ESA Support to Science Element

Pathfinders OA – Final Report

ESA Contract No. 4000110778/14/I-BG

Deliverable: D-12

FINAL

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STSE Pathfinders OA

Final Report

Customer	ESA / ESRIN
Authors	PML, IFREMER
ESRIN Contract Number	4000110778/14/I-BG
Document Reference	Pathfinders OA D12
Version/Rev	1.1
Date of Issue	08/01/2017

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AMENDMENT HISTORY

Version	Date	Change Description	Author
1.0	31/10/16	Structure and content	Jamie Shutler
1.1	08/01/17	Updated based on ESA feedback	Jamie Shutler

DISTRIBUTION

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Contents

1. Introduction

Since the beginning of the industrial revolution humans have released approximately 500 billion metric tons of carbon into the atmosphere from burning fossil fuels, cement production and land-use changes. About 30% of this carbon dioxide has been taken up (or absorbed) by the oceans. The oceanic uptake of carbon dioxide leads to a change in marine carbonate chemistry resulting in a decrease of seawater pH and carbonate ion concentration, a situation which is commonly called 'Ocean Acidification' (OA).

To date, the majority of the scientific studies into the potential impacts of OA and efforts for monitoring the effects of OA have focussed on the use of models and in situ studies (such as buoys, research cruises and lab or field based mesocosm studies). Space observations from satellite Earth observation (EO) have yet to be fully exploited and could play an important role in this area of science through providing quasi-synoptic, reproducible and well-calibrated measurements for investigating processes on global scales.

We propose to deliver a feasibility study, called *Pathfinders-OA*, to evaluate the role that satellite EO can play in supporting and expanding OA research. We propose to achieve this by bringing together multidisciplinary expertise and capability in:

- Marine carbonate chemistry (*in situ* and numerical modelling)
- Marine EO (active and passive sensors)
- Algorithm development and validation
- Efficient data processing

Pathfinders Ocean Acidification (OA) aims to exploit Earth Observation (EO) data to quantify parameters required for OA research. It will implement existing algorithms and generate new ones in five geographical regions (global, Arctic seas, Bay of Bengal, The greater Caribbean and the Amazon Plume), find which algorithms perform best in each region and validate the algorithms using in situ data and model output. The result will be a set of regional algorithms and monthly datasets of EO derived pH and aragonite saturation state (Ω_{ar}).

Purpose and Scope of the Final Report

This is the Final Report (FR) (deliverable D12) for the Pathfinders Ocean Acidification (OA) project. It is intended to satisfy the original requirements for the Final Report specified by the ESA [SOW]. It is intended that this document presents the mains aims and objectives of the project and then provides a detailed overview of the advancements and achievements that have been made within Pathfinders Ocean Acidification.

Structure of this Report

The report is structured as follows:

- Section 1 (this section) the introduction gives an overview of the document aims and structure.
- Section 2 contains the objectives and intended benefits.
- Section 3 contains the Pathfinders OA final report.
- Section 4 contains the priority areas for future work as identified by the project, partners and discussions.
- Annexs provide copies of publications and abstracts.

Contributions

The table below details the people who contributed to this report and the sections that they contributed to.

Table 1 Table of contributions.

Section	Primary author(s)	Contributing author(s)
Section 1	Jamie Shutler (UoE)	
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Reference documents

This document makes reference to the documents listed in Table 2.

Table 2: Documents Referred to in this Report

Reference	Document
[SoW]	Pathfinders-OA Statement of Work 4000110778/14/I-BG Support to Science Element Pathfinders Ocean Acidification
[RB]	Pathfinders Ocean Acidification Reference Baseline.
[RB-Annex2]	Pathfinders Ocean Acidification Literature review.
[ATBD]	Pathfinders Ocean Acidification Algorithm Theoretical Basis Document.
[IAR]	Pathfinders Ocean Acidification Impact Assessment Report.

Definitions and acronyms

AATSR	Advanced Along Track Scanning Radiometer (ESA instrument)
ATBD	Algorithm theoretical basis document
A_T	Total alkalinity
AVHRR	Advanced Very High Resolution Radiometer (NOAA instruments)
CARINA	CARbon dioxide IN the Atlantic Ocean
CCI	ESA Climate Change Initiative
Chl	Chlorophyll-a
CLIM	Climatology
CMIP5	Climate Model Inter-comparison Project 5
CORA	Coriolis Ocean Dataset for Reanalysis
CO_2	Carbon dioxide
DIC	Dissolved inorganic carbon
ECMWF	European Centre for Medium-Range Weather Forecasts
Envisat	Environmental monitoring satellite
EO	Earth observation
EOS	Earth Observing System
ERSEM	European Regional Seas Ecosystem Model (and now global oceans ecosystem model)
ESA	European Space Agency
EUMETSAT	European Organization for the Exploitation of Meteorological Satellites
FTP	File transfer protocol
GLODAP	Global Ocean Data Analysis Project
GOA-ON	Global Ocean Acidification Observing Network
GOOS	Global Ocean Observing System
HADGEM2-ES	Hadley Centre Global Environment Model version 2 - Earth System
IPCC	Intergovernmental Panel on Climate Change
ITT	ESA invitation to tender
KO	Project kick off (November 2012)
LDEO	Lamont Doherty Earth Observatory
MERIS	Medium Resolution Imaging Spectrometer (ESA instrument)
MLD	Mixed layer depth
MODIS	Moderate Resolution Imaging Spectrometer (NASA instrument)
NASA	National Aeronautics and Space Administration (US)
NEMO	Generalised European oceanic physics modeling framework
NIVA	Norsk Institutt for Vannforskning, Norway
NOAA	National Oceanographic and Atmospheric Administration (US)
NSF	US National Science Foundation
$npCO_2$	pCO_2 normalized to a standard temperature
OA	Ocean acidification
OAPS	Ocean Acidification Product Suite
OSI-SAF	EUMETSAT Ocean & Sea Ice Satellite Application Facility
pCO_2	Partial pressure of CO_2

pH	Acidity (or basic) scale
PIC	Particulate inorganic carbon
PML	Plymouth Marine Laboratory
PMP	Project Management Plan
POC	Particulate organic carbon
RA2	Radar altimeter 2 (ESA instrument)
RMSD	Root Mean Squared Difference
RMSDe	Normalized Root Mean Squared Difference
Rrs	Remote sensing reflectance
SCOT	ESA special conditions of tender
SMOS	Soil Moisture and Ocean Salinity (ESA satellite)
SOCAT	Surface Ocean CO_2 Atlas
SOM	Self organizing map
SOOP	Ship of Opportunity Programme
SoW	ESA statement of work
SSM/I	Special Sensor Microwave/Imager
SSS	Sea surface salinity
SST	Sea surface temperature
STSE	Support to Science Element
Sv	Sverdrups (a unit of volume transport)
US	United States of America
WP	Work package
WPD	Work package description
WOA	World Ocean Atlas
ΔpCO_2	Difference between in-water pCO_2 and atmospheric pCO_2
Ω_A	Aragonite saturation state

2. Introduction to Ocean Acidification

The latest IPCC report (AR5) highlights that the ocean has absorbed about 30% of the emitted anthropogenic carbon dioxide (CO_2) (IPCC, 2013). This CO_2 addition into the surface ocean has caused a shift in the seawater carbonate system (Figure 1), termed Ocean Acidification (OA), resulting in a 0.1 unit decrease in pH (a 26% increase in acidity) and a 16% decrease in carbonate ion concentration since the industrial revolution (Fabry et al., 2008). Recently there has been recognition that OA is not occurring uniformly across the global oceans, with some regions (e.g. polar oceans) having faster rates of acidification than others (e.g. Turley et al., 2010) and regional hydrodynamics causing local acidification events on seasonal time-scales (e.g. upwelling, Feely et al., 2008). However, the overall cause of OA remains consistent: adding CO_2 into the oceans, and as such, remains a global issue. Continual emissions of CO_2 into the atmosphere over the next century have been projected to cause a continued decrease in average surface ocean pH by as much as 0.32 units (RCP8.5 scenario) by the end of the 21st Century (IPCC, 2013). The seawater carbonate system is relatively complex (Figure 2), however the important parameters required to monitor and assess OA are pH (basity) and calcium carbonate saturation state (Ω), with aragonite generally considered to be the most important calcium carbonate mineral to be monitored for OA because of its relevance to marine organisms and its relative solubility. Aragonite saturation state Ω_A is important because many marine organisms use aragonite to form shells and structures. Thermodynamically aragonite minerals form when seawater is oversaturated with calcium and carbonate ions ($\Omega_A > 1$) and dissolve when seawater becomes undersaturated with these ions ($\Omega_A < 1$). There has been some experimental evidence that there is a relationship between organisms building and maintaining their calcium carbonate shells and calcium carbonate saturation state (Kroeker et al., 2013).

One of the major concerns with ocean acidification is that it will affect these calcifying marine organisms, and this will not only reduce biodiversity (Widdicombe and Spicer, 2008) but will have knock-on effects for the food chain, and protein supply for humans (Turley et al. 2010), but additionally for the functioning of the ecosystem and feedbacks to climate (Ridgwell et al. 2009). Without knowledge of the current state of the oceanic carbonate system, as well as the ability to detect and monitor ocean acidification, we would be unable to know whether our efforts to reduce CO_2 emissions are working, and increasingly importantly, how to manage adaptation and mitigation in the instance that CO_2 emissions are not drastically reduced. Therefore there is an urgent need to develop monitoring and detection tools, locally, regionally and globally.

The carbonate system can be understood and probed through four key parameters, total alkalinity (T_A), dissolved inorganic carbon (DIC or C_T), fugacity of CO_2 (fCO_2) and basity (pH). The relationships between the different carbonate system parameters are fundamentally controlled by thermodynamics, so knowledge of the salinity and temperature is key to fully understand the system. In principle knowledge of any two of the carbonate parameters is sufficient to enable the complete system to be determined These characteristic enable remote sensing and Earth observation to support this important area of science and were the starting point of the Pathfinders-OA project. Salinity and temperature can now both be observed from space, which combined with empirical algorithms can enable two of the carbonate system parameters to be determined (A_T and C_T), in turn enabling the complete carbonate system to be studied.

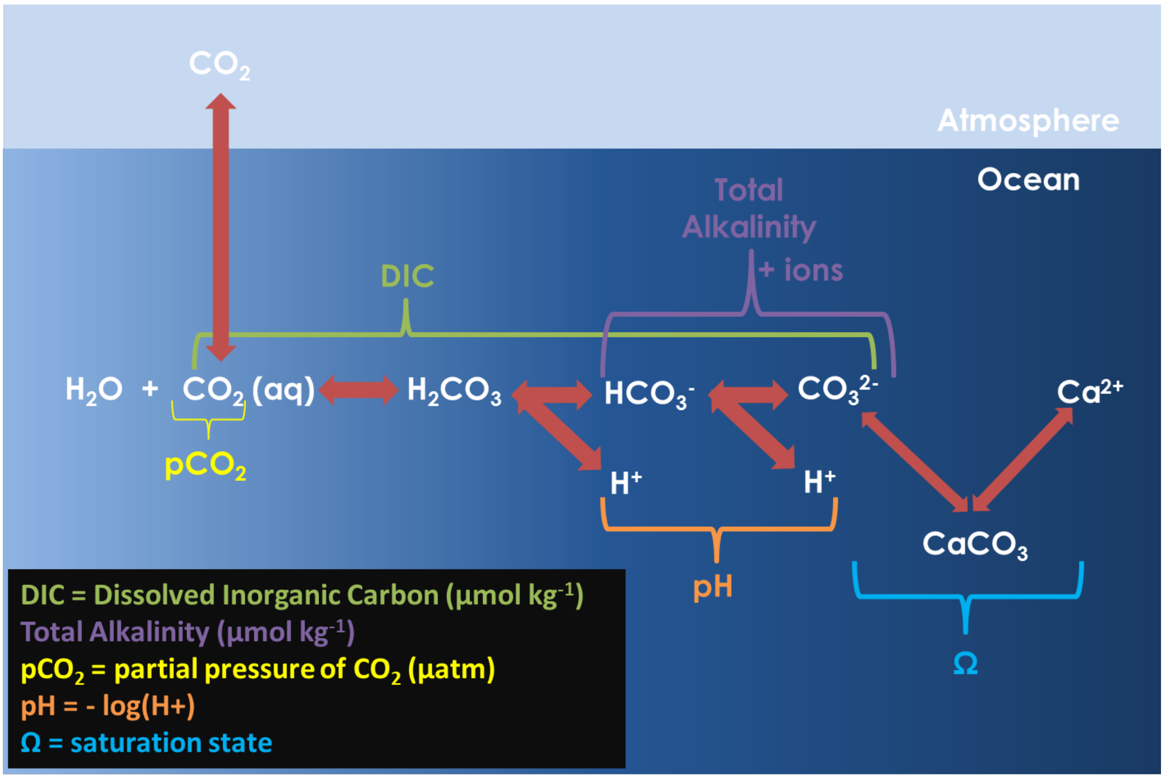


Figure 1 Overview of the seawater carbonate system, illustrating the reaction of carbon dioxide (CO_2) with water (H_2O) to form carbonic acid (H_2CO_3), which dissociates to form bicarbonate (HCO_3^-) and hydrogen (H^+) ions. HCO_3^- can further dissociate to carbonate ions (CO_3^{2-}) and H^+. Whether calcium carbonate mineral forms or dissolves is dependent on the concentrations of CO_3^{2-} and calcium ions (Ca^{2+}) and this is often monitored by the saturation state (Ω). DIC (or C_T) is the sum of all the carbon species, total alkalinity (A_T) is the sum of all the ion species, and pH is the measure of hydrogen ions (acidity). Measuring any two of the four "key" parameters (DIC/C_T, A_T, pCO_2 or pH) can be used to calculate the remaining components of the carbonate system.

3. Objectives and intended benefits

From the [SoW]: the Support To Science Element (STSE) Pathfinder projects focus on:

[obj-1] Exploring the potential offered by the synergistic use of existing Earth Explorers (GOCE, CryoSat and SMOS) al- so in combination with other ESA or non-ESA satellite data sets;

[obj-2] Maximise the scientific exploitation of the synergies offered by the ESA historical archives (including ERS-1, ERS-2, Envisat data and Third Party Missions (TPM) also in synergy with non-ESA satellite data;

In this context, the Pathfinder project should address at least one of the following points:

[obj-3] Novel products and innovative retrieval methods: Develop novel products and innovative retrieval methods exploiting in a synergistic manner different existing ESA EO missions and datasets also in combination with non-ESA satellite data.

[obj-4]New Earth Science Results: Exploiting multi-mission observation capacities offered by different ESA missions (also in combination with non-ESA satellite data) to address key open questions in Earth system science advancing our knowledge of the Earth system and its processes.

As clarified above, the core of this activity is the synergistic use of different satellites data. However, in addition, their combination with in-situ and airborne data and models is also considered.

In the medium and long-term, this activity aims at contributing to develop a new generation of EO products, novel scientific results and future applications maximising the complementary capabilities of the ESA and non-ESA multi-mission capacity.

The above were the generic objectives for all STSE Pathfinder projects. From the submitted proposal, the main outputs and objectives specific to the Pathfinders-OA project were (and that map directly onto the generic STSE Pathfinder objectives) were:

[obj-5] New validated multi-sensor products complete with uncertainty information.

[obj-6] Positive impact from the international OA community.

[obj-7] Improved understanding of the issues involved in future systematic monitoring of O.

[obj-8] Increased uptake of ESA and third party mission EO datasets.

[obj-9] Clear scientific roadmap for future activities in OA research and monitoring.

[obj-10] At least three peer reviewed journal publications.

4. The pathfinders Ocean Acidification project

Challenges and advances – The Pathfinders-OA narrative

Biogeochemical drivers

The Pathfinders-OA project began with a large review of all of the published empirical algorithms for T_A, C_T, fCO_2 (or pCO_2) and pH. This meta-analysis not only identified existing empirical algorithms but also identified regions that could potentially be studied. Figure 2 (reproduced from Land et al., 2015) shows the regions where empirical algorithms were available and thus identifies the regions where the greatest analysis could be achieved. This meta-data analysis and the potential of using space based salinity observations to support ocean acidification research was then highlighted to the international community in the first project journal publication and media output (Land et al., 2015, see section 4.3 below for papers and media outputs). From this analysis five regions of focus were chosen; these were deliberately chosen to include regions of importance for OA monitoring, but also regions where salinity from space observations were well characterised and regions where salinity retrievals from space were know to be complex and problematic.

