Sampling with water bottles can’t be done by vessel underway, but, underway data is essential if we want to capture the changes that take place in surface water properties on relatively small scales (a few km) as opposed to the frequency that a research-ship can be stopped at when crossing an ocean basin this is usually a few 10s of km on intense surveys such as those carried out in the World Ocean Circulation Experiment - WOCE (view <http://www.ewoce.org/> to see the illustrations of WOCE data and find out more about that multi-national project).

Systems designed to measure the concentrations of dissolved gasses in the surface layer of the ocean in a stream of water pumped continuously onboard while a research-ship is underway were developed in several labs round the world in the early 1990s. These development were linked by the International Joint Ocean Fluxes Study (JGOFS). In 1996 a system was trialled for a year on board a merchant ship working between the UK and the Caribbean by Andrew Watson’s group at Plymouth Marine Laboratory (now at the University of East Anglia). From 2000 onwards a number of such routes started to be operated on a more



Figures 4.3 and 4.4. Above sampling water from the water collecting bottle on board HMS Challenger in 1874. Below sampling water form the a 24 bottle “rosette” on RRS Discovery in 2012.



Figure 4.5 An underway system for measuring $p\text{CO}_2$ in surface seawater. Seen on board MV Falstaff in 2002 operated by IfM Kiel, Germany, designed and built by JAMSTEC Japan.

permanent basis when and where possible. In Europe the work was supported by the EU-FP4 project CAVASSOO, in the USA by NOAA and in Japan by JAMSTEC.

These systems were in 2000 and still in 2012 remain complex and time-consuming to keep in operation at sea. They require regular maintenance by trained scientific and engineering staff, often each time the system arrives in port and frequently need to be adjusted and tested by a scientist sailing with the ship. The aim of the SNOMS project was to develop and then run a system that could be maintained by a small amount of effort from the ship’s crew and consequently required only infrequent visits from the scientists involved in the project. However a project’s scientists should put in some time on the ship, to help

give the crew a feeling of “ownership” and involvement in the effort.

4.2 SNOMS system evaluation, data products and interpretation

In this section we look at some of the finding so far from work on the data produced by the SNOMS system. We give answers to three main questions:-

- How reliable are the data from a low maintenance system?
- What is the evidence that SNOMS data will improve the reliability of future global budgets of the air-sea flux of CO₂?
- Does the SNOMS system provide valuable insight into the processes controlling air-sea gas exchange?
- Is knowledge emerging from the SNOMS system that contributes to the study of ocean acidification?

4.2.1 The SNOMS system is reliable and produces good quality data

In June 2007, the new SNOMS low maintenance system for measuring in-water pCO₂ was fitted to a ship-of-opportunity, the Swire Group CNCo *MV Pacific Celebes*. The system is based around the ProOceanus Inc. CO₂-ProTM and GTD-ProTM measuring devices mounted in a flow-through-tank flushed by surface seawater when the ship underway. The ship’s engineers maintain the cleanliness inside the tank. The CO₂-Pro continuously measures the mole fraction of CO₂ in an air stream that has equilibrated with seawater flowing through the tank and GTD measures the total pressure of dissolved gases within the water. To validate the system, samples for the determination of Total Alkalinity (TA) and Total Dissolved Inorganic Carbon (DIC) are collected each day the ship is at sea.

The reliability of the data is assessed in three ways, a paper on these comparisons is being written (Jiang et al., 2013b) :-

(1) On the basis of the underway and sample data collected on *Pacific Celebes* itself: The data from the water samples collected by the ships crew can be used to calculate a value for pCO₂ that can be compared with the value being recorded by the underway measurement system at the time the water sample was collected. This provides a check on the consistency of the data from the ProOceanus CO₂-Pro instruments over the periods of their use.

(2) By comparison to data obtained by NOAA: A system was operated by NOAA-PMEL laboratory on the same route at various times between 2004 and 2010. In late 2010 the SNOMS and NOAA ships crossed the Pacific on the same track on the same dates but in opposite directions so this data can be compared.

(3) In medium term laboratory tests on the whole SNOMS system: After the completion of the work on the *Pacific Celebes* the SNOMS system was transferred to Dalhousie University in Halifax, Canada. Tests were done there working with Prof. Wallace’s group. These tests were aimed at the development of a Dalhousie version of the SNOMS system. In these tests the SNOMS system was run along side new sensors for pCO₂ and pH and an equilibrator based system. The equilibrator-based system is regularly calibrated with standard gasses and so provides a reliable check on the performance of the other units.

(1) Consistency of the SNOMS measurements of pCO₂ made on board the ships and calculated from analyses of the crew-collected samples -

A first assessment was possible following SNOMS system’s first crossing of the Atlantic. The match between measured and calculated pCO₂ was 0.99 ± 0.03 . This confirmed that the system was performing at the level expected from it. The error between the two sets of measurements was less than has been found in the comparison data on the carbonate system collected on research ship cruises (Lamb et al., 2002). Assembly of a convincing data set for publication was hindered by inconsistent performance of the system until into 2009 shortly before the move of operations in the Pacific. The consistency of the data from the Pacific crossings has now been reviewed in detail by Jiang et al (2013b). After calibrating each crossing on the basis of the sample data the standard deviation between the adjusted CO₂-Pro data and the data for pCO₂ calculated from the sample data was ± 6.5

μatm ($n=180$) which is similar to the uncertainty in the calculated value which is $\pm 6.0 \mu\text{atm}$. This is very good agreement.

(2) Comparison of data from the SNOMS system and with that from the NOAA-PMEL system in the Pacific

Between October 2009 and March 2012 the *Pacific Celebes* made 9 return voyages between Australia/New Zealand and USA/Canada. The route between New Zealand and California coincided with a route that the NOAA-PMEL laboratory has been able to operate intermittently since 2004. All the data collected by the PMEL laboratory on the route have been made available to the Swire Student by Richard Feely, the project's principal-investigator at PMEL. Their operations are shown along side those of the SNOMS system in Table 4.1 below.

Table 4.1 Table indicating availability of data from the SNOMS and NOAA-PMEL operations **PMEL only**, **Celebes only**, **Both**. **PT(red) PC crossing number** when the routes between Long Beach New Zealand on same track as PMEL ship

	2004	2005	2006	2007	2008	2009	2010	2011	2012
Jan									PT17
Feb							PT3		PT18
Mar									
Apr							PT4		
May							PT5	PT12	
Jun								PT13	
Jul							PT6		
Aug							PT7	PT14	
Sep								PT15	
Oct						PT1	PT8		
Nov						PT1	PT9	PT16	
Dec						PT2	PT9		

The spread of the data obtained from two operations agrees well as shown in Figure 4.6 below. the data from 2004 to 2012 is currently being examined to determine the scale of intra- and inter-annual variations. In addition the scale of variation is being compared to the values predicted in the Takahashi Atlas (see later).

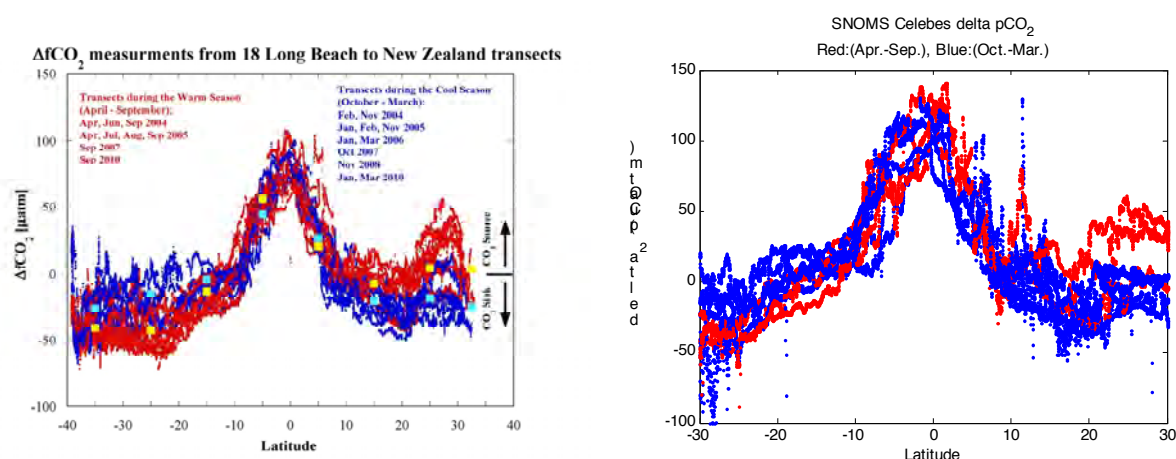


Figure 4.6 Latitudinal distribution of the air-sea CO_2 difference measured by the Celebes (right panel) compared to those measured by the PMEL (left panel). The data were divided into two periods: April-Sep. and Oct.-Mar. Higher $\Delta p\text{CO}_2$ were observed in the relatively warmer period: the April-Sep. in the Northern Hemisphere and Oct.-Mar. in the Southern Hemisphere, suggesting that water temperature rather biological activity is the dominant control of $p\text{CO}_2$ in these regions, at towards California the waters become a strong source of CO_2 to the atmosphere in summer.