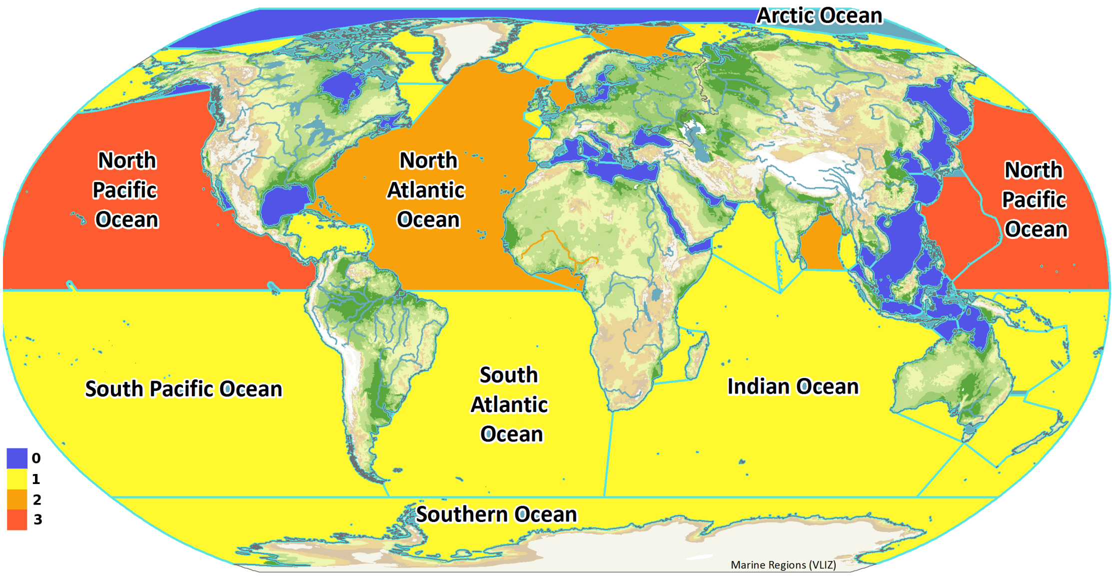


Figure 2. The number of key carbonate parameters (fCO_2 or PCO_2, T_A, C_T, pH) for which regional algorithms exist in the literature that can be implemented using just satellite Earth observation data.

A large data collation exercise followed to collate and consistency check all of the freely available in situ data that could be used to evaluate each of algorithms in each region. This included the need to cross check for duplicate data (e.g. data from the same cruise/ship/date/time that appeared as different values in different datasets). The large round-robin inter-comparison for each region and model (in this context a 'model' hereafter refers to a specific algorithm and input data pairing) was then performed for the global, Great Caribbean, Bay of Bengal and Amazon plume regions (on the global

1° × 1° degree gridded data). The Arctic analysis was performed last (on the 25 km × 25 km polar stereo graphic grid) and all results were presented at various international meetings and workshops, and a second journal paper was submitted for review (see section 4.3 below).

Following feedback from the international meetings and the journal paper review comments it was clear that the sparsity of the in situ data itself could potentially bias the results. For example, consider the plausible situation in which all models perform poorly in coastal waters. All else being equal, a model that does not use coastal observations will produce better statistics than one that does. Therefore the analysis was re-visited and revised to include both the traditional approach (evaluate each model with all possible in situ data, RMSD) and one that normalizes the results based on the available in situ data and its spatial coverage (RMSDe). The details of this A_T and C_T analysis are captured and used within the revised journal paper (Findlay et al., in-review) for Global, Bay of Bengal, Greater Caribbean and Amazon Plume areas. Whereas Annex 4 gives the A_T and C_T results for the Arctic region and Annex 5 gives pCO_2 results for all regions. Annex 6 gives a detailed description of the datasets and methods for the round robin exercise.

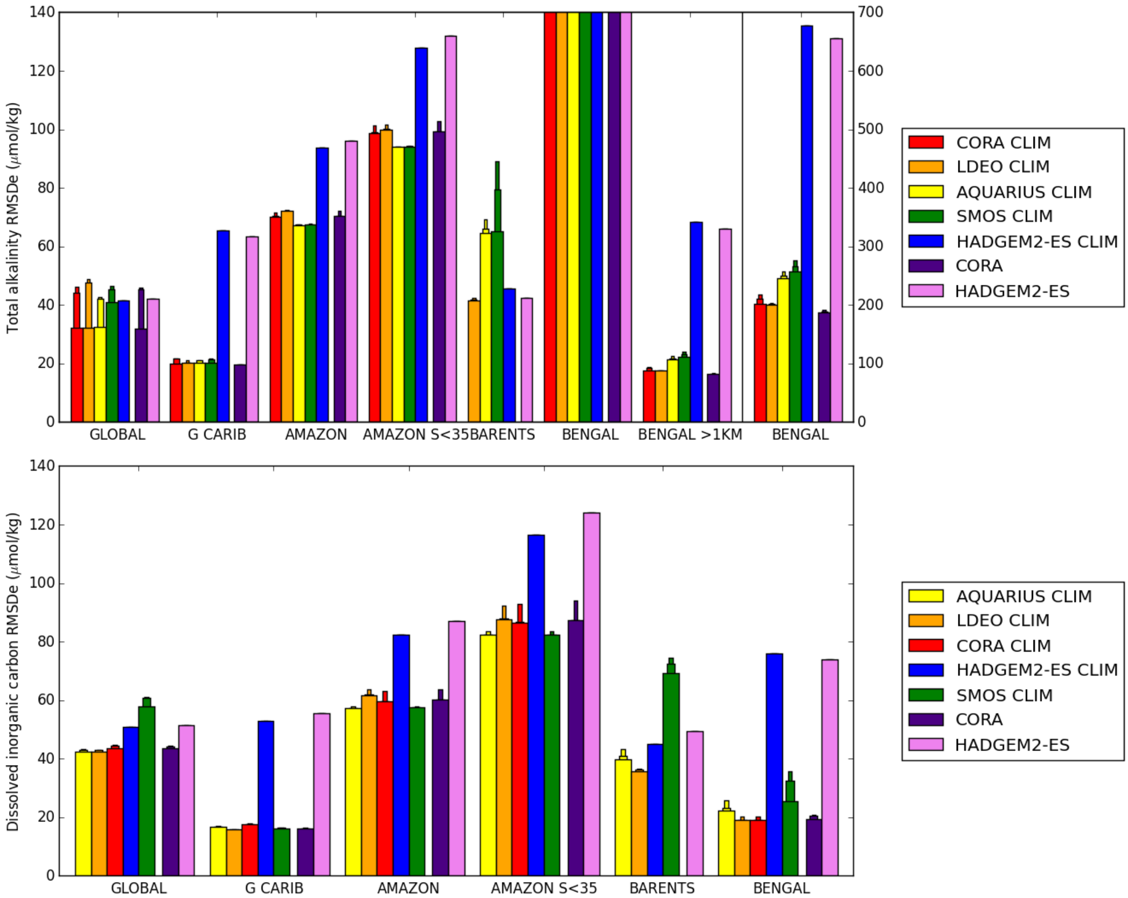


Figure 3 The overall A_T (top) C_T (bottom) normalised root mean squared differences across all models (algorithm and input pairing) grouped by region and chosen salinity input. The normalised approach allows the A_T and C_T results between regions to be compared (care should be taken when comparing across regions).

The analysis demonstrated the suitability of using empirical algorithms to calculate total alkalinity (A_T) and total dissolved inorganic carbon (C_T), assessing the relative performance of satellite, interpolated *in situ*, climatology and HadGEM2-ES Earth system model datasets in reproducing the wider spatial patterns of these two variables. Both A_T and C_T *in situ* data are reproducible, both regionally and globally, using salinity and temperature datasets, with satellite observed salinity from Aquarius and SMOS providing performance comparable to other datasets for the majority of case studies, and significantly better in the Amazon plume (both low and high salinity) – see figure 3. Use of satellite data inputs for the Bay of Bengal region and Arctic Barents Sea were less successful which highlighted both satellite and in situ data limitations in these regions. Only one published pCO_2 algorithm was found and regional performance is acceptable for some applications (Annex 5), whilst very few pH in situ data and a complete lack of empirical algorithms made the assessment of pH algorithms or the development of novel ones, impossible. Figure 4 shows an example annual mean A_T derived from SMOS observations as input to an empirical model. The square pixels represent the data points were comparisons were possible for this particular region within the round-robin inter-comparison.

The clear success in the approach of using Earth observation to drive empirical A_T and C_T algorithms means that it is now possible to produce spatially resolved monthly estimates of A_T and C_T, along with all other components of the carbonate system including pH and Ω_A (the latter two can be calculated using of A_T and C_T along with temperature and salinity data). Importantly the uncertainties in these spatially resolved estimates are also characterised. Figure 5 shows the example results for deriving A_T and C_T and then calculating the remainder of the marine carbonate system allowing pCO_2, pH and Ω_A to be calculated.

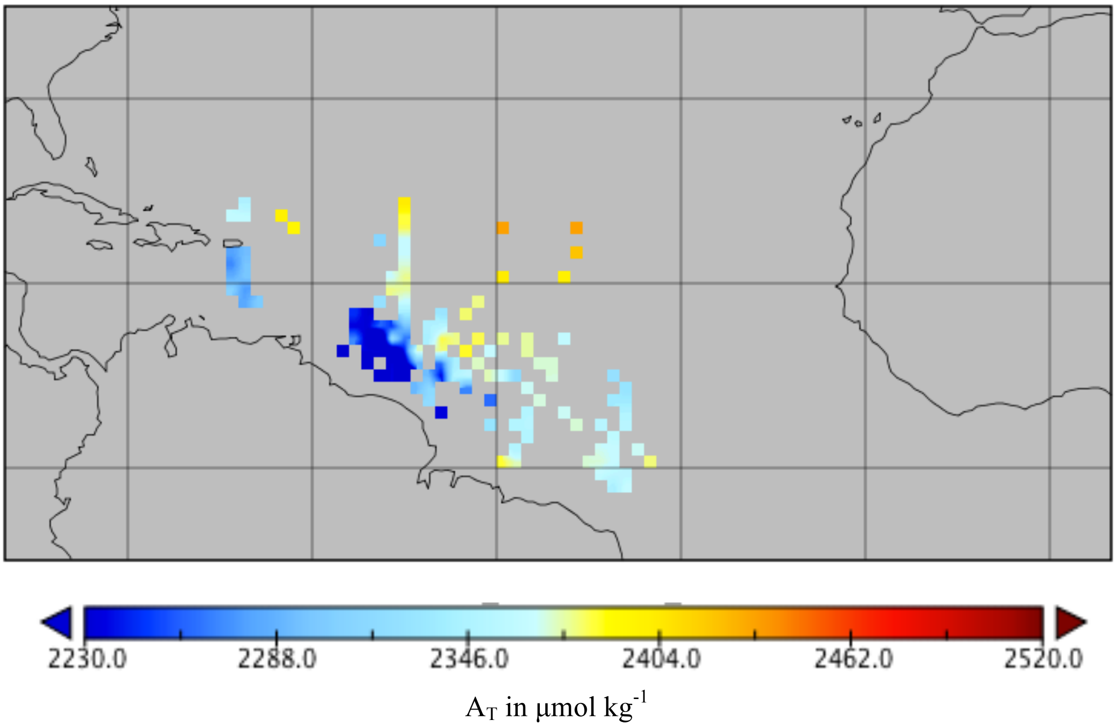
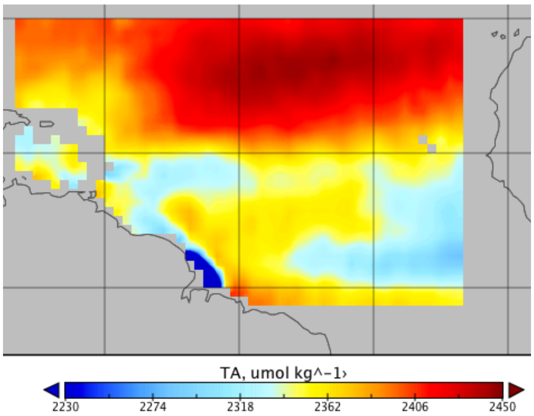
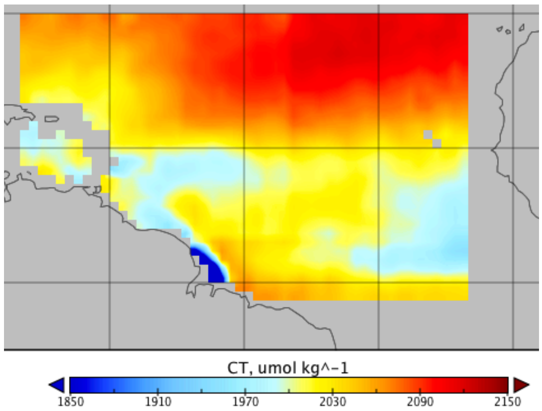


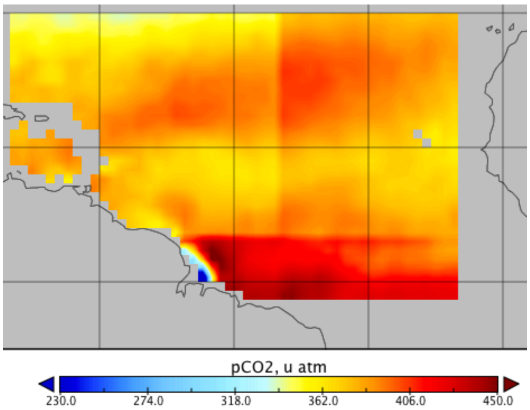
Figure 4 An example SMOS salinity driven model annual mean A_T in µmol kg^{-1} (empirical algorithm used Takahashi et al., 2014) for the Amazon region showing the common data points used within the round robin inter-comparison exercise.



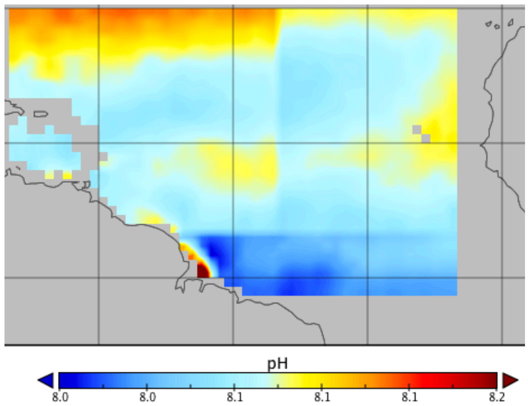
a) A_T



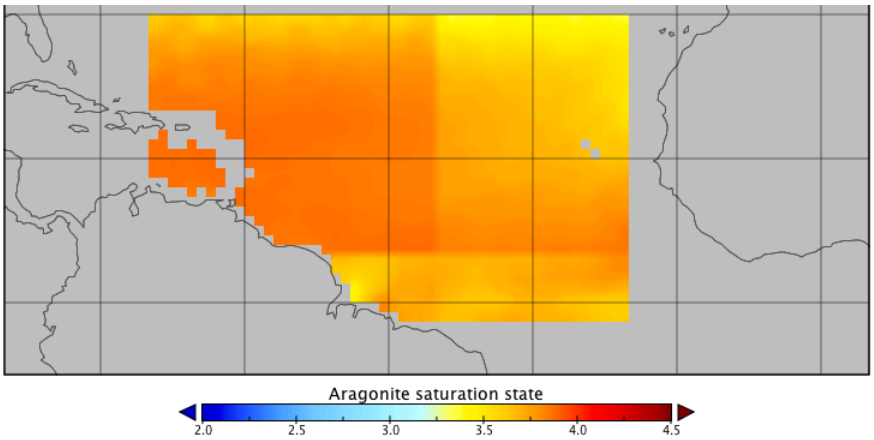
b) C_T



c) pCO_2



d) pH



e) Ω_A

Figure 5 Example Aquarius (satelilite observed) salinity driven model outputs for the Amazon region, derived using the best model (algorithm and input pairings) as identified for this region by the round robin exercise; a) A_T (µmol kg^{-1}), b) C_T (µmol kg^{-1}), c) SeaCarb derived pCO_2 (µatm) calculated using A_T and C_T and Aquarius salinity and temperature, d) the equivalent SeaCarb derived pH, e) the equivalent SeaCarb derived in aragonite saturation state (Ω_A).

Physical drivers

All of the work described so far has focussed on the biogeochemical parameters of the marine carbonate system that are of interest for studying ocean acidification. In parallel to this work and for studying one of the possible physical drivers of ocean acidification a novel remote sensing upwelling indicator method was developed based on known physical oceanography and ocean-atmospheric interactions. It was initially intended to derive an experimental upwelling algorithm for the Amazon Plume region, but it was later decided to produce a global result since the method and input data appeared to be very robust. The indicator data provides the potential to evaluate the distribution of episodic upwelling events, such as hurricanes, storms, frontal- and eddy-driven upwelling. The data also identify processes that lead to vertical fluxes of properties across the base of the surface mixed layer (ML) of the ocean and possible perturbation of the mean state of surface parameters. This work was written up into a technical report (Quilfen et al., 2016, see section 4.3 and appendix 3).

The future

Whilst all of this work was being carried out the project team also developed an extensive roadmap for future research and opportunities. This roadmap (3-5 year vision) contains content discussed at project meetings, external meetings and conferences, along with ideas that build upon the achievements from Pathfinders-OA. The roadmap contains individual process and algorithm studies and also identifies regions where we could now trial the routine provision of data to help support OA research and monitoring. Each of these trial areas has a clear societal linkage and justification for this data provision. Furthermore, the process and algorithms studies have been designed so that the outputs from these will help support and enhance the regional data provision. Two concept ideas for potential OA satellite missions are also presented and included here are the scientific meta-analysis that would form the first stage of any mission feasibility study.

The process and algorithm studies section importantly identifies the potential to improve and refine the SMOS global estimates of A_T and C_T and the exploitation of NASA Soil Moisture Active Passive (SMAP) data. The similarity of the SMOS and Aquarius sensors suggest that they should exhibit similar performance and provide similar capability, yet Aquarius driven models appear to outperform SMOS for global A_T and C_T (see figure 3). The demise of Aquarius in 2015 means that SMOS and SMAP are the only sensors in orbit capable of providing global salinity from space observations. Therefore attempts to improve SMOS (and test SMAP) global A_T and C_T retrievals have the potential for considerable impact and exploitation e.g. such data could be used for evaluating Earth System models (ESM) as used in the international Coupled Model Inter-comparison Project (CMIP) series of experiments and provide input to future IPCC assessments. The Pathfinders-OA project has already identified the potential for this within Findlay et al., (in-review) which included the evaluation of the HadGEM2 ESM.