In late 2010 both system were in operation at the same time. The PMEL system was installed on board the *MV Nathalie Schulte* (see Figures 4.7 and 4.8) below. The two ships left port heading in opposite direction within two days of one another and arrived three days apart at the other end of the track (*Pacific Celebes* 23/11 to 11/12/2010 and *Nathalie Schulte* 25/11 to 8/12/2010).



Figure 4.7 The *MV Nathalie Schulte* the ship used by NOAA-PMEL in 2010



Figure 4.8 General Oceananics™ type 8050 $p\text{CO}_2$ measuring system on board ship

The data for the temperature and salinity of the water suggest that the waters through which the ships passed changed little over the course of the voyages and were particularly close north of 10°S .

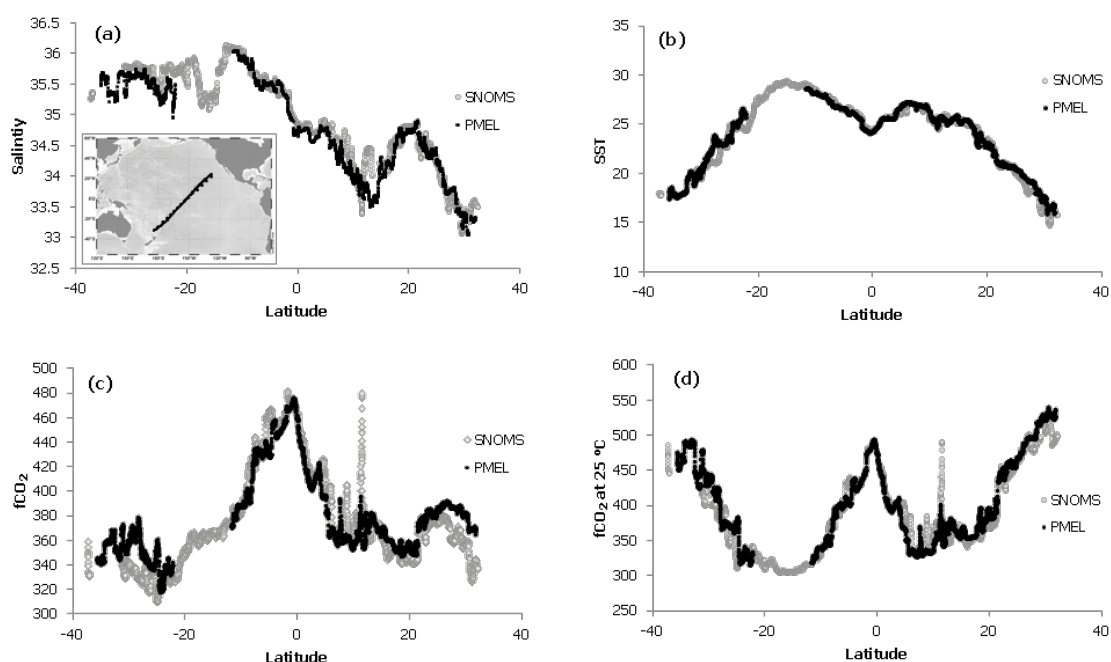


Figure 4.9 Comparison of data for surface water $p\text{CO}_2$ recorded by *MV Nathalie Schulte* and *MV Pacific Celebes* crossing the Pacific on the same route in November December 2010. Data are adjusted to the same temperature to adjust for temperature changes between the crossings that were made in opposite directions. Latitudinal distributions are shown (a) salinity, (b) SST, (c) $f\text{CO}_2$, and (d) temperature normalized $f\text{CO}_2$ at 25°C . Their routes were shown in the panel (a).