The following sub sections now describe how the project has addressed each of the objectives set by ESA and by the project team within the original bid document (section 4.2), giving an overview of the project outputs (section 4.3) and ends with the lessons learnt by the project team (section 4.4).

Responding to the objectives and outputs

The follow sections details how the project addressed each of the original objectives set by ESA in the [SoW] and in the original proposal submission. All of the abstracts of the journal papers that are referred to in this section can be found in Appendix 1.

[obj-1] Exploring the potential offered by the synergistic use of existing Earth Explorers (GOCE, CryoSat and SMOS) also in combination with other ESA or non-ESA satellite data sets

The project has performed an extensive evaluation of the potential of using EO sea surface salinity and sea surface temperature in synergy (as input to 12 different empirical algorithms). For example this included using SMOS salinity data in conjunction with ESA sea surface temperature CCI data. Non-ESA datasets that were used were salinity observations from Aquarius. The performance of these synergy approaches are detailed in Findlay et al., (in-review).

[obj-2] Maximise the scientific exploitation of the synergies offered by the ESA historical archives (including ERS-1, ERS-2, Envisat data and Third Party Missions (TPM) also in synergy with non-ESA satellite data

All of the data used and analysed within the Pathfinder-OA project were historical data. This included the use of ERS-1, ERS-2, Envisat (through the ESA SST CCI dataset which exploits the ATSR, ATSR2 and AATSR data). All of the biogeochemical algorithms evaluated within the Pathfinders-OA project were synergy approaches.

[obj-3] Novel products and innovative retrieval methods

The project was the first to exploit satellite salinity observations from SMOS and Aquarius platforms to study the oceanic carbonate system and ocean acidification. The project was the first to highlight the potential (Land et al., 2015) and we are now awaiting the second review of the journal paper demonstrating the potential of these novel retrievals concerning A_T and C_T (Findlay et al., in-review). For this work on enabling the carbonate system biogeochemical parameters (A_T, C_T, pH and pCO_2) to be derived from EO data, the project has focused on verifying existing published empirical algorithms in five different geographical regions.

For studying the physical drivers of ocean acidification a novel upwelling indicator method and dataset has been developed based on physical oceanography and atmospheric interactions. It was initially intended to derive an experimental algorithm for the Amazon Plume region, but it was decided to produce a global result since the method and input data appeared to be very robust. The indicator data provides the potential to evaluate the distribution of episodic events, such as hurricanes, storms, frontal- and eddy-driven upwelling, to better document processes that lead to vertical fluxes of properties across the base of the surface mixed layer (ML) of the ocean and possible perturbation of the mean state of surface parameters. The resultant output provides a open ocean and coastal upwelling component and more information can be found in Appendix 3 of this report.

[obj-4] New Earth Science Results

The Pathfinder-OA project has demonstrated that EO driven empirical carbonate system algorithms can outperform in situ driven equivalent algorithms for some specific regions. The EO driven approach showed the highest performance in the Amazon plume (both low and high salinity regions) and Greater Caribbean.

The Pathfinders-OA project has identified the potential for using these EO derived A_T and C_T for evaluating CMIP model outputs (within Findlay et al., in-review), which included the evaluation of the HadGEM2 ESM. Globally the HadGEM2 Earth System Model performed well, whereas regionally its performance was poor when compared to that of in situ and Earth observations.

[obj-5] New validated multi-sensor products complete with uncertainty information

The round-robin inter-comparison has extensively validated 12 previously published algorithms and methods (in total across all regions = 6 A_T, 4 C_T, 2 pCO_2 methods) and an Earth system model (HadGEM2) with respect to driving these algorithms with EO and climatology data as input. This validation included the propagation of errors through these empirical algorithms. The full analysis can be found in Findlay et al., (in-review).

[obj-6] Positive impact from the international OA community

The project's media exposure based on the Land et al., (2015) publication was a mixture of supportive and negative feedback. However, evidenced through interactions and discussions at meeting and conferences the international scientific community have been very positive about the project achievements and outputs. In general the community has been pleasantly surprised at the potential and performance of the EO methods. On the 26th February we received a congratulatory email from Dr Phil Williamson (International Atomic Agency Ocean Acidification International Coordination Centre and former co-chair of he Global Ocean Acidification Observing Network, GOA-ON). He had become aware of our work via the UK Department for the Environment and Climate Change (DECC).

The Pathfinders-OA project has identified the potential for using these EO derived A_T and C_T (and thus the whole carbonate system via SeaCarb) for evaluating global CMIP model outputs. This work appears within Findlay et al., (in-review), which included the evaluation of the HadGEM2 Earth System Model.

[obj-7] Improved understanding of the issues involved in future systematic monitoring of OA

The project has identified the best performing C_T and A_T algorithms for each of the five regions. These outputs data plus SST and salinity data can then be used as input to SeaCarb modelling package to provide all of the carbonate system parameters, including pH and aragonite saturation state. Section 5 identifies regions where we could now trial the routine provision of EO derived carbonate system data to help support OA research and monitoring

[obj-8] Increased uptake of ESA and third party mission EO datasets

Collectively the Pathfinders-OA project has used data from >4 ESA sensors and >3 third party EO missions and the existence and scientific exploitation of these data has been published in all of the project outputs and conference presentations. Open ftp access to these data is provided on the project website.

[obj-9] Clear scientific roadmap for future activities in OA research and monitoring

A clear scientific roadmap has ben produced that contains individual process and algorithm studies, whilst also identifying regions where we could now trial the routine provision of data to help support OA research and monitoring. Each of these trial areas has a clear societal linkage and justification for this data provision. Furthermore the process and algorithms studies have been designed so that the outputs from these will help support and enhance the regional data provision. It also details some experiments that could identify the potential for a specific Ocean Acidification satellite sensor mission. Please see Section 5 of this document for more information.

[obj-10] At least three peer reviewed journal publications

This project has led and/or contributed to three journal papers.

Thus far the project has published one paper (Land et al., 2015), contributed to another (Shutler et al., 2016) and a third paper on the project's round-robin experiment is in-review (Findlay et al., in-review). The titles of each of these papers are given in the next section. The project team has content and results focusing on the Arctic that will form the basis of a fourth journal publication.

The Pathfinder-OA outputs

Listed below are the main outputs from the Pathfinders-OA project. These outputs fall under the following six categories i) published journal paper, ii) journal papers in review, iii) published conference abstracts, iv) technical report, v) community datasets and tools and vi) a media outputs.

Published peer review journal papers

P.E. Land, J. D. Shutler, H. Findlay, F. Girard-Ardhuin, R. Sabia, N. Reul, J.F. Piollé, B. Chapron, Y. Quilfen, J. E. Salisbury, D. Vandermark, R. Bellerby, P. Bhadury, (2015) Salinity from space unlocks satellite-based assessment of ocean acidification, *Environmental Science and Technology*, 49, 1987-1994. doi : 10.1021/es504849s **[5 citations]**

Shutler JD, Quartly GD, Donlon CJ, Sathyendranath S, Platt T, Chapron B, Johannessen JA, Girard-Ardhuin F., Nightingale PD, Woolf DK, Høyer JL (2016), Progress in satellite remote sensing for studying physical processes at the ocean surface and its borders with the atmosphere and sea ice, *Progress in Physical Geography*, 40: 215-246, doi:10.1177/0309133316638957. **[1 citation]**.

Journal paper in review

H. Findlay, P.E. Land, J. D. Shutler, I. G. Ashton, A. Grouazel, F. Girard-Ardhuin, R. Sabia, N. Reul, J.F. Piollé, B. Chapron, Y. Quilfen, R. Bellerby, P. Bhadury, J. E. Salisbury, D. Vandermark, R. Sabia (in-review) Optimum satellite and in situ inputs for empirical carbonate system algorithms in the Global Ocean, the Greater Caribbean, the Amazon Plume and the Bay of Bengal, *submitted to Geophysical Research Letters*.

Conference abstracts

During 2014-2016 the project team has presented its findings at **twelve** international conferences. In addition Peter Land gave an invited talk on Pathinders-OA at University College London, UK and results of the project were presented by the PI (Jamie Shutler) at the 2016 ESA/GCP/CEOS Carbon From Space workshop in Exeter, UK.

The twelve conference abstract titles were:

1. Shutler, JD (2016) The other CO_2 problem from a different angle: Studying Ocean Acidification using satellite Earth observation, *Air-sea gas flux: progress and future prospects*, Brest, France, 6-9 September 2016.

2. Shutler, JD, P. Land, H Findlay, F Girard-Ardhuin, J-F Piolle, N Reul, B Chapron, Y Quilfen, J Salisbury, D Vandemark, R Bellerby, P Bhadury, R Sabia, D Fernandez (2016) The other CO_2 problem from a different angle: Studying Ocean Acidification using satellite Earth observation, *The ESA living Planet Symposium*, Prague, Czech Republic, 9-13 May 2016.

3. R. Sabia, D. Fernández-Prieto, J. Shutler, C. Donlon, P. Land, N. Reul, Surface Ocean pH Estimation: a Satellite Perspective, Hobart, Australia, 3-6 May 2016.

4. R. Sabia, D. Fernández-Prieto, J. Shutler, C. Donlon, P. Land, N. Reul, Satellite Remote Sensing of Ocean Acidification and its Relevance within the SOLAS framework, SOLAS Open science Conference 2-15, Kiel, Germany, September 7-11, 2015.

5. R. Sabia, D. Fernández-Prieto, J. Shutler, C. Donlon, P. Land, N. Reul, Remote Sensing of Surface Ocean pH Exploiting Sea Surface Salinity Satellite Observations, IGARSS '15 (International Geoscience and Remote Sensing Symposium), Milano, Italy, July 27 –31, 2015.

6. R. Sabia, D. Fernández-Prieto, J. Shutler, C. Donlon, P. Land, N. Reul, Estimation of surface ocean pH exploiting SMOS salinity observations, 2nd SMOS Science Conference, 25-29 May 2015, Madrid, Spain.

7. Shutler, JD, P. Land, H Findlay, F Girard-Ardhuin, J-F Piolle, N Reul, B Chapron, Y Quilfen, J Salisbury, D Vandemark, R Bellerby, P Bhadury, R Sabia, D Fernandez (2015) The other CO_2 problem from a different angle: Studying Ocean Acidification using satellite Earth observation, *The 7th international symposium on Gas Transfer at the Water Surface*, Seattle, US, 18-21 May 2015.

8. R. Sabia, D. Fernández-Prieto, J. Shutler, N. Reul, P. Land, C. Donlon; Preparatory activities to estimate surface ocean pH exploiting sea surface salinity satellite observations; Ocean salinity science and salinity remote sensing workshop, Exeter, UK, November 26-28, 2014.

9. P. Land, J. Shutler, H. Findlay, F. Girard-Ardhuin, J.-F. Piolle, N. Reul, B. Chapron, Y. Quilfen, R. Sabia, D. Fernandez, J. Salisbury, D. Vandemark, R. Bellerby, P. Bhadury, P. Williamson; The other CO2 problem from a different angle: studying Ocean Acidification using satellite Earth observation; ESA-SOLAS-EGU Earth Observation for Ocean-Atmosphere Interactions Science 2014, Frascati, Italy, October 28-31, 2014.

10. R. Sabia, D. Fernández-Prieto, J. Shutler, N. Reul, P. Land and C. Donlon; Preparatory activities to estimate surface ocean pH from satellite observations; ESA-SOLAS-EGU Earth Observation for Ocean-Atmosphere Interactions Science 2014, Frascati, Italy, October 28-31, 2014.

11. Shutler, JD, P. Land, H Findlay, F Girard-Ardhuin, J-F Piolle, N Reul, B Chapron, Y Quilfen, J Salisbury, D Vandemark, R Bellerby, P Bhadury, R Sabia, D Fernandez (2014) The other CO_2 problem from a different angle: Studying Ocean Acidification using satellite Earth observation, *The Challenge Society for Marine Science Conference 2014*, Plymouth, UK, 8-11 September, 2014.

12. R. Sabia, D. Fernández-Prieto, C. Donlon, "A preliminary attempt to estimate surface ocean pH from satellite observations", IMBER Open Science Conference, Bergen, Norway, 23-27 June 2014.

Technical reports

A technical report describing the derivation and outputs from the upwelling indicator algorithm development and global dataset has been written:

Quilfen, Y., (2016) Upwelling indicators from Earth observation, *Ifremer technical report*.

Community datasets and tools

The experimental dataset contains T_A, C_T, and resultant SeaCarb output data for each of the five study regions (Global, Amazon plume, Greater Caribbean, Bay of Bengal, Arctic). The T_A, C_T model (algorithm and input pairings) used for each region are those that provided the best performance based on the results from the round-robin inter-comparison (presented in Findlay et al. in-review) and these are then used to calculate the remainder of the carbonate system parameters. Each regions' data consists of a NetCDF4 file containing T_A, C_T outputs and a second NetCDF4 file containing the SST, SSS, latitude and longitude for the year 2010 and the resultant calculated pH, pCO_2, Ω, at a regular global geospatial resolution of 1° × 1° grid (Global, Amazon plume, Greater Caribbean, Bay of Bengal), or polar stereographic nominal spatial resolution of 25 km (Arctic). The global upwelling indicator output dataset for 2010-2015 is available for at 0.25° × 0.25° and 1° × 1° outputs. The latter is provided so that the upwelling indicator data are available on a grid that is consistent with the biogeochemical data within the experimental dataset. All of these will be made available through the project website. Therefore the experimental dataset covers all of the novel outputs specified in the original bid document (see table 1 for a list of the parameters covered). The project team are in the process of preparing the software tools for provision on github under an open-source (not for profit) licence.

Table 1: Reproduced from the original bid document. Novel products that have been developed, validated and exploited within Pathfinders-OA and that are now available within the experimental dataset.

No.	Variable	Variable	Method/source
1.	Partial pressure of CO_2 in seawater	pCO_{2W}	SeaCarb modelled (using optimal A_T and C_T as input, and SST and SSS).
2.	Total alkalinity	A_T	Optimal empirical algorithm from literature (region specific).
3.	Dissolved inorganic carbon	C_T (DIC)	Optimal empirical algorithm from literature (region specific).
4.	Aragonite saturation state	Ω_{ar}	SeaCarb modelled (using optimal A_T and C_T as input, and SST and SSS).
5.	Basicity of seawater	pH	SeaCarb modelled (using optimal A_T and C_T as input, and SST and SSS).
6.	Upwelling incidence indicator	UII	Multi-sensor and model combination.

Published media and social media outputs

Following the publication of Land et al., (2015) press releases from ESA and the university of Exeter resulted in stories in 21 news outlets, 6 blogs, 9 Facebook pages and 72 twitter accounts. A synopsis of all of this media attention can be found here: https://www.altmetric.com/details/3076776

The ESA press release is here:
http://www.esa.int/Our_Activities/Observing_the_Earth/SMOS/SMOS_on_acid

The university of Exeter press release is here:
http://www.exeter.ac.uk/news/featurednews/title_435490_en.html

Feedback to ESA

The Pathfinders-OA project has clearly made a large amount of progress in a relatively short period of time with a small budget. For instance, the project has led 2 journal papers (one published, one in its second review), contributed to a third with enough content and results for a fourth paper. This equates to a cost of €37500 per journal paper (i.e. total budget of €150000/4 papers). The main reason for the low cost per journal paper within the project is that the project team built on previous work, efforts and experience has greatly increased and accelerated the outputs from the project. The high level of output from Pathfinders-OA would not have been possible if the team had started completely from the beginning. Examples of this include:

- Pre-processing of all data benefitted from Nephelae cloud and ESA GlobWave tools and the outputs from previous projects (e.g. ESA SST CCI, SMOS CATDS, ESA OceanFlux Greenhouse Gases).

- Data formats exploited ESA GlobWave NetCDF formats.

- The use of generic data formats across projects eased their use within the project ie OceanFlux Greenhouse Gases used ESA Ocean Colour CCI, ESA Sea surface temperature CCI and ESA GlobWave, all data that were available in NetCDF formats.

5. Scientific priority areas for future work

In this section we identify a pathway to fully exploit the scientific and technical progress that has been made within the Pathfinders-OA project, both in relation to the priorities of the broader OA community and also considering the Earth observation perspective.

This roadmap has been developed to provide a 3-5 year vision and identifies where real gains and advances (that enable impact both scientifically and from a societal point of view) could be made. The roadmap presented is the result of discussions at project meetings, scientific workshops, between project partners and colleagues within the wider OA community and during the final Pathfinders-OA project meeting.

The roadmap contains individual process and algorithm studies, whilst also identifying regions where we could now trial the routine provision of data to help support OA research and monitoring. Each of these trial areas has a clear societal linkage and justification for this data provision. Furthermore the process and algorithms studies have been designed so that the outputs from these will help support and enhance the regional data provision.

The regions where we could trial the provision of data are i) global, ii) Amazon plume, iii) North East Atlantic, iv) Caribbean, Pacific and Mediterranean Seas, v) Arctic waters (Barents Sea), and vi) Baltic Sea. The reasons for these region choices (or groupings) are described in the following sections.

The process and algorithm studies section identifies the potential to improve and refine the SMOS global estimates of A_T and C_T and the exploitation of NASA Soil Moisture Active Passive (SMAP) data. Attempts to improve SMOS (and test SMAP) global A_T and C_T retrievals have the potential to increase the impact and exploitation of Earth observation data. Such data could be used for evaluating Earth System models (ESM) as used in the international Coupled Model Inter-comparison Project (CMIP) series of experiments and provide input to future IPCC assessments. This application has already been illustrated within Findlay et al., (in-review) which included the evaluation of the HadGEM2 ESM.