The $p\text{CO}_2$ data from the two ships are compared Figure 4.9 above. Given the actual separation between the two crossings the agreement is remarkably good. The mean difference between the data sets was $3.4 \mu\text{atm}$. This is actually better agreement than we found between the SNOMS underway data and the sample data and surprisingly good for data collected from two different ships. This

particularly so when the separation in time between the measurements is considered. This comparison confirms the quality of the data from the CO₂-Pro equipment.

(3) Validation in extended laboratory tests at the Aquatron Laboratory Dalhousie University

Because the ocean is a constantly swirling and poorly mixed soup the agreement shown in Figure 4X above is surprisingly good. The work in the Aquatron Laboratory has enabled us to carryout essentially similar tests in which the different instruments were measuring the same water. In these tests the complete SNOMS system was directly compared to an equilibrator based pCO₂ measurement system. This used a Licor 7000™ non dispersive infra-red detector for the precise measurement of concentrations of CO₂ in the equilibrated gas stream (kindly loaned by Helmuth Thomas) the same type of high precision detector is used in the PMEL system.

The Aquatron experiment was of similar duration to a SNOMS voyage and lasted over three months. The SNOMS instruments were serviced and recalibrated by ProOceanus before they were placed in the tank in May, 2012. During these tests the SNOMS tank system was operated as at sea with the tank being opened and rinsed with fresh water on average every 10 days. We were able to obtain data at environmentally realistic concentrations for the later two of the three months between July and September 2012. As on the *Pacific Celebes* samples of the water flowing through the systems were collected on a near daily basis for analysis of Total Alkalinity (TA) and Total Dissolved Inorganic Carbon (DIC) from which pCO₂ was calculated. (Over the key period 38 water samples were collected.)

A comparison of the different data sets is shown in Figure 4.10.

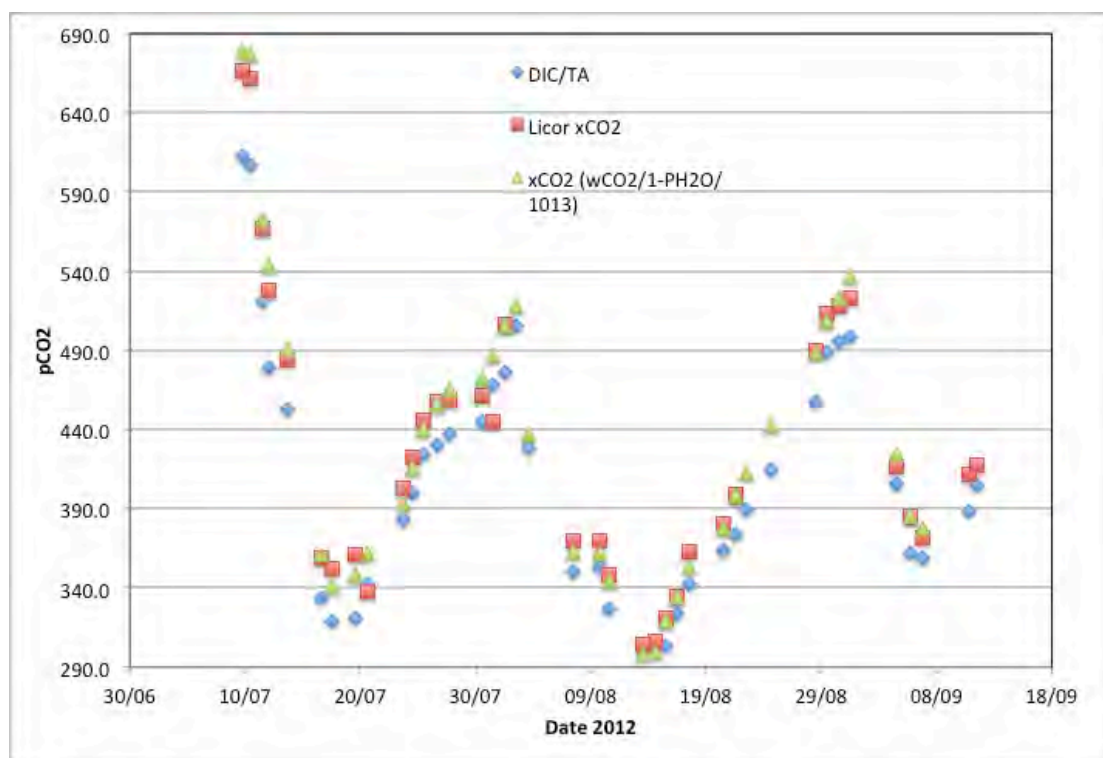


Figure 4.10 Aquatron Tests. Comparison of the data from the SNOMS system, the Licor-Equilibrators and pCO₂ calculated from the measurements of DIC and TA in water samples.