Regions to focus the trialing of routine data provision

The following sections describe the regions identified where the Pathfinders-OA methods work well and where there are clear societal and research needs that could benefit from the routine provision of EO supported and derived OA datasets. For each section the justification for the region selection is given and region specific process or development studies are identified. In this way a future OA focussed project will be able to exploit the outputs from Pathfinders-OA, whilst also further building and developing the methods and approaches. Therefore, the trialling of data provision for each of these regions is not simply a data provision exercise, as it also includes scientific advancement. Furthermore, all of these regions will benefit from the work proposed within Section 5 of this roadmap.

Global

The second publication from the Pathfinders-OA project (Findlay et al., in-review) has highlighted the potential for EO driven model outputs for evaluating global and regional output from Earth System Models. Identifying the reasons for the poorer global performance of SMOS driven models, when compared to Aquarius driven models is first required and is clearly achievable (see section page 28 of this report). By providing routine global coverage carbonate system data and a suite of simple comparison metrics (e.g. Saux-Picart et al., 2012) would provide a rich source of evaluation data for ongoing and future evaluation of any Earth System Models (e.g. as used within the CMIP series and the analyses for future IPCC reports).

Amazon plume and trend analyses

The 3rd Carbon From Space workshop (January 2016, Exeter, UK, http://www.carbonfromspace.info) highlighted the lack of research that is focussing on the flow of carbon from the land into the ocean, and thus there is little knowledge on how this flow has changed through space and time, and its resultant impact on the regional marine carbonate system.

Clearly this carbon flow from large river systems like the Amazon is likely to be linked to deforestation. Pathfinders-OA has identified how the Amazon plume is one of the regions where SMOS salinity driven empirical carbonate algorithms out perform in situ re-analysis driven methods. Visible spectrum ocean colour data can be used to characterise and estimate suspended particulate loadings within large river systems (e.g. Martinez et al., 2015). Therefore there is a clear opportunity to use remote sensing EO to investigate and quantify temporal and spatial variations in land-ocean carbon flow and the resulting impact that this flow has on the regional marine carbonate system e.g. its promotion of CO_2 outgassing, the modulation of the regional CO_2 sink and alterations to the A_T pH in the region of the Amazon plume.

Due to the large salinity gradients in this region there is also the potential to exploit AMRS-E salinity data for such a study, enabling a 14+ year time series analysis (2002-present day) (Reul et al., 2009). Therefore information on longer-term trends could also be quantified.

North East Atlantic and Shellfish aquaculture

Aquaculture, the farming of marine life as a source of food, has been identified as one of the routes towards ensuring future global food security. Popular species for aquaculture include shellfish and oysters (and more recently Lobsters), and all of these carbonate forming marine animals require specific carbonate conditions for shell and/or exoskeleton growth (e.g. Fitzer et al., 2014). These species, and calcifying organisms in general, are threatened in the foreseen scenario of progressive undersaturation of seawater, as depicted by the expected changes in the Aragonite saturation state Ω. In the case of mussels, the carbonate conditions have also been shown to impact their ability to securely latch on to a substrate (O'Donnell et al., 2013). The need to study and monitor carbonate conditions to support aquaculture is one of the underlying reasons for the development of the US NOAA OAPS service that was established in 2011. The outputs from OAPS were used as a baseline comparison for the Pathfinders-OA Caribbean data.

Within the EU the expansion of aquaculture, including the farming of shellfish, has been identified as one component to enable future food security. Despite the increasing demand for sea food in the EU, the EU aquaculture production is stagnating in the freshwater and mollusc segments. The results of a recent mapping exercise to identify the reason for this stagnation concluded that tools and methods to identify new regions for aquaculture development would help support the industry (JRC, Mapping aquaculture, https://fishreg.jrc.ec.europa.eu/web/mappingaquaculture). This would allow the industry to expand through using regions that are currently overlooked.

Due to increasing pressures within coastal environments and the resulting concerns over water quality offshore shellfish farms are now beginning to appear. This movement to offshore farms (in contrast to those in estuaries) is likely to increase as populations continue to expand. Furthermore, the advantage of co-locating shellfish farms in offshore wind farms (to mutual benefit of both industries) has also been identified (e.g. Crown Estate (2010); Syvret et al., 2013; Hattam et al., 2015).

Offshore shellfish farms are typically 1-10 km offshore and are located in sheltered areas (e.g. St Austell Bay, Lyme Bay) that have little or no riverine inputs, meaning that the carbonate system is less complex than the estuarine equivalent. European offshore wind farms (of interest here with respect to aquaculture and wind farm co-location) are located 2-23 km from the coast, with some, but not all, near to large estuaries.

The movement to offshore installations means not only that the carbonate system is likely to be less complex than estuarine equivalents but also importantly that remote sensing could be used to characterise these environments.

Clearly climatological data on carbonate parameters could be useful to EU agencies and government organisations for marine planning purposes (e.g. to identify the optimal locations for new aquaculture sites and regions to avoid due to poor carbonate system conditions).

The Pathfinders-OA work has shown that EO driven empirical algorithms of A_T and C_T work well in some regions. So we have the methodology, tools and data to perform a similar analysis for European waters. A multitude of large research programmes have collated carbonate system data for the European Shelf Seas (e.g. the £10 Million UK Ocean Acidification programme) and a recent initiative (led by one of our Pathfinders-OA project partners, Dr Phil Williamson) has collated these data into a large database.

Therefore a future project could exploit the software and methods developed within Pathfinders-OA, along with the large carbonate datasets to evaluate and develop specific empirical carbonate system algorithms for the European shelf seas. The resulting spatial data could be provided to European agencies responsible for marine planning helping to underpin sustainable expansion of aquaculture in Europe towards improving future food security. Such information would also be useful for aquaculture farm managers.

Caribbean, Pacific and Mediterranean Sea sponge aquaculture

Sea sponge aquaculture is the process of farming sea sponges under controlled conditions or managed harvesting from the natural environment and it has been conducted in the world's oceans for centuries. It is an important industry for island nation communities (e.g. Micronesia) and Mediterranean countries including Greece and it was previously an important industry in the U.S. Sponge farming was originally developed to support local use of the product (e.g. as bathing sponges) but has since expanded into tourism, medicine and cosmetics. Indeed recent advances within cancer drug development have exploited algae that grow on sea sponges (e.g. Twelves, 2014). The increasing demand for sponges suggests that this is an industry likely to grow in the near future.

There are many factors such as light, salinity, pH, dissolved oxygen and the accumulation of waste products that influence the growth rate of sponges. However, the key parameters are considered to be pH, salinity and suspended sediment. Sponge aquaculture is typically performed in equatorial or mid-latitude regions, which also coincide with the regions where SMOS shows the highest performance.

Therefore a future project could exploit the software and methods developed within Pathfinders-OA, along with the large carbonate datasets to evaluate and develop empirical carbonate system algorithms for the regions of sea sponge aquaculture. The resulting spatial data could be provided to agencies responsible for marine planning helping to underpin sustainable expansion of sponge aquaculture.

The Arctic for climate, food webs, gateways and climate model evaluation

Cold water can absorb more CO_2 than warmer water, and so the polar oceans are taking up CO_2 at a faster rate than elsewhere on the planet, therefore they are already experiencing the impacts of ocean acidification. One of the additional issues with the Arctic Ocean is the potential for enhanced ocean acidification in the future by the increase input of freshwater as sea ice retreats and the planet warms. It is thought that the addition of freshwater into the Arctic will dilute the ocean’s ability to cope with increases in acidity, but this is yet to be tested or verified by observations. Baseline data is required to understand the current carbonate chemistry and biology in the Arctic, and the processes that could potentially enhance the rate of ocean acidification. Without this knowledge, it is difficult to make predictions about how ecosystems will respond to ocean acidification in the future, and this impedes our ability to mitigate change, as well as manage the environment.

The inhospitable and heterogeneous nature of the Arctic make if difficult and expensive to rely solely on in situ observations for monitoring and understanding its changing environment. Synergistic use of satellite observations, in conjunction with in situ data and models, provide a solution to providing more spatially complete observations. Such data can be used for driving innovative process studies, climate model evaluation and data assimilation, and developing monitoring methodologies. The carbonate system can be separated into its chemical, physical and biological aspects and satellite Earth observation can be used to support the study of all of these components, in relation to both the forcing and the impacts.

Issues highlighted by the international community where satellite Earth observation can be exploited in relation to studying ocean acidification in the Arctic include i) developing novel methods for monitoring alkalinity (e.g. SMOS, Land et al., 2015) and air-sea CO_2 flux and studying their monthly to inter-annual variations, ii) characterising seasonal dynamics at the lower latitude Arctic gateways to link primary production observations (and food webs) with other factors including ice cover, carbonate chemistry and air-sea gas exchange, iii) develop upwelling indices that can identify when and where upwelled events occur along coasts (lower temperature water upwelled with lower pH) and ice edges (warmer water upwelling with higher pH) and to characterise which coasts and regions are most at risk from this phenomenon and iv) further improvements and advances in estimating ice cover, ice thickness, snow depth and sea ice densities (e.g. reliable snow depth and sea ice densities will improve estimates of ice thickness). The study of these parameters in the marginal ice zone is especially important, as this is where gas exchange is likely to occur.

Therefore a future project could exploit the outputs for the Arctic Barents sea and provide these data routinely for this area. Data would include the empirical derived A_T and C_T outputs and the modeled SeaCarb derived pCO_2 and pH data. These would be complemented by the upwelling indicator datasets and additional data from published algorithms (e.g. ice cover, snow depth, sea ice densities). The region of data provision could be expanded to include the Arctic gateways (e.g. the northern Greenland Sea).

Baltic Sea and new ESA member states (Estonia and Poland)

The Baltic Sea, bordered by two new ESA member states, Poland and Estonia, is an inland sea connected to the North Sea through the shallow Kattegat. There is little exchange of seawater between the North Sea and Baltic, resulting in the Baltic Sea exhibiting a very low salinity of the order of 7 on the Practical Salinity Scale (PSS). For comparison the Atlantic open ocean salinity is of the order of 35 PSS. Biological water quality within the Baltic has been of international concern for many years due to a history of pollution events and the impact of a changing climate, but as yet no concerted effort has been made to monitor and study the carbonate system health and thus chemical water quality. Initiated and encouraged by the International Carbon Observing System (ICOS) three countries that border the Baltic Sea (Finland, Sweden and Germany) are now part of ICOS and routinely collecting carbonate measurements through ships of opportunity that routinely transect the sea, providing an extensive dataset and basis for the development of empirical carbonate system algorithms and the monitoring of air-sea gas fluxes through the collection of pCO_2 data (e.g. Parard et al., 2015). Poland and Estonia are currently in the process of developing a strategy for ICOS.

The consistently cold temperature of the northern Baltic Sea water suggests that it has the capacity to become a significant sink of CO_2 and not surprisingly OA is an area of concern for Baltic states due to their reliance on the Baltic as a source of food, both through wild fisheries and aquaculture. It is estimated that on average the waters will exhibit a reduction of 0.2-0.4 pH by 2100 (Havenhand, 2012). However, the carbonate system in the Baltic is highly influenced by runoff and regional conditions, so significant regions variations can exist. For example the Kiel fjord varies seasonally by up to 0.7 pH (Thomsen et al., 2010) and diurnal variations (within one day) of ±0.15 pH have been identified in particularly shallow areas (Havenhand, 2012).

SMOS data have recently been used in the Baltic to characterise sea ice thickness and some Baltic Sea SMOS salinity data are now becoming available. Ocean colour and sea surface temperature Earth observation observations have been routinely collected over the Baltic Sea since the 1990s.

Therefore there appears to be a large enough dataset of EO and in situ carbonate data to evaluate the potential for EO to monitor at least pCO_2 in this region. The enclosed nature of the Baltic Sea and the low water temperatures are likely to make SMOS salinity retrievals difficult, but its low salinity suggests that the carbonate system is highly temperature controlled (temperatures in the southern Baltic range seasonally between 2 – 18 ^{o}C, whereas the northern Baltic typically contains some sea ice for 6 months of the year), highlighting the important and dominant role that EO SST is likely to play in any carbonate system analysis.

Therefore there is a clear scientific basis to apply the techniques already developed within Pathfinders-OA to evaluate the use of EO in the Baltic to study and monitor OA. Whilst clearly providing a challenging environment for such a study, datasets and algorithms developed would contribute to Baltic national activities and aims, and they have clear links to societal impact and benefit.

Process and algorithm studies

The following sections describe process studies and algorithm development that will support the regional data provision described in the previous section.

Impact of rain

Rain is known to alter the physical and chemical conditions at the sea surface, and thus influence the marine carbonate system. It can influence the carbonate system through enhanced gas transfer velocity, the direct export of carbon from the atmosphere to the ocean, by altering the sea skin temperature, and through surface layer dilution. The impacts of rain on the carbonate system are likely to be significant in the Inter-tropical convergence Zone (ITCZ). To date, very few studies quantifying these effects on global OA parameters exist, and EO provides ideal datasets to evaluate and characterise the impact of rain, and therefore elucidate how changes in rain distribution and intensity (as predicted by the IPCC) will impact on the future marine carbonate system.

The OceanFlux Greenhouse Gases project has recently characterised the impact that rain can have on the air-sea flux of CO_2, so this is an example of synergy where a future Pathfinders-OA project could benefit from exploiting experience and data already held by the OceanFlux team.

Mapping of upwelling and vertical water flow produced during tropical cyclones

There are two main effects related to tropical cyclones (known as hurricanes in the Atlantic) that can influence ocean CO_2 concentrations, and in turn air-sea CO_2 fluxes: wind speed, and changes in mixed layer depth. A change in wind speed has a direct effect on the flux, whilst the upwelling of colder, deeper waters leads to SST changes, altering both surface ocean pCO_2 and the flux rate. A significant change in the mixed layer depth also brings material to the surface that is normally held away by stratification, e.g. carbon and nutrients. For a given ocean basin and a particular year, tropical cyclones are likely to contribute greatly to air-sea exchanges, as stated by Nemoto et al., 2009: "The efflux enhanced by three typhoons accounted for 60% of the efflux of CO_2 in the North Pacific warm season". This is the result of the exceptional intensity of such events in regions where the background wind is relatively moderate or regular.

It can be exemplified in the Figure 6 that shows the Ekman pumping velocity field, (from the Pathfinders-OA upwelling indicator dataset) during the hurricane Igor on September 17th, 2010. For that particular day the background field is very low comparatively to the upwelling indicator in the Igor wake, and one can anticipate that such a long lasted phenomenon (> 10 days) may contribute very significantly to the variations in the carbonate system for this basin and season. This is area of science is very active (Levy et al., 2012; Foltz et al., 2015; Mei et al., 2015), but the unique Pathfinders-OA upwelling data could certainly help to contribute to existing international efforts as no such upwelling dataset currently exists.

The OceanFlux Greenhouse Gases project has recently characterised the impact that cyclones can have on some aspects of the air-sea flux of CO_2. However, the impact of upwelled water, the increase in nutrients that they bring and how this impacts on the surface water carbonate system has not been investigated. This is an example of how the OceanFlux team could benefit from the experience and outputs from the Pathfinders-OA projects.

Characterising the impact of the cyclone driven upwelling on the carbonate system (e.g. use the Pathfinder-OA EO upwelling indicator dataset to initiate a hydrodynamic model) could be an area of future work which would then feed into the OceanFlux studies and international efforts to understand how tropical cyclones impact on the marine carbonate system.

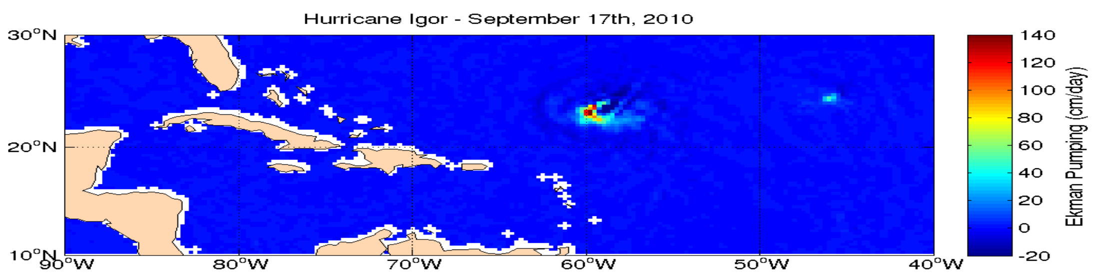


Figure 6 Ekman pumping velocity field in hurricane Igor from the OA Pathfinder project.

Towards improving global SMOS A_T ad C_T outputs to support CMIP and IPCC assessments

Figure 2 shows that SMOS driven models perform better than all other methods in the Greater Caribbean and Amazon Plume (low and high salinity) for both A_T ad C_T. This is likely due to the inability for the in situ SST and SSS observations to fully capture the variability in this region.

Clearly, the relatively low spatial resolution possible from salinity from space methods means that these sensors are well placed to study global variations in carbonate parameters. The demise of Aquarius in 2015 means that SMOS and the new NASA Soil Moisture Active Passive (SMAP) are the only sensors in orbit capable of providing global salinity from space observations. Therefore attempts to improve SMOS (and test SMAP) global A_T and C_T retrievals have the potential for the large amount of impact and exploitation e.g. such data could be used for evaluating Earth System models (ESM) as used in the international Coupled Model Inter-comparison Project (CMIP) series of experiments and provide input to future IPCC assessments. The potential for using these EO derived A_T and C_T for evaluating CMIP model outputs has been demonstrated within Findlay et al., (in-review) which included the evaluation of the HadGEM2 ESM.