These data collected on the *MV Pacific Celebes* and *MV Nathalie Schulthe* and in Aquatron tests establish that the SNOMS system working with the ProOceanus CO₂-Pro™ is now a reliable system capable of providing data of good accuracy and precision over periods of operation in excess of three months. The initial targets for the SNOMS system have been fully met.

4.2.2 The SNOMS data will improve the reliability of future assessments global budgets of the air-sea flux of CO₂

Each voyage of the Pacific Celebes is being examined at the moment. A key point of interest is the degree to which the new in situ observations fit the model developed by Takahashi and his co-workers to extrapolate the existing sparse data to provide estimates of the likely change month by month across the surface of the ocean. Figure 4.12 shows an example preliminary comparison from data from one of the last voyages of the *Pacific Celebes* (PT18).

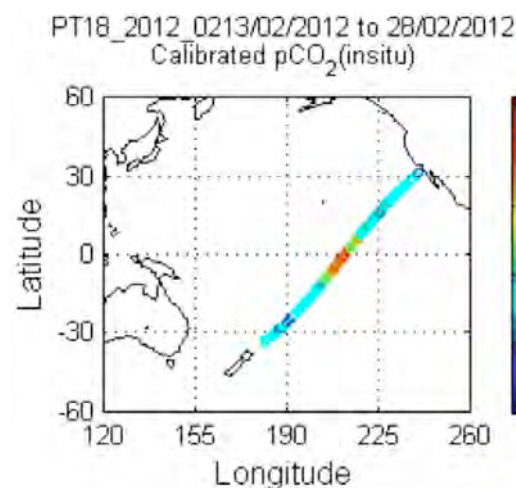


Figure 4.11 Map of the values of pCO₂ measured by the SNOMS system between 13 and 28 Feb, 2012.

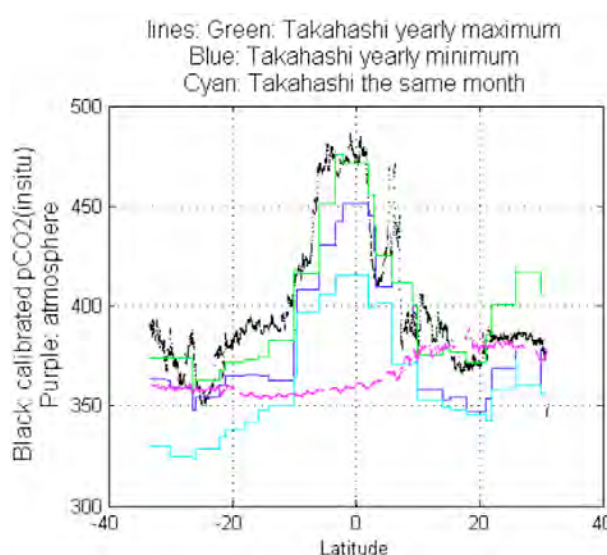


Figure 4.12 Plot with respect to the latitude along the track shown in Fig. 4.11 of the observed pCO₂ compared to the minimum and maximum values estimated along the track and the values estimated for February given in Takahashi et al., (2009).

In this case the values for February are tending to agree at both ends of the track where more data was available to Takahashi and the agreement is least good least data was available. For the data in the centre of the plot from the equatorial plume the in-situ data match the highest values expected by Takahashi. A general feature of the period covered by the new data from the *Pacific Celebes* is that the concentrations observed in the plume were consistently high being less variable than expected from the Atlas. A numerical assessment of these differences and their effect on the air-sea fluxes along the track for the period of the SNOMS and PMEL observations is being worked on at the moment.

An example of where the SNOMS work has been able to explain the differences between the observations and the expectation set out in the Takahashi Atlas is provided by one of the first SNOMS data sets which was studied from the North Atlantic.

Figure 4.13 shows a plot of surface seawater temperature and SNOMS pCO₂ data from the first crossing of the north Atlantic from Halifax to Livorno in August and September 2007. Delta pCO₂ is plotted. This is the difference between the concentration of pCO₂ in the atmosphere and surface sea water. If delta pCO₂ is positive the concentration in seawater is higher than in the air and there will be a net movement of CO₂ from the sea into the air. During this crossing it can be seen that delta pCO₂ is closely related to the temperature of the water to the east of about 20 °W. This is consistent with the predictions of the Atlas. It predicts that in summer, pCO₂ will be controlled by temperature along the route taken. However, the observed values of delta pCO₂ were negative in the western Atlantic basin. It is possible to explain this observation by taking into account biological activity. Estimates of chlorophyll-a and biological production were obtained from data from the SeaWiFS satellite along the track and in surrounding waters prior to and during the crossing (provided by Tim Smyth and Peter Miller at the Plymouth Marine Laboratory). The satellite data show that plankton had continued to bloom in the western basin into summer, during 2007. Consequently concentrations of CO₂ were lower than those estimated by the simple model used in the Takahashi Atlas work. That work assumes

significant growth of plankton only occurs in springtime, and that subsequent transfer of CO₂ into the sea from the air and increasing temperature of the water would have restored the deficit of CO₂ caused by the growth of plankton. Team work like this with groups making different types of observations is an essential part of making it possible to explain where data deviate from expectation.

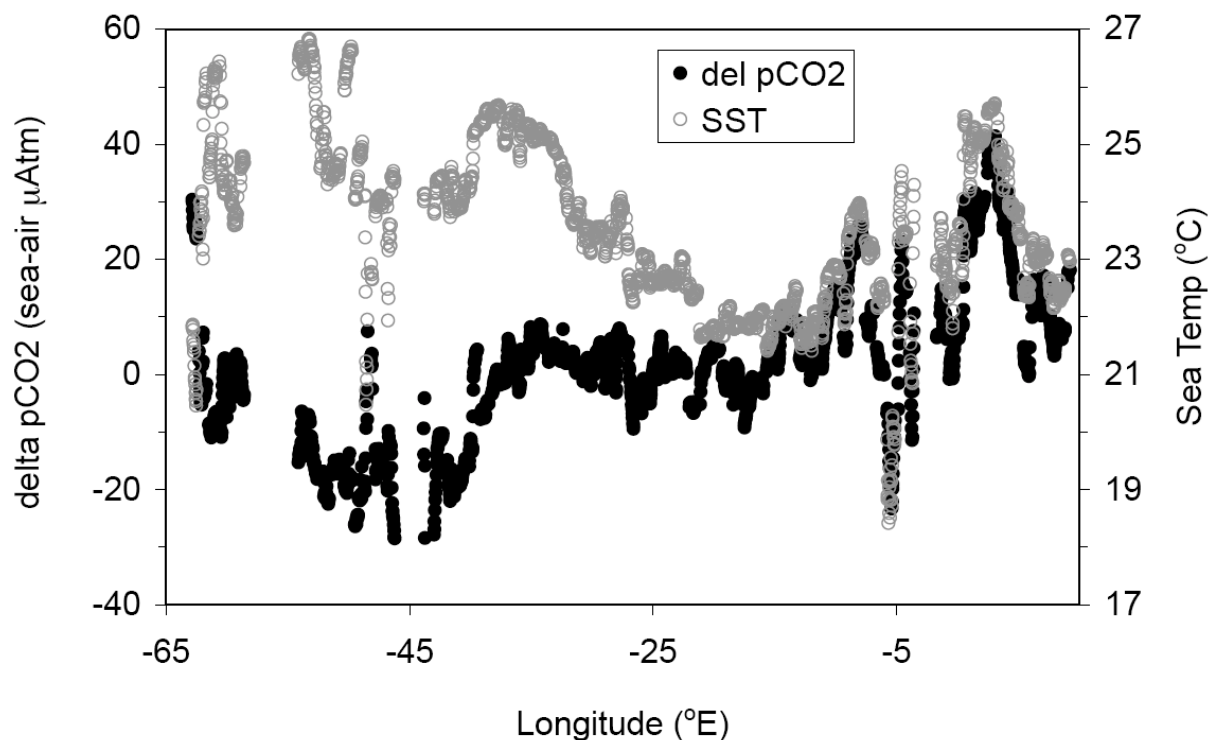


Figure 4.13 Data from the Pacific Celebes collected across the North Atlantic and eastern Mediterranean in August and September 2007. Values of sea surface temperature and delta pCO₂ (sea-air) are plotted relative to longitude along the track between Halifax in Canada and Livorno, Italy.