For global C_T, SMOS driven models performs poorly when compared to all other in situ driven models and even to that of Aquarius driven models. Whereas Aquarius driven models show performance similar to that of in situ driven models and the HagGEM2. This situation is also true for the Barents Sea. Clearly work to identify the reason for the poorer performance of the SMOS driven models and to improve their estimates will enable space based global monitoring of C_T. Comparing Aquarius model output with the equivalent from SMOS (e.g. latitudinal analyses and comparisons) should enable the reasons for the differences to be easily identified and investigated. The difference in Arctic Barents Sea performance between the SMOS and Aquarius driven models is a good starting point for this work (as the reasons for these differences are likely to be apparent by simply comparing the Aquarius and SMOS latitudinal SSS and C_T data).

For global A_T, Aquarius and SMOS driven model performance is comparable across all of the regions, except global. For the global case Aquarius driven models outperform SMOS equivalents. The reasons for these differences should be apparent from studying the individual observations used within the performance analysis to identify any conditions or regions that lead to the lower performance.

Exploiting SMAP

The launch of SMAP in 2015, and the subsequent demise of Aquarius, suggests that SMAP observations should be exploited within any future OA from space analysis and SMAP salinity data are already available e.g. http://www.remss.com/blog/SMAP-Ocean-Salinity.

Refitting and re-tune published carbonate algorithms

There is a clear need to re-fit and re-tune existing carbonate system algorithms. Many of the algorithms used within Pathfinders-OA were globally applicable (or tuned), rather than being region specific. Clearly, due to the complex nature of the marine carbonate system region specific algorithms will generally always out perform globally derived algorithms. Developing tools to allow existing carbonate system algorithms to be easily retuned will allow new in situ data to be exploited, whilst also allowing users to overcome the disadvantage of relying on empirical algorithms i.e. as climate changes, the response of the carbonate system is also likely to change, so empirical algorithms will need to be updated to ensure that they continue to accurately represent and reproduce the carbonate system.

Sensor studies – the potential for Future satellite missions

The following sections describe two studies that are focussed on identifying and developing the potential for directly remotely sensing ocean pH.

The potential of observing pH via infrared remote sensing

Since the beginning of the industrial revolution humans have released approximately 500 billion metric tons of carbon into the atmosphere from burning fossil fuels, cement production and land-use changes. About 30% of this carbon dioxide has been taken up (or absorbed) by the oceans. The oceanic uptake of carbon dioxide leads to a change in marine carbonate chemistry resulting in a decrease of seawater basity (pH) and carbonate ion concentration, a situation that is commonly called ‘Ocean Acidification’. We rely on the oceans as a source of food and Ocean Acidification can make it difficult for some marine life to exist, thus it directly impacts on our future food security.

Arguably satellite remote sensing is the most cost efficient method of monitoring our global oceans. Currently none of the carbonate parameters can be directly observed from space using existing remote sensing satellites. Recent work (Land et al., 2015) highlighted how satellite derived salinity measurements will help us to use the salinity-alkalinity relationship; numerous regional empirical algorithms exist that can be used to exploit salinity and temperature relationships for deriving the carbonate parameters globally. However, globally applicable algorithms for deriving pH remain illusive.

The oceanic carbonate system can be characterized and studied through four key parameters: total alkalinity (A_T), fugacity of CO_2 (fCO_2), dissolved inorganic carbon (often referred to as DIC or CT) and basity (pH). Knowing any two of these parameters (e.g. pH and A_T) along with temperature and salinity allows the complete carbonate system to be determined. Thus if we were able to estimate A_T and pH (e.g. using satellite remote-sensing), then fCO_2 can also be determined – a key parameter for studying air-sea gas exchange.

pH is a logarithmic measure of hydrogen ion activity (H^+). Lin and Brown (1993) list the major ions and their concentrations in a standard seawater sample. Figure 1 shows these ions as a function of pH (-log[H^+]), including borate (B-), boric acid (HB), bicarbonate (HC-) and carbonate (C2-). Referring to Figure 1, it appears that variations in the pH of seawater (i.e. pH of 7-8.3) can be determined by observing variations in B- and HB or C2-. The total Boron concentration (sum of B- and HB) will very with salinity.

Goulden and Manning (1967) show the infra-red (IR) absorption features of common inorganic compounds in aqueous solution. B- appears to have distinct absorption features at ~8.3µm and ~10.3µm (see figure 1 of Goulden and Manning, 1967) and HB has an absorption feature at ~8.75µm. It is possible to observe these wavelengths from space, as water vapour within the atmosphere does not absorb strongly at these wavelengths. Bands centred at 10µm are extensively used to study sea skin temperature. Lin and Brown (1993) have shown how some of these ion absorption features are likely to exhibit temperature dependence.

Early work focused on measuring spectra of ion molar concentrations of the order 0.2 moles (0.2 mol $litre^{-1}$). More recent work (Peak et al., 2003) has demonstrated how the IR spectra of much smaller B- ion concentrations (50μM – 1mM which is 50×10^{-6} mol $litre^{-1}$ to 1×10^{-3} mol $litre^{-1}$) can also be observed. From Lin and Brown (1993) the borate ion concentration in a standard seawater sample of 35% salinity is of the order 10×10^{-3} mol $litre^{-1}$ which is within the concentration range successfully studied by Peak et al., (2003).

Total alkalinity, T_A, is the ability of the water to buffer a change in acidity and it is highly correlated with salinity (Land et al., 2015). Lin and Brown (1993) have demonstrated the potential to determine salinity from near-IR spectrometry by observing how groups of ions vary with salinity, thus observing a change in the combined ion derived IR spectrum, rather than focusing on specific ions. The near-IR bands studied by Lin and Brown (1993) are similar to some of the bands used by Sentinel 2, suggesting that data from Sentinel 2 could be used to estimate salinity over the ocean, although it is currently unclear if Sentinel 2 could provide the required sensitivity.

Attenuated Total Reflectance (ATR) Fourier Transform Infrared (FTIR) spectroscopy has been previously used to measure the IR spectrum of borate ions in aqueous solution (Peak et al., 2003). This method enables low concentration solutions to be studied and the sample can be presented to the instrument in a temperature controlled and enclosed (but not guaranteed airtight) sample holder (called an accessory).

We propose a simple study to analyse a small range of seawater samples using ATR FTIR spectroscopy with the aim of observing how the concentrations of groups of ions vary with pH and thus alter the IR spectrum.

A further route of investigation would be to determine if the ion control of A_T is detectable via near-IR spectrometry (rather than relying on salinity data – existing empirical methods to model A_T typically exploit the salinity-A_T relationship).

The Pathfinders-OA project team have developed a pilot study plan and identified potential partners to enable an initial investigation.

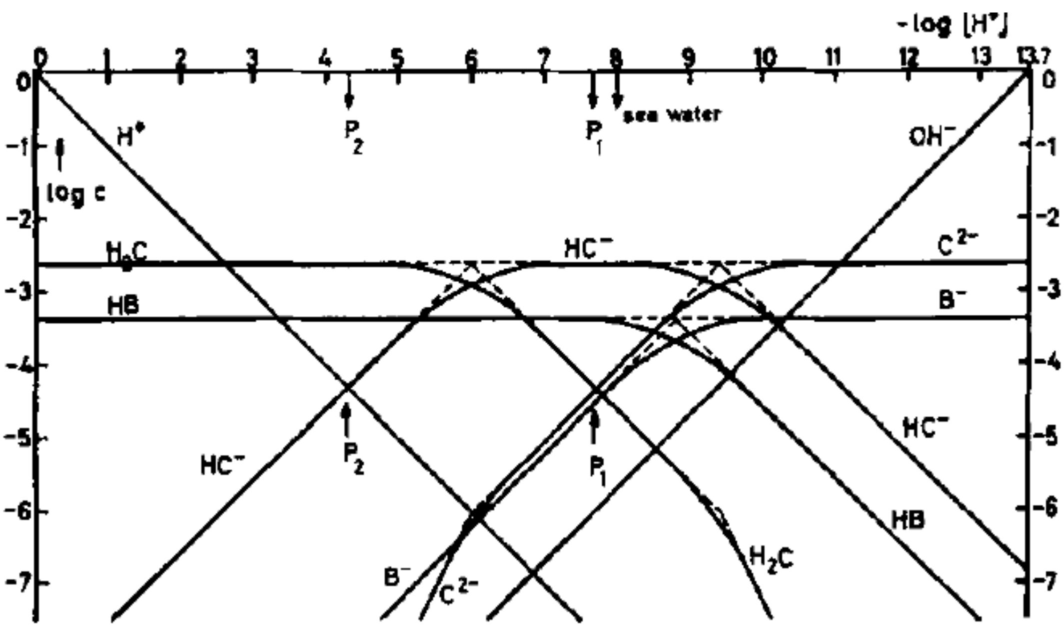


Figure 7 Seawater ions as a function of pH (-log[H^+]), including borate (B-), boric acid (HB), bicarbonate (HC-) and carbonate (C2-).

The potential of observing pH via microwave remote sensing

As described in the previous section, pH is a logarithmic measure of hydrogen ion activity (H^+). Lin and Brown (1993) list the major ions and their concentrations in a standard seawater sample. Figure 5 shows these ions as a function of pH (-log[H^+]), including borate (B-), boric acid (HB), bicarbonate (HC-) and carbonate (C2-). Referring to Figure 5, it appears that variations in the pH of seawater (i.e. pH of 7-8.3) can be determined by observing variations in B- and HB or C2-. The total Boron concentration (sum of B- and HB) will vary with salinity. The dielectric properties of the water are influenced by the concentrations of these ions in the water (e.g. Navarkhele et al., 1998) and L-band SMOS essentially observes the dielectric properties of water and then uses this to determine the salinity (i.e. as the total Boron ion concentration varies with salinity).

Therefore it is possible that observations of the dielectric properties of the water (e.g. from an L-band sensor like SMOS) could be used to directly determine the ocean pH.

To study this potential from a sensor physics point of view, we must return to fundamental aspects and gain an improved and consistent understanding of the dielectric properties of the water. We must therefore explore the full electromagnetic spectrum from all available measurements (from L-band to optical wavelengths) in relation to the dielectric properties of the water. The unique multi-angle aspects of SMOS could also be exploited. Only by doing this will we be able to move away from using L-band inferred SSS as an input to empirical formulations.

In the first instance such a piece of work could be used to study regions where large in situ anomalies have been observed, such as those driven and associated with local 'events' captured by satellite observations (for example from blooms, to internal waves, wind bursts, rain down drafts, fresh water lenses, diurnal events and the impact of storms).

Scientific software engineering development strategy

The following development activities and potential aims have been identified during workshop discussions and project meetings.

1. Open source toolbox: Experience has shown that the easiest way to increase uptake of an open source toolbox within the scientific community is to publish a scientific paper that accompanies the tools and explains how they work, what they can be used for and provides information on how the software has been verified. There is therefore a clear need therefore for a short journal paper to be written that can accompany the open source software tools that have been developed within Pathfinders-OA.

2. SOCAT and GLODAP: There is a need to work with the Surface Ocean CO_2 Atlas (SOCAT) team (especially D. Bakker, UEA, UK) and Global Ocean Data Analysis Project (GLODAP) and to exploit the new versions of the SOCAT and GLODAP datasets. SOCAT is an international effort that is gaining momentum and they have begun to include full carbonate system data within the SOCAT database. This means that future version of SOCAT will contain C_T, A_T and pH data, in conjunction with pCO_2 data. GLODAP have also recently made the GLODAP2 database available. These two teams have essentially repeated some of the work that the Pathfinders-OA team performed by collating large carbonate system datasets and then providing them in a common format. The GODAP2 and SOCAT data are now more up to date than the original Pathfinders-OA datasets. Therefore any future OA project should simply exploit these two datasets for in situ data, rather than collating the data themselves.

Therefore there is a need to modify and update the round robin analysis code to work with these data formats as this would allow accelerated progress, especially with respect to re-tuning algorithms (see section 5 of this roadmap).

The advantages of integrating with larger initiatives and large international scientific efforts

It is clear that there are multiple routes that can be exploited to increase the uptake and exploitation of the Pathfinders-OA outputs.

1. The International Surface Ocean - Lower Atmosphere Study (**SOLAS**) project is an international research initiative aiming to understand the key biogeochemical-physical interactions and feedbacks between the ocean and atmosphere. International SOLAS has supported the OceanFlux projects from their gestation and they are aware of the Pathfinders-OA project. It remains an important vehicle for ensuring both that this and similar projects are genuinely targeted to recognised scientific priorities and for enabling the promotion of the project and its interactions with related projects. We expect any future projects to benefit from an active involvement with and from SOLAS.

2. The Surface Ocean pCO_2 Atlas (**SOCAT**) and Global Ocean Data Analysis Project (**GLODAP** Carbon Synthesis project) are large international data collation exercises. Future OA focussed projects are likely to need to exploit these data (see Section 6) and so working alongside and building a good relationship with these communities is key to any future success. The recent provision of the GLODAPv2 dataset will mean that any future OA focussed work will be accelerated as the majority of the in situ data collation exercise (that Pathfinders-OA had to construct) has now been completed and updated by the GLODAP effort and team.

3. There are many synergies and common themes between atmosphere-ocean gas flux research and OA research. Certainly Pathfinders-OA has exploited much of the infrastructure, staff and partners that were first established through the ESA STSE **OceanFlux** Greenhouse Gases projects. We can see that future OA projects would benefit from being involved in, or existing within, an ESA atmosphere-ocean flux project (e.g. merging Pathfinders-OA and OceanFlux Greenhouse Gases). This approach would also reduce the management overhead.

4. By attending the “Oceans in a High-CO_2 World Symposium – Ocean Acidification”, in Hobart, Australia, in May 2016, it was still evident the quite limited awareness of the OA community of the potential and benefits of remote sensing techniques in the OA world. However, remote sensing usefulness has been mentioned several times in different talks and the dedicated project talk received a very encouraging feedback and raised many questions. It has been discussed in the Pathfinder-OA Final Meeting the fact that an “amplifier” of the potential of satellites for monitoring OA is needed to leverage the community interest. The best bottom-up approach could be to organize a dedicated “Remote Sensing for Ocean Acidification” workshop, in ESRIN, a first of its kind, targeting about 20/30 people with invited talks to also liaise with additional relevant stakeholders.

Conclusions on the future directions and foci

In common with other scientific and technical endeavours, it is far too easy to write an ever-expanding list of future objectives. The Pathfinders-OA study using remote sensing Earth observation has overcome some substantial and technical obstacles. It is also the case that retrieving the most appropriate information by Earth observation is not simple. Nevertheless, a roadmap has been established that identifies strategically significant tasks with tractable solutions. Firstly we have identified specific regions where Earth observation and technical expertise can be immediately brought to bear. All of these region choices have clear societal and scientific justification. A second group of priorities identifies areas that will underpin and expand the regional data provision. This second set of priorities also includes work that would underpin a future OA focussed satellite mission. The development and use of Cloud computing is central to much of the proposed roadmap and the roadmap includes highly novel and high impact scientific investigations, along with initiatives that will help ensure the uptake and exploitation of the outputs by the international community. We have also outlined a process by which future projects can work with major umbrella organisations and initiatives (e.g. SOLAS, SOCAT, GCP) and with individual scientists with varying backgrounds.

Finally we have highlighted the potential benefit of more closely linking future Ocean Acidification research with that of atmosphere-ocean gas flux research. There are many synergies between the work of the two existing STSE projects (Pathfinders-OA and OceanFlux Greenhouse Gases Evolution). So far these synergies have been exploited due to the common staff and partners within these projects. However, it is possible that greater impact could be achieved by fully integrating these two areas of work. Such integration would also reduce the management overhead, enabling more of the project staff time to be used for generating outputs and impact.

6. Overall conclusions

The study of the marine carbonate system and ocean acidification has been slowed and complicated by some technical obstacles and the sparcity of data to evaluate the methods and algorithms.

Nevertheless, the Pathfinders-OA project has made some significant advances in first identifying the potential that Earth observation can play in this important area of science to the international community, and then by assessing the accuracy of Earth observation driven empirical methods in comparison to in situ and an Earth System Model. The analysis shows that there are regions in the world where Earth observation driven empirical algorithms outperform other methods for studying ocean acidification parameters (Amazon plume and Greater Caribbean). Globally the performance of Earth observation driven empirical algorithms equals that of other methods. These result emphases the important and substantial role that Earth observation can play in future large spatial scale monitoring of Ocean acidification parameters. The potential of this was first highlighted by the Pathfinders-OA team (Land et al., 2015), and now the team have provided an extensive analysis and considerable evidence to support this claim (Findlay et al., in-review).

The interdisciplinary team composition of modellers, Earth observation, computing, carbonate and in situ specialists was key to the success of the project

The project has also constructed the first spatially complete set of carbonate parameters for 5 regions (Global, Amazon plume, Greater Caribbean, Bay of Bengal, Arctic); key information that helps to illustrate the potential that Earth observation has in providing observations to support future international monitoring efforts. All of these data are freely available.

The project has also identified a large range of future possibilities and ways in which Earth observation and remote sensing in general could help to further expand our capability to study and understand Ocean acidification and its impacts on the marine environment. This includes areas where routine monitoring could now be trialled, the potential for specific novel satellite missions, and how this work can feed into and underpin Earth System Model performance evaluation helping to support future Intergovernmental Panel on Climate Change (IPCC) assessments.

7. References

Clements, J. C. and Chopin, T. (2016), Ocean acidification and marine aquaculture in North America: potential impacts and mitigation strategies. Reviews in Aquaculture. doi: 10.1111/raq.12140

Crown Estate (2010) co-location report (Aquaculture and wind farms) - http://www.gov.scot/Resource/0040/00408280.pdf

EU (2011) Guide to best practices for ocean acidification research and data reporting, Edited by Riebesell, U., Fabry, V. J., Hanson, L., Gattuso, J-P., *European Commission*, 258pp.

Fabry, V. J., Seibel, B. A., Feely, R. A., and Orr, J. C., (2008) Impacts of ocean acidification on marine fauna and ecosystem processes, ICES Journal of Marine Science: *Journal du Conseil*, 65, 414-432.

Feely, R. A., Sabine, C. L., Hernandez-Ayon, J. M., Ianson, D., and Hales, B., (2008) Evidence for upwelling of corrosive" acidified" water onto the continental shelf, *Science*, 320, 1490-1492.

Fitzer, S. C., Phoenix, V. R., Cusack, M. Kamenos, N. A. (2014) Ocean acidification impacts mussel control on biomineralisation, *Scientific Reports* 4, 6218, doi:10.1038/srep06218

Foltz, G. R., K. Balaguru, and L. R. Leung (2015), A reassessment of the integrated impact of tropical cyclones on surface chlorophyll in the western subtropical North Atlantic, *Geophys. Res. Lett.*, 42, 1158–1164, doi:10.1002/2015GL063222.

Goulden, J. D. S., Manning, D. J. (1967) Infra-red spectroscopy of inorganic materials in aqueous solution, *Spectrochmica*, 23A, 2249-2254.

Hattam, C., Hooper, T. and Papathanasopoulou, E. 2015. 'Understanding the Impacts of Offshore Wind Farms on Well-Being', The Crown Estate, 77 pages, ISBN: 978-1-906410- 65-0. See (p27-28) http://www.thecrownestate.co.uk/media/501972/ei-understanding-the-impacts-of-offshore-wind-farms-on-well-being.pdf

Havenhand (2012) How will Ocean Acidification Affect Baltic Sea Ecosystems? An Assessment of Plausible Impacts on Key Functional Groups, *Ambio*, 41(6), 637-644

IPCC (2013) Working Group I Contribution to the IPCC Fifth Assessment Report, Climate Change 2013: The Physical Science Basis, Summary for Policymakers: http://www.ipcc.ch/report/ar5/wg1/-.Ul7CrUpwbos .

Kroeker, K. J., R. L. Kordas, R. Crim, I. E. Hendriks, L. Ramajo, G. S. Singh, C. M. Duarte, and J.-P. Gattuso, (2013), Impacts of ocean acidification on marine orgnaisms: quantifying sensitivities and interaction with warming. *Glob. Change Biol.*, 19, 1884-1896, doi:10.1111/gcb.12179.

Land, P.E., Shutler, J.D., Findlay, H., Girard-Ardhuin, F., Sabia, R., Reul, N., Piolle, J., Chapron, B., Quilfen, Y., Salisbury, J.E., et al (2015). Salinity from space unlocks satellite-based assessment of ocean acidification. *Environmental Science & Technology*, doi: 10.1021/es504849s.

Levy, M., M. Lengaigne, L. Bopp, E. M. Vincent, G. Madec, C. Ethe, D. Kumar and VVSS Sarma (2012), Contribution of Hurricanes to the air-sea CO2 flux: a global view, *GBC*, vol 26, doi:10.1029/2011GB004145

Lin, J., Brown, C. W. (1993) Near-IR spectroscopic measurement of seawater salinity, *Environmental Science and Technology*, 27, 1611-1615.

Martinez, J.-M., R. Espinoza-Villar, E. Armijos, and L. Silva Moreira (2015), The optical properties of river and floodplain waters in the Amazon River Basin: Implications for satellite-based measurements of suspended particulate matter. J. Geophys. Res. Earth Surf., 120, 1274–1287. doi: 10.1002/2014JF003404.

Navarkhele, V. V., Agrawal, R. S., Kurtadikar, M. L., (1998) Dielectric properties of electrolytic solutions, *Pramana*, 51(3), 511-518.

Nemoto, K., T. Midorikawa, A. Wada, K. Ogawa, S. Takatani, H. Kimoto, M. Ishii, and H. Y. Inoue (2009), Continuous observations of atmospheric and oceanic CO2 using a moored buoy in the East China Sea: Variations during the passage of typhoons, *Deep Sea Res*., Part II, 56(8–10), 542–553, doi:10.1016/j.dsr2.2008.12.015.

O'Donnell, M. J., George, M. N., Carrington, E. (2013) Mussel byssus attachment weakened by ocean acidification, *Nature Climate Change* 3, 587–590, doi:10.1038/nclimate1846

Parard, G., Charantonis, A., Rutgersson, A. (2015). Remote sensing the sea surface CO2 of the Baltic Sea using the SOMLO methodology. *Biogeosciences*, 12, 3369–3384, doi:10.5194/bg-12-3369-2015

Peak, D., Luther, G. W., Sparks, D. L. (2003) ATR-FTIR spectroscopic studies of boric acid adsorption on hydrous ferric oxide, *Geochimica et Cosmochimica Acta*, 14, 2551-2560.

Reul, N., S. Saux-Picart, B. Chapron, D. Vandemark, J. Tournadre, and J. Salisbury (2009), Demonstration of ocean surface salinity microwave measurements from space using AMSR-E data over the Amazon plume, *Geophys. Res. Lett*., 36, L13607, doi:10.1029/2009GL038860.

Ridgwell A, Schmidt DN, Turley C, Brownless C, Maldonado MT, Tortell P, Young JR., (2009) From laboratory manipulations to Earth system models: scaling calcification impacts of ocean acidification. *Biogeosciences*, 6: 2611-2623.

Saux Picart S, Butenschön M, Shutler JD (2012). Wavelet-based spatial comparison technique for analysing and evaluating two-dimensional geophysical model fields. *GMD*, *5*(1), 223-230.

Syvret, M., FitzGerald, A., Gray, M., Wilson, J., Ashley, M. and Ellis Jones, C. (2013) Aquaculture in Welsh Offshore Wind Farms: A feasibility study into potential cultivation in offshore wind farm sites. Report for the Shellfish Association of Great Britain, 250p.

Thomsen, J., M.A. Gutowska, J. Saphorster, A. Heinemann, K. Trubenbach, J. Fietzke, C. Hiebenthal, A. Eisenhauer, et al. (2010). Calcifying invertebrates succeed in a naturally CO_2-rich coastal habitat but are threatened by high levels of future acidification. *Biogeosciences*, 7: 3879–3891.

Turley, C., Eby, M., Ridgwell, A. J., Schmidt, D. N., Findlay, H. S., Brownlee, C., Riebesell, U., Fabry, V. J., Feely, R. A., and Gattuso, J. P., (2010) The societal challenge of ocean acidification, *Marine Pollution Bulletin*, 60, 787-792.

Twelves (2014) https://www.leeds.ac.uk/news/article/3618/sea_sponge_drug_could_boost_advanced_breast_cancer_survival_by_up_to_five_months

Wei, M., Chun-Chi Lien, I.-I. Lin, and Shang-Ping Xie, (2015): Tropical Cyclone–Induced Ocean Response: A Comparative Study of the South China Sea and Tropical Northwest Pacific. *J. Climate,* 28, 5952–5968. doi: http://dx.doi.org/10.1175/JCLI-D-14-00651.1

Widdicombe S, Spicer JI., (2008) Predicting the impact of ocean acidification on benthic biodiversity: What can animal physiology tell us? J. Exp. Mar. Biol. Ecol. 366: 187-197.

8. Annex 1 - Abstracts of each journal paper

Salinity from space unlocks satellite-based monitoring of ocean acidification

Peter E. Land, Jamie D. Shutler, Helen S. Findlay, Fanny Girard-Ardhuin, Roberto Sabia, Nicolas Reul, Jean-Francois Piolle, Bertrand Chapron, Yves Quilfen, Joseph Salisbury, Douglas Vandemark, Richard Bellerby, and Punyasloke Bhadury

Abstract

Approximately a quarter of the carbon dioxide (CO_2) that we emit into the atmosphere is absorbed by the ocean. This oceanic uptake of CO_2 leads to a change in marine carbonate chemistry resulting in a decrease of seawater pH and carbonate ion concentration, a process that is commonly called 'Ocean Acidification'. Recent studies

have highlighted the need for the development of new *in situ* technology for monitoring ocean acidification, but the potential monitoring capabilites of space-based measurements remain largely untapped. Routine measurements from space can provide quasi-synoptic, reproducible and well-calibrated data for investigating processes on global scales; they are also arguably the most efficient way to monitor the global oceans. As the carbon cycle is dominantly controlled by the balance between the biological and solubility carbon pumps, innovative methods to exploit existing satellite sea surface temperature and ocean color, and new satellite sea surface salinity measurements, will enable frequent monitoring of ocean acidification over large spatial scales.

Optimum satellite and in situ inputs for empirical carbonate system algorithms in the Global Ocean, the Greater Caribbean, the Amazon Plume and the Bay of Bengal

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Abstract
Improving our ability to monitor ocean chemistry, particularly with respect to the carbonate system, has become a priority as the ocean continues to absorb carbon dioxide from the atmosphere. The use of satellite Earth Observation has not yet been thoroughly explored as an option for routinely observing ocean carbonate chemistry, although its potential has been highlighted. We demonstrate the suitability of using empirical algorithms to calculate total alkalinity (A_T) and total dissolved inorganic carbon (C_T), assessing the relative performance of satellite, interpolated *in situ*, climatology and HadGEM2-ES Earth system model datasets in reproducing the wider spatial patterns of these two variables. Both A_T and C_T *in situ* data are reproducible, both regionally and globally, using salinity and temperature datasets, with satellite observed salinity from Aquarius and SMOS providing performance comparable to other datasets for the majority of case studies, and significantly better in the Amazon plume. Use of satellite data inputs in the Bay of Bengal region were less successful, highlighting both satellite and in situ data limitations there.

Progress in satellite remote sensing for studying physical processes at the ocean surface and its borders with the atmosphere and sea-ice

Shutler JD, Quartly GD, Donlon CJ, Sathyendranath S, Platt T, Chapron B, Johannessen JA, Girard-Ardhuin F, Nightingale PD, Woolf DK et al.,.

Physical oceanography is the study of physical conditions, processes and variables within the ocean, including temperature-salinity distributions, mixing of the water column, waves, tides, currents, and air-sea interaction processes. Here we provide a critical review of how satellite sensors are being used to study physical oceanography processes at the ocean surface and its borders with the atmosphere and sea-ice. The paper begins by describing the main sensor types that are used to observe the oceans (visible, thermal infrared and microwave) and the specific observations that each of these sensor types can provide. We then present a critical review of how these sensors and observations are being used to study i) ocean surface currents, ii) storm surges, iii) sea-ice, iv) atmosphere-ocean gas exchange and v) surface heat fluxes via phytoplankton. Exciting advances include the use of multiple sensors in synergy to observe temporally varying Arctic sea-ice volume, atmosphere-ocean gas fluxes, and the potential for 4 dimensional water circulation observations. For each of these applications we explain their relevance to society, review recent advances and capability, and provide a forward look at future prospects and opportunities. We then more generally discuss future opportunities for oceanography-focussed remote-sensing, which includes the unique European Union Copernicus programme, the potential of the International Space Station and commercial miniature satellites. The increasing availability of global satellite remote-sensing observations means that we are now entering an exciting period for oceanography. The easy access to these high quality data and the continued development of novel platforms is likely to drive further advances in remote sensing of the ocean and atmospheric systems.

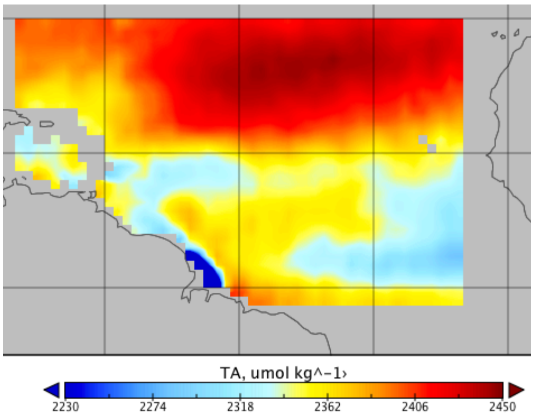
9. Annex 2 - Overview of the Experimental Dataset and examples

Overview

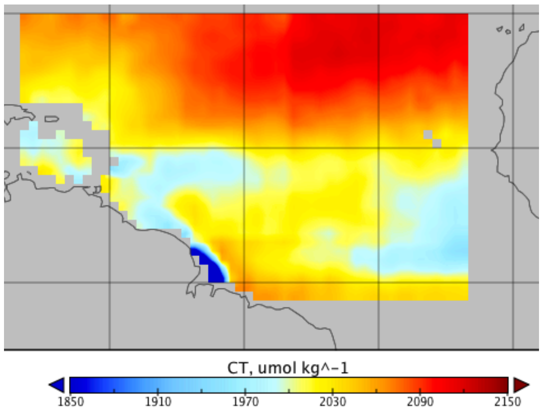
The experimental dataset contains A_T, C_T, and resultant SeaCarb output data for each of the five study regions (Global, Amazon plume, Greater Caribbean, Bay of Bengal, Arctic). The A_T, C_T model (algorithm and input pairings) used for each region are those that provided the best performance based on the results from the round-robin inter-comparison (presented in Findlay et al. in-review) and these are then used to calculate the remainder of the carbonate system parameters. Each regions' data consists of a NetCDF4 file containing T_A, C_T outputs and a second NetCDF4 file containing the SST, SSS, latitude and longitude for the year 2010 and the resultant calculated pH, pCO_2, Ω, at a regular global geospatial resolution of $1° \times 1°$ grid (Global, Amazon plume, Greater Caribbean, Bay of Bengal), or polar stereographic nominal spatial resolution of 25 km (Arctic). The global upwelling indicator output dataset for 2010-2015 is available for at $0.25° \times 0.25°$ and $1° \times 1°$ outputs. The latter is provided so that the upwelling indicator data are available on a grid that is consistent with the biogeochemical data within the experimental dataset. All of these will be made available through the project website. Therefore the experimental dataset covers all of the novel outputs specified in the original bid document (see table A2.1 for a list of the parameters covered). The project team are in the process of preparing the software tools for provision on github under an open-source (not for profit) licence. Figure A2.1 shows example spatial data from the EDS for the Amazon Plume region as viewed in panopaly.

Table A2.1: Reproduced from the original bid document. Novel products that have been developed, validated and exploited within Pathfinders-OA and that are now available within the experimental dataset.

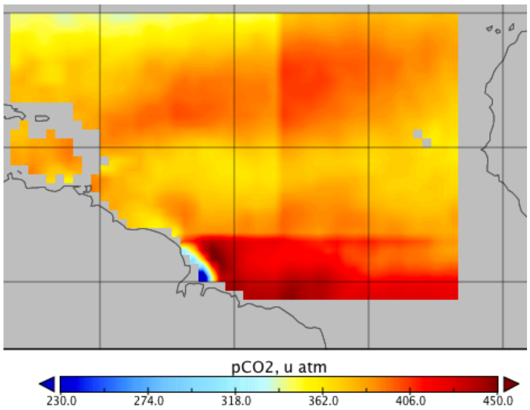
No.	Variable	Variable	Method/source
1.	Partial pressure of CO_2 in seawater	pCO_{2W}	SeaCarb modelled (using optimal A_T and C_T as input, and SST and SSS).
2.	Total alkalinity	A_T	Optimal empirical algorithm from literature (region specific).
3.	Dissolved inorganic carbon	C_T (DIC)	Optimal empirical algorithm from literature (region specific).
4.	Aragonite saturation state	Ω_{ar}	SeaCarb modelled (using optimal A_T and C_T as input, and SST and SSS).
5.	Basicity of seawater	pH	SeaCarb modelled (using optimal A_T and C_T as input, and SST and SSS).
6.	Upwelling incidence indicator	UII	Multi-sensor and model combination.