4.2.3 The SNOMS system provides valuable insight into the processes controlling air-sea gas exchange

The SNOMS system was developed to take the measurement of gas exchange processes further than the solely measuring levels of pCO₂. By adding measurements of total dissolved gas pressure a more accurate adjustment of the value of pCO₂ measured inside the ship can be made to true conditions outside the ship. Other systems assume the dissolved gas pressure is the same as the air pressure. However as we showed in the paper mentioned below it can be around 10 % different in storm conditions. It can also be substantially different in calm conditions when the sea surface is warming rapidly. By measuring oxygen we obtain data on biological production that is stoichiometrically related to the amount of CO₂ that has been taken up from or released to the water by primary biological production or respiration of organic matter.

The first SNOMS paper to be published appeared in the Journal of Operational Oceanography (Hydes et al., 2008). It is based on data collected during tests of the completed system that were carried out on board the P&O ferry the *MV Pride of Bilbao* in 2007. The paper examined the performance of the system with respect to measurements of concentrations of dissolved oxygen and the estimation of concentrations of dissolved nitrogen calculated from measurements of total dissolved gas pressure and dissolved oxygen. The markedly different weather conditions experienced during these tests enhanced the interest of the data sets. Weather states ranging from calm seas to storm conditions were encountered over the 22 days of the tests. In addition the paper showed how the data set from SNOMS system could be linked with information from other data collection systems operating in the area to interpret the observations. The sources of data used were:- (1) From the SNOMS system - measurements of temperature, salinity and dissolved gas concentrations (2) From the FerryBox system

- measurements of chlorophyll-fluorescence and dissolved nutrients; (3) From UK Met Office and Meteo France data buoys - data for wind speed and direction and wave height (4) From Argo floats - data on depth of the surface mixed layer. (5) From a numerical model of the hydrography - data on surface currents.

Two findings came from examining the data. Firstly, that the sustained winter storms at the start of the observations period had increased the saturation of dissolved nitrogen to levels only previously observed during hurricane conditions. The high dissolved nitrogen concentrations are shown in Figure 4.14. Secondly, we confirmed that measurements of dissolved oxygen in a ship of opportunity system are an effective way of determining biological production. The observed increase in the oxygen concentration anomaly closely matched the observed changes in concentrations of nutrients and changes in temperature of the water.

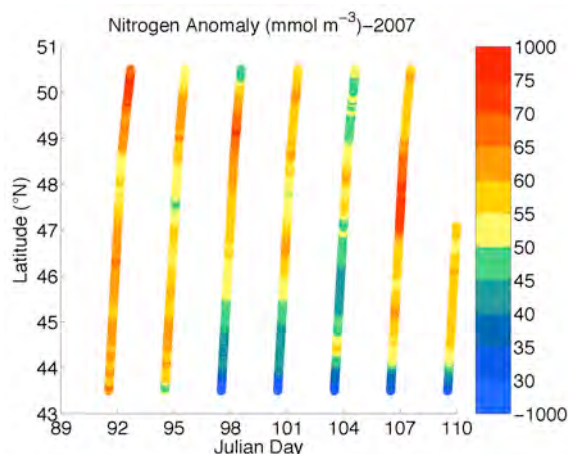


Figure 4.14 Data from the SNOMS trials on the P&O Pride of Bilbao - April 2007. Dot plot of the calculated anomaly in the observed concentration of dissolved nitrogen (DN) relative to the equilibrium saturation concentration at the in-situ temperature and salinity of the water. Data are from north bound crossing during which the route of the ship is less variable than when south bound. DN values are calculated from the measurement of total dissolved gas pressure measured by the SNOMS GTD instrument.

This work demonstrated the considerable added value that can be gained from adding extra sensors for dissolved oxygen and total dissolved gas pressure to a underway system principally designed for measuring pCO₂. The physical design of the flow through tank used in the SNOMS system makes addition of these measurements easy to do. The paper in the Journal of Operational Oceanography also demonstrated the real progress that is now being made in linking a range of *in-situ* data sets and numerical models.

4.2.4 SNOMS alkalinity data helps the assessment of ocean acidification.

The absorption of anthropogenic CO₂ by the oceans is now recognised as a two-edged sword. The process is slowing down the rate of accumulation of CO₂ in the atmosphere and is therefore reducing the immediate impact of CO₂ on climate as a green house gas. On the other hand as the ocean takes up more CO₂ it is becoming more acidic.