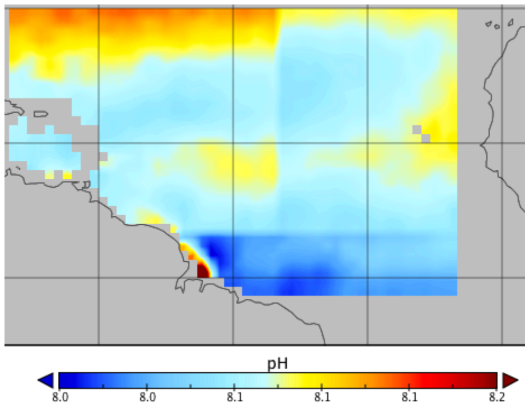
a) A_T



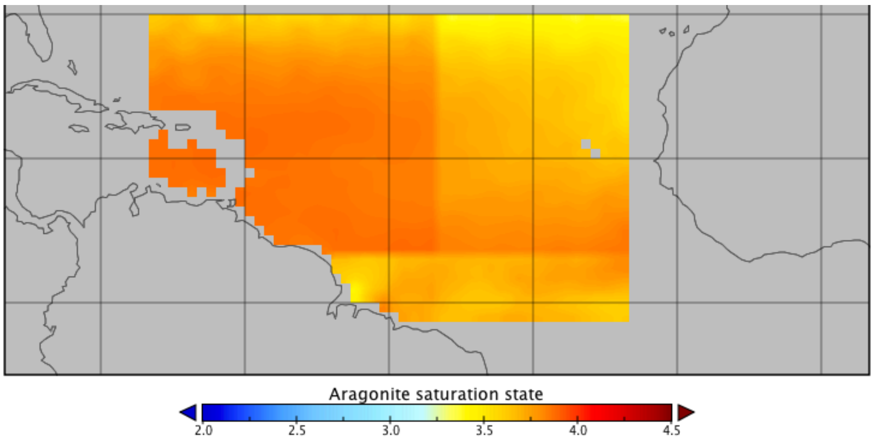
b) C_T



c) pCO_2



d) pH



e) Ω_A

Figure A2.1 Example Aquarius (satelilite observed) salinity driven model outputs for the Amazon region, derived using the best model (algorithm and input pairings) as identified for this region by the round robin exercise; a) A_T (μmol kg^{-1}), b) C_T (μmol kg^{-1}), c) SeaCarb derived pCO_2 (μatm) calculated using A_T and C_T and Aquarius salinity and temperature, d) the equivalent SeaCarb derived pH, e) the equivalent SeaCarb derived in aragonite saturation state (Ω_A).

10. Annex 3 - Upwelling (Quilfen et al., 2016)

1 - Introduction

There are several direct and indirect aspects where satellite data from multiple sensors and platforms can help to improve our understanding of ocean carbonate dynamics and acidification. Accordingly, the remote sensing of ocean acidification (OA) can be interpreted and first separated between chemical, physical, and biological forcing, further recognizing that some sensors can be used to study forcing and impacts. Remotely sensed chemical forcing includes multi-sensor estimates of pCO2 and air-sea CO2 fluxes, and estimates of alkalinity relying heavily on remotely sensed salinity. Water mass, ocean currents and ecological province designations can further be obtained from temperature, altimeter and colour sensors. Ecological responses can then be estimated from satellite products including chlorophyll, coloured dissolved organic matter (CDOM), and productivity relying on sensor measurements in the visible spectrum. Particulate inorganic carbon concentrations that are of relevance for forcing due to impact on alkalinity and response as an indicator of calcifiers can further be determined from their unique spectral features.

Moreover, elaborated key parameters, such as depth of the mixed layer and its wind-impacted advection, along with associated biochemical influx and transformations can today benefit from the improved spatio-temporal view of salinity, temperature, precipitations, ocean colour, wind, wave, and ocean circulation dynamics that can come from the present satellite complement. In particular, upper ocean currents contribute to water mass exchange by horizontal advection to redistribute different constituent concentrations, and can further enhance vertical mixing to possibly entrain lower pH water at larger depth. Conversely, upwelling will entrain lower pH waters to the surface to also possibly stimulate productivity.

This work-package is dedicated to the development of a meaningful upwelling indicator algorithm. It was initially intended to derive an experimental algorithm for the Amazon Plume region, but it was decided to produce a global one since methods and input data appeared to be very robust for that purpose and because its usefulness will be much more evident. Indeed, it will provide the potential to jointly evaluate the distribution of episodic events, such as hurricanes, storms, frontal- and eddy-driven upwelling, to better document processes that lead to vertical fluxes of properties across the base of the surface mixed layer (ML) of the ocean and possible perturbation of the mean state of surface parameters, using all combined observations (especially targeting the available 5 years SMOS observations), and, thanks to the high spatial resolution we are able to evaluate, to focus on any coastal area of interest .

2 – Basic concepts

Upwellings are ubiquitous, wind-driven phenomena (mostly), and they occur at various scales.

They differ in involved processes at offshore and coastal locations. Both are important to consider for the Pathfinders-OA project.

Offshore, the main process that triggers an upwelling is the so-called Ekman pumping. It is the consequence of the divergence of the surface Ekman transport, as illustrated on Figures 1 and 2 for two of the major phenomena leading to open ocean upwelling. The figure 1 shows the mechanisms for a storm-induced upwelling, whose intensity is mainly wind stress curl dependent. Stronger the curl, stronger the divergence of the transport and the associated upwelling. This is modulated by the Coriolis force. These phenomena are ubiquitous and occur at the meso-scale 0(100km).

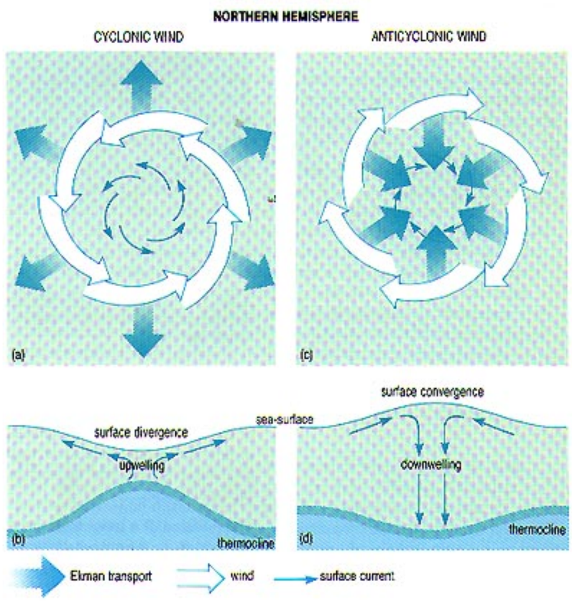


Figure 1: Left: upwelling of cold waters (bottom) induced by cyclonic winds(top). Right: downwelling of cold waters (bottom) induced by anticyclonic winds(top)

Another important upwelling, but occurring at larger scale, is the equatorial upwelling driven by the divergence of the Ekman transport caused by the variability of the Coriolis force on each part of the equator, as illustrated on figure 2. It is varying at seasonal and inter-annual scales depending on the location and strength of the trade winds.

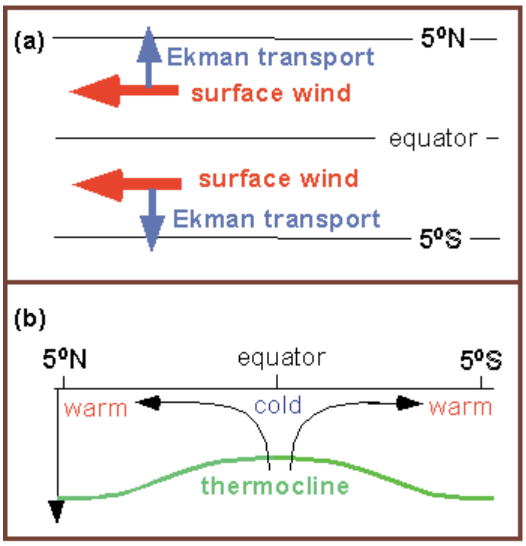


Figure 2: Left: upwelling of cold waters (bottom) induced by divergence of the Ekman transport (top)

At smaller scale, it has also been shown (Chelton, 2010) that SST-induced (cross-front wind gradient induced via air-sea coupling) upwelling are also ubiquitous, and eddy-driven upwelling are also of concern for ocean acidification studies.

Near the shore, upwelling occur over most of the continental shelves as shown on Figure 3, but more systematically close to the eastern boundaries of ocean basins, driven by the main wind systems.

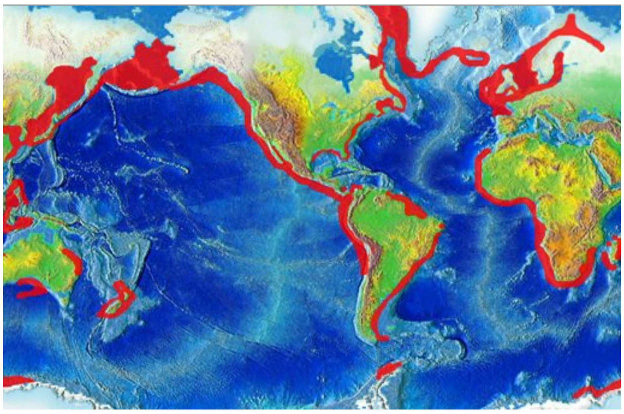


Figure 3: Location, in red, of the main coastal areas of up-welled waters.

Near the shore, the main process leading to an upwelling was long thought to be mainly driven by the divergence of the Ekman transport caused by the along-shore component of an equator-ward wind flow (Bakun, 1973, 1990). The associated offshore Ekman transport causes the coastal upwelling as illustrated in the case of the Benguela upwelling system shown on Figure 4.

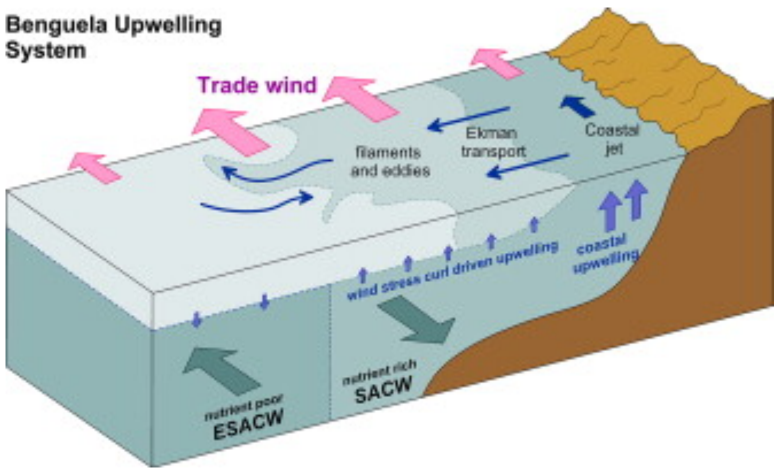


Figure 4: Processes taking place in the Benguela upwelling system.

However, as illustrated on Figure 4, in numerous coastal upwelling systems, other processes contribute significantly and could even be the leading processes (Chelton, 1982; Halpern, 2002; Pickett and Paduan, 2003; Capet et al., 2004; Castelao, 2012). This is for example the case of the California current system. Indeed, large wind stress curl patterns can produce Ekman pumping and up-welled waters in various configurations: cross-shore wind gradients due to weakening of the wind stress very near to the shore caused by the land drag or to SST gradients (air/sea coupling), presence of coastal promontories. Pickett and Paduan (2003) show that Ekman pumping from wind stress curl is as important as Ekman transport from alongshore winds in the California current.

While a simple upwelling indicator can be defined for open ocean conditions as a signed vertical velocity derived from the Ekman pumping, a meaningful upwelling indicator for coastal areas should take into account the different possible processes. The difficulty is that both Ekman pumping and Ekman transport estimates cannot be combined in a single parameter in a global way because each process must be scaled with characteristic lengths that are regionally dependent. In particular these scales depend heavily on the shape of the continental shelves (Estrade et al., 2008), and other process such as onshore geostrophic flow may further complicate the situation.

We then choose to provide both indicators separately in a same product, to evaluate the Ekman pumping and Ekman transport contributions, that can be further combined for a specific upwelling area or analysed in a combined approach as discussed in Halpern (2002).

One important point is that this upwelling indicator should retain the useful scales, which was not possible with the data sets previously available (Pickett and Paduan, 2003; Capet et al., 2004). Thanks to the large coverage of the satellite instruments operating during the recent years, we are able, in the frame of the OA project, to derive upwelling indicators at daily scale and 0.25 degree of spatial resolution.

3 – Upwelling indicators

Accounting for the basic concepts developed in the previous section, we can define two different indicators that can be used differently in case its use concerns an offshore or a coastal upwelling.

3.1 Upwelling indicator offshore

Offshore, the upwelling indicator is related to the Ekman pumping/suction, and can be defined as the vertical velocity at the base of the Ekman layer. Direct mapping and quantification of the upwelling (positive velocity) and downwelling (negative velocity) patterns is given by:

$$\mathrm{EKP}=W_{\mathrm{EK}} = (\mathrm{curl}\tau)/(\rho f) + (\beta\tau_x)/(\rho f^2)$$

where $(\mathrm{curl}\tau)$is the wind stress curl, $\rho$is the air density, $f$is the Coriolis parameter.

The second term of the right hand part of the equation is a correction term for the βplane effect (derivative of f with latitude), and $\tau_x$is the wind stress zonal component.

Details of the Ekman surface layer model and Ekman pumping calculation and interpretation can be found in several publications (Stommel, 1958; Halpern, 2002; Risien and Chelton, 2008).

Units are generally given in m/s, cm/day, or m/day.

The Ekman model breaks down close to the equator where f approaches 0, resulting in unrealistic large values of Ekman pumping. Therefore, indicator values are not computed equator-ward of 5 degrees of latitude.

The Ekman pumping calculation also does not hold very close to the coast where the surface Ekman layer merges with the bottom Ekman frictional layer.

The figure 5 illustrates the Ekman pumping climatology at mean monthly scale, derived from the QuikScat scatterometer (Riesen and Chelton, 2008). It shows mainly the equatorial upwelling (positive values) and the large upwelling patterns in the mid-latitude storm tracks areas.

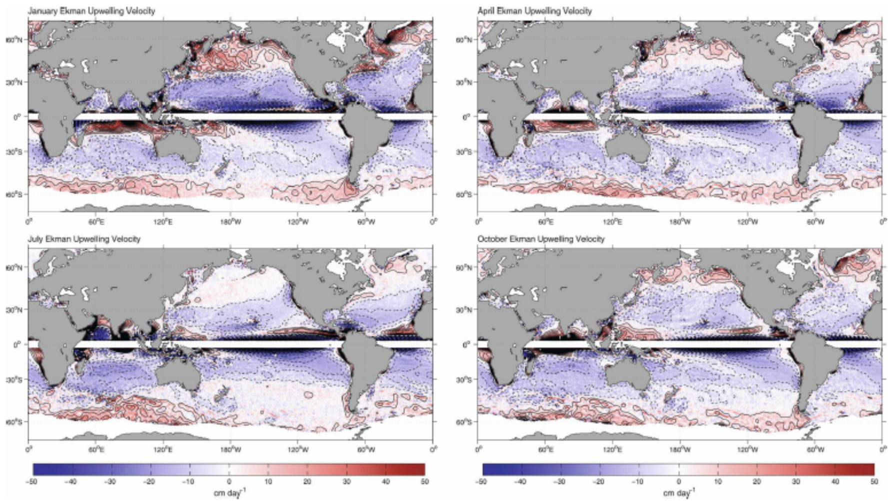


FIG. 7. Average SCOW Ekman upwelling velocity (w) maps for (a) January, (b) April, (c) July, and (d) October. Given that curl(τ/f) is undefined at the equator, values of w are not plotted between 3°S and 3°N. Contours of w with an interval of 5 cm day^{-1} are overlaid to aid interpretation. Dashed and solid contours correspond to negative and positive upwelling velocities, respectively. The zero contour is omitted for clarity.

Figure 5: Climatology of the Ekman upwelling velocity in cm/day for January (top left), April (top right), July (bottom left), October(bottom right). From Riesen and Chelton (2008).

3.2 Upwelling indicator near the coastline

Near the coast, upwelling is also driven by the equator-ward component of the wind stress and can be defined by the cross-shore Ekman transport by unit of coast length:

$EKT = \tau_{\parallel} / (\rho f)$ where $\tau_{\parallel}$ is the wind stress component parallel to the coast line.

Units in m^3/s

Near the coast, both EKP and EKT indicators should be considered to account for the different upwelling types at work, but they cannot be combined in a single indicator on a general basis because such combination requires to define a local cross-shore scale and to account for the local sea floor shape.

3.3 Products for the OA Pathfinder

One single product in netcdf format is produced, grouping the Ekman pumping and Ekman transport components parameters.

Two temporal resolutions are processed. A monthly climatology is produced, in line with other products of the OA database. Daily fields are also produced to map episodic events such as upwelling associated with storms and to retain the short-term variability near the coast that triggers many upwelling events (Feely et al, 2008).

A spatial resolution of 0.25^{o} in latitude and longitude is chosen for both temporal resolution because a 1^{o} resolution is much too crude to account for the variability of the parameters (wind stress and curl, SST) that triggers the upwelling. It enables a better intensity and variability mapping.

The products cover the global ocean for the time period 2010/2015.

The input wind stress products are the blended fields (produced at CERSAT, Bentamy et Croize-Fillion, 2012) computed using a kriging algorithm to grid ASCAT-A and –B winds together, and a spatial coherency constraint towards ECMWF wind vectors. The blended approach benefits from the global coherency of ECMWF numerical winds patterns but is mainly weighted towards the more accurate satellite winds.

An example of a product dump is given in the appendix.

4 – Examples from the OA Pathfinder data-base

This section intends to illustrate the upwelling indicator data-base usefulness for a variety of applications, and to also validate the choices made concerning the indicators and the product space/time resolution.

4.1 Upwelling of the California current

Near-shore waters of the California Current System already have a low carbonate saturation state, making them particularly susceptible to ocean acidification (Feely et al., 2008; Hauri et al., 2013).

The California current upwelling is a characteristic feature of the ocean dynamics in this area due to the uneven coastline and its wind climatology, and is thus one of the most studied system. It is also the subject of an operational monitoring by the NOAA CoastWatch project, as illustrated on Figure 6.