An important contribution to value of the SNOMS data set has been provided by the data from the daily samples collected by the ship's crews. The Total Dissolved Inorganic Carbon (DIC) and Total Alkalinity (TA) contents of these samples have been measured at NOC. It is the concentrations of these two components in a water that along with the temperature determine the actual pCO₂ and pH of that water. The alkalinity of a water can be considered to provide its "buffer capacity" - its resistance to change. When a water with a high alkalinity absorbs CO₂, for the same amount of CO₂ absorbed the pCO₂ increases less than in a water with lower alkalinity. As a general rule the alkalinity of water is directly proportional to the total amount of salt in the water - its salinity. However as more data are collected across the ocean we are beginning to identify regions where this is not strictly true.

Presently, direct measurement of ocean acidity is problematic because it is difficult to measure pH with the accuracy and precision needed to monitor the on-going changes in the ocean. Methods of measuring pH are improving and some laboratories can make measurements to the required high levels of precision. However, an appropriate record of historical changes in pH does not exist. A solution is that historical values pH can be calculated if the pCO₂ and alkalinity of the water are known. SOO operations now provide historical records of pCO₂ that extends back for a decade or more in some regions. So if the associated alkalinity in the water at the time of the measurements of pCO₂ is known a record of change in acidity can be arrived at. Unfortunately, much of the data collected for pCO₂ does not have associated data on alkalinity to go with it. The SNOMS data for TA in the

samples collected by the ship's crew and their wide global coverage are contributing to improving to a knowledge of how well TA can be estimated from measurements of salinity in different regions and therefore a knowledge of how reliably pH can be estimated from measurements of pCO₂ in different regions.

In the SNOMS data it possible to distinguish areas of the ocean in which the existing equations for the estimation of alkalinity work well and those areas in which significant anomalies exist. For example the alkalinity in the Mediterranean is higher than predicted and the Red Sea lower. A scientific paper reviewing these observations is being prepared (Jiang et al., 2013c). The data from the Pacific crossings shown in Figure 4.16, is one area of interest. When the alkalinity signal is adjusted for the change in the salinity of the water (normalised to salinity of 35) the plotted value of nTA₃₅ reveals that the alkalinity north of the equator is effectively increasing progressively towards the coast of N. America. Possible causes of this change may be high concentrations of alkalinity in the major rivers that enter the North Pacific along this coast or it may be a combination of this with the upwelling of deeper more alkaline waters that is known to occur in this region. The effect of this increase in alkalinity is to buffer these waters resulting in slower change in their acidity as the take up CO₂ each year. The SNOMS data helps to identify that this anomaly exists over a wide region of the N. Pacific.

This a clear demonstration of how simple tasks performed well each day by the crews of the *Pacific Celebes* greatly enhanced the scientific value of the SNOMS project.

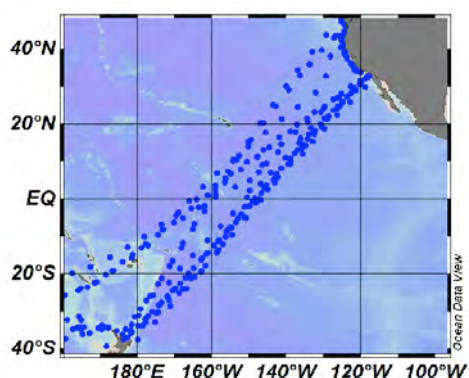


Figure 4.15. Positions at which TA samples were collected by the Pacific Celebes crews between Australasia and N. America.

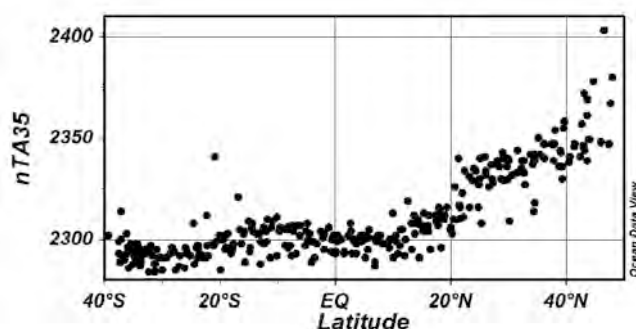


Figure 4.16 Values of TA adjusted to a salinity of 35 in the samples collected at the positions shown in Fig. 4.15. The progressive increase in nTA₃₅ north of 20°N is a significant finding in the SNOMS data.

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