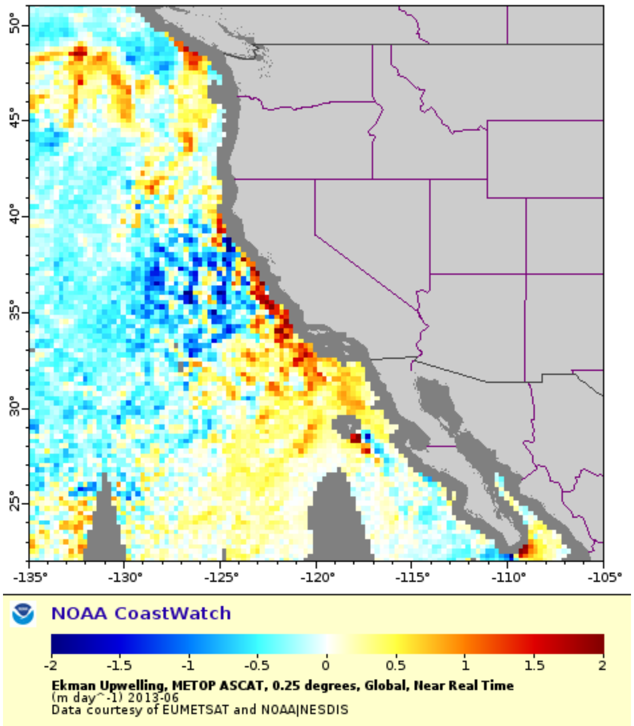


Figure 6: Ekman upwelling indicator from the NOAA CoastWatch project for June 2013.

This picture shows rather complex patterns that are mostly related to the wind stress curl patterns. This small-scale variability is characteristic of the influence of the California current coastal topography and is enhanced near capes and points. The California current is a particular upwelling system where the EKP contribution is shown to be as large or greater than the EKT contribution (Pickett and Paduan, 2003). This is certainly why the CoastWatch project provides the EKP as a unique indicator to trace the upwelling events.

However, contribution of the cross-shore Ekman transport is as significant as discussed in Pickett and Paduan (2003) and combination of both EKP and EKT upwelling indicators is certainly needed to map the upwelling patterns, as illustrated on Figure 7 that maps the OA Pathfinder data for June 2013 as on Figure 6. EKP patterns on figures 6 and 7 compare well as expected, both using the METOP ASCAT data. However, it is expected that the OA Pathfinder product is more accurate since it makes use of a state-of-art interpolation analysis while the near real time NOAA product uses simple averaging methods of the ASCAT winds. Further, the figure below shows that the cross-shore Ekman transport significantly contributes to the upwelling intensity and patterns. Using this data-set, one can analyse separately the different contributions as discussed in Halpern (2002) or go beyond with a combination of the two quantities following Pickett and Paduan (2003).

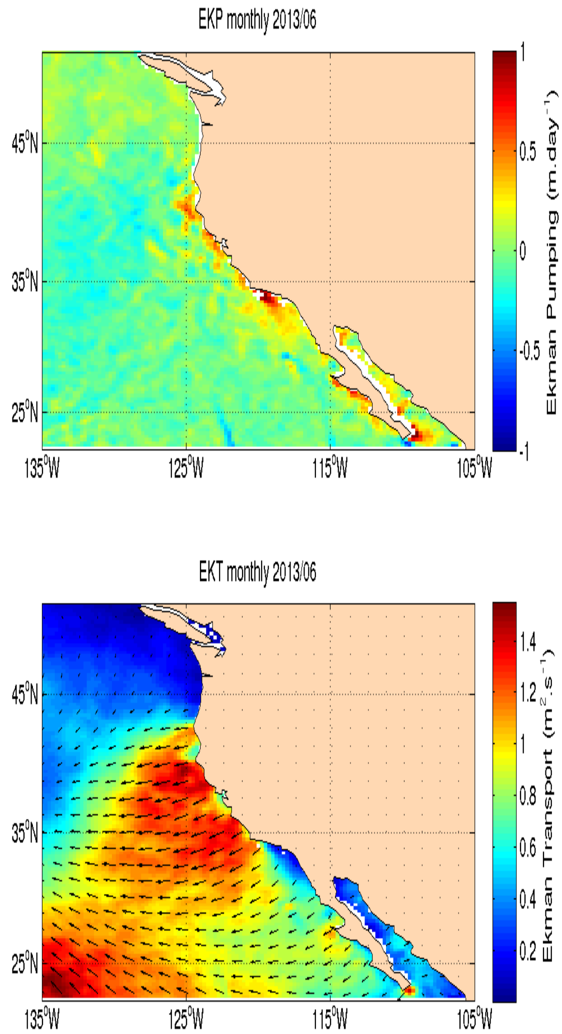


Figure 7: Ekman upwelling indicators from the OA Pathfinder project for June 2013.

4.2 Mapping of upwelling produced during tropical cyclones

Episodic events such as tropical cyclones contribute to local air/sea CO2 flux and variations of primary productivity, depending on the ocean saturation state at the time of the TC passage. For a given ocean basin and a particular year, tropical cyclones are likely to contribute greatly to air/sea exchanges, as stated by Nemoto et al., 2009: "The efflux enhanced by three typhoons accounted for 60% of the efflux of CO2 in the North Pacific warm season". This is the result of the exceptional intensity of such events in regions where the wind is relatively moderate or regular. It can be exemplified in the Figure 8 represents the Ekman pumping velocity field, from the OA Pathfinder, during the hurricane Igor on September 17th, 2010. For that particular day the background field is very low comparatively to the upwelling indicator in the Igor wake, and one can anticipate that such a long lasted phenomenon (> 10 days) may contribute very significantly to the total outcome for this basin and season.

However this is a field of active and controversial research (Levy et al., 2012; Foltz et al., 2015; Mei et al., 2015), this OA data set can certainly help to contribute.

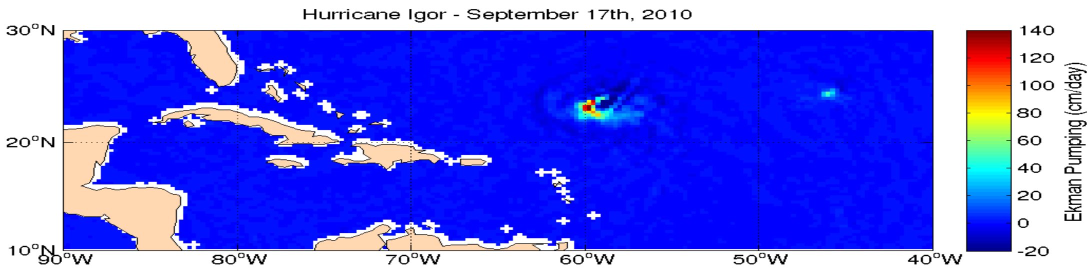


Figure 8: Ekman pumping velocity field in hurricane Igor from the OA Pathfinder project.

4.2 Upwelling episodic event in the Western Arctic Ocean

Episodic meteorological events in the Western Arctic Ocean occur frequently when traveling storms generate winds parallel to the coastline, as in the Beaufort Sea. Storm-induced upwelling of high pCO2 waters onto the continental shelf of the western Arctic Ocean and implications for carbonate mineral saturation states are discussed in the Mathis et al study (2012). The figure 9 is a picture of the numerical winds they used to map the monthly stormy wind conditions in October 2011. It shows that the zonal winds (bottom plot) blowing parallel to the coastline generate a cross-shore Ekman transport and an upwelling of boundary current water that likely caused aragonite undersaturation along the entire coast of the Beaufort Shelf.

The figure 10 shows the OA Pathfinder monthly upwelling indicators for the same month in October 2011 (top), and the daily fields corresponding to the passage of the strongest winds (2011, October 18th). The daily field of the EKT (bottom right) indicator very well depicts the cross-shore transport that produced the upwelling, and with better accuracy than the monthly field. Moreover, the daily EKP field (bottom left) clearly shows a significant contribution of the wind stress curl to the upwelling, that was not discussed in Mathis et al. (2012). It is clear that the ¼ degree resolution of the fields enables to map the cross-shore wind gradients and associated wind stress curl, which is a strength of these data.

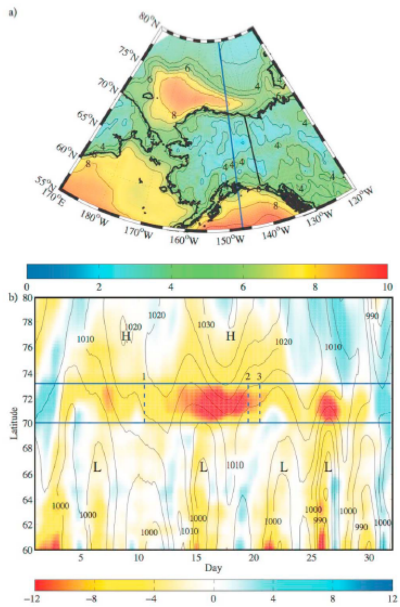


Figure 9: Atmospheric conditions over the Beaufort Sea during October 2011. Top: monthly mean 10 m wind speed (m/s). Bottom: Hovmoller plot of the sea-level pressure (contours- mb) and the zonal component of the 10 m wind (color, m/s) along 147 W.

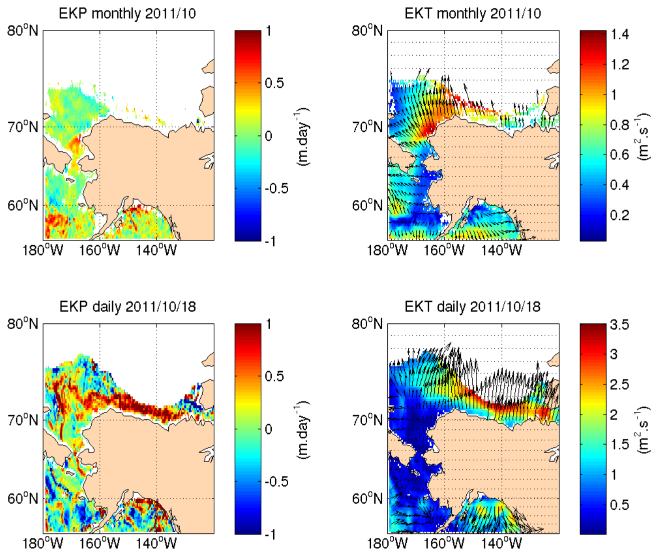


Figure10: EKP (left) and EKT (right) indicators of the OA Pathfinder at monthly scale (top, 2011/10) and daily scale (bottom, 2011/10/18).

5 - Appendix: Example of an upwelling indicator product dump

Dimensions:

time = 1 (UNLIMITED)

lat = 641

lon = 1440

Variables:

lat

Size: 641x1

Dimensions: lat

Datatype: single

Attributes:

_FillValue = 9.97e+36

long_name = 'latitude'

standard_name = 'latitude'

units = 'degrees_north'

lon

Size: 1440x1

Dimensions: lon

Datatype: single

Attributes:

_FillValue = 9.97e+36

long_name = 'longitude'

standard_name = 'longitude'

units = 'degrees_east'

time

Size: 1x1

Dimensions: time

Datatype: double

Attributes:

_FillValue = 9.97e+36

long_name = 'time'

standard_name = 'time'

units = 'days since 1970-01-01 00:00:00Z'

northward_ekman_transport

Size: 1440x641x1

Dimensions: lon,lat,time

Datatype: double

Attributes:

_FillValue = 9.97e+36

long_name = 'Northward component of Ekman transport'

units = 'm^2.s-1'

ekman_pumping

Size: 1440x641x1

Dimensions: lon,lat,time

Datatype: double

Attributes:

_FillValue = 9.97e+36

long_name = 'Ekman pumping velocity'

units = 'm.s-1'

comment = 'no values between 5North and 5South'

eastward_ekman_transport

Size: 1440x641x1

Dimensions: lon,lat,time

Datatype: double

Attributes:

_FillValue = 9.97e+36

long_name = 'Eastward component of Ekman transport'

units = 'm^2.s-1'

6 - References

Bakun, A. (1973), Coastal upwelling indices, west coast of North America, 1946–71, *NOAA Tech. Rep.* NMFS SSRF□671, 103 pp.

Bakun, A. (1990), Global climate change and intensification of coastal ocean upwelling, *Science*, 247, 198–201.

Bentamy A..; D. Croize-Fillon (2012), Gridded surface wind fields from Metop/ASCAT measurements. *Inter. Journal of Remote Sensing*, 33(6), 1729-1754. DOI 10.1080/01431161.2011.600348.

Capet, X.J., Marchesiello, P., McWilliams, J.C. (2004). Upwelling response to coastal wind profiles. *Geophys. Res. Lett*. 31, L13311. Doi:10.1029/ 2004GL020123.

Castelao, R. M. (2012), Sea surface temperature and wind stress curl variability near a cape, *J. Phys. Oceanogr.*, 42, 2073–2087.

Chelton, D., and S.-P. Xie (2010), Coupled ocean-atmosphere interactions at oceanic mesoscales, *Oceanography*, 23, 52–69.

Chelton, D. (1982), Large-scale response of the California current to forcing by the wind stress curl, *CalCOFI Rep.*, 119, 130–148.

Estrade, P., Marchesiello, P., De Verdière, A.C., and C. Roy (2008), Cross-shelf structure of coastal upwelling : a two – dimensional extension of Ekman's theory and a mechanism for inner shelf upwelling shut down. *J. Mar. Res.*, 66, http://dx.doi.org/10.1357/002224008787536790

Feely RA, Sabine CL, Hernandez-Ayon JM, Ianson D, Hales B. (2008). Evidence for upwelling of corrosive “acidified” water onto the continental shelf. *Science* 320:1490–92

Foltz, G. R., K. Balaguru, and L. R. Leung (2015), A reassessment of the integrated impact of tropical cyclones on surface chlorophyll in the western subtropical North Atlantic, *Geophys. Res. Lett.*, 42, 1158–1164, doi:10.1002/2015GL063222.

Halpern, D. (2002). Offshore Ekman transport and Ekman pumping off Peru during the 1997–1998 El Nino. *Geophys. Res. Lett*. 29 (5), 1075. doi:10.1029/2001GL014097.

Hauri, C., N. Gruber, M. Vogt, S. C. Doney, R. A. Feely, Z. Lachkar, A. Leinweber, A. M. P. McDonnell, M. Munnich, and G.-K. Plattner (2013), Spatiotemporal variability and long-term trends of ocean acidification in the California Current System, *Biogeosci*., 10, 193–216, doi:10.5194/bg-10-193-2013.

Levy, M., M. Lengaigne, L. Bopp, E. M. Vincent, G. Madec, C. Ethe, D. Kumar and VVSS Sarma (2012), Contribution of Hurricanes to the air-sea CO2 flux: a global view, *GBC*, vol 26, doi:10.1029/2011GB004145

Lin, I.-I., W. T. Liu, C.-C. Wu, G. T. F. Wong, C. Hu, Z. Chen, W.-D. Liang, Y. Yang, and K.-K. Liu (2003), New evidence for enhanced ocean primary production triggered by tropical cyclone, *Geophys. Res. Lett.*, 30(13), 1718, doi:10.1029/2003GL017141.

Mathis, J. T., et al. (2012), Storm-induced upwelling of high pCO2 waters onto the continental shelf of the western Arctic Ocean and implications for carbonate mineral saturation states, *Geophys. Res. Lett.*, 39, L07606, doi:10.1029/2012GL051574.

Wei Mei, Chun-Chi Lien, I.-I. Lin, and Shang-Ping Xie, (2015): Tropical Cyclone–Induced Ocean Response: A Comparative Study of the South China Sea and Tropical Northwest Pacific. *J. Climate,* 28, 5952–5968. doi: http://dx.doi.org/10.1175/JCLI-D-14-00651.1

Nemoto, K., T. Midorikawa, A. Wada, K. Ogawa, S. Takatani, H. Kimoto, M. Ishii, and H. Y. Inoue (2009), Continuous observations of atmospheric and oceanic CO2 using a moored buoy in the East China Sea: Variations during the passage of typhoons, *Deep Sea Res*., Part II, 56(8–10), 542–553, doi:10.1016/j.dsr2.2008.12.015.

Pickett, M. H., and J. D. Paduan (2003), Ekman transport and pumping in the California Current based on the U.S. Navy's high-resolution atmospheric model (COAMPS), *J. Geophys. Res.*, 108(C10), 3327,doi:10.1029/2003JC001902.

Risien, C.M., and D.B. Chelton (2008): A Global Climatology of Surface Wind and Wind Stress Fields from Eight Years of QuikSCAT Scatterometer Data. *J. Phys. Oceanogr*., 38, 2379-2413.

Stommel, H. M. (1958), The Gulf Stream: A Physical and Dynamical Description, 202 pp., *Univ. Calif. Press*, Berkeley, Calif..

11. Annex 4 – Artic region A_T and C_T round-robin inter-comparison results

The figures below show the A_T and C_T results for all regions analysed. The columns labelled ‘Barents’ are for the Barents Arctic Sea. For A_T the Aquarius and SMOS results are comparable and at around 60 µmol kg^{-1}, whereas the in situ (LDEO climatology) driven models and HadGEM2 results are around 40-42 µmol kg^{-1}. Note there are no CORA data within the Barents Sea so the red column is missing from the plots. For C_T the Aquarius and in situ (LDEO clim) driven model results are around 38-40 µmol kg^{-1}, HadGEM2 climatology are slightly higher, whereas the SMOS results are much higher at around 70 µmol kg^{-1}. Overall Aquarius and SMOS driven A_T models perform poorly in the Barents Sea. Aquarius driven C_T models show skill comparable to that of in situ driven models in the Barents Sea. Whereas, in comparison SMOS driven C_T models performs poorly. These results are captured in figure A4.1 below and figure A4.2 shows example spatial data using the best performing model (algorithm and input pairings).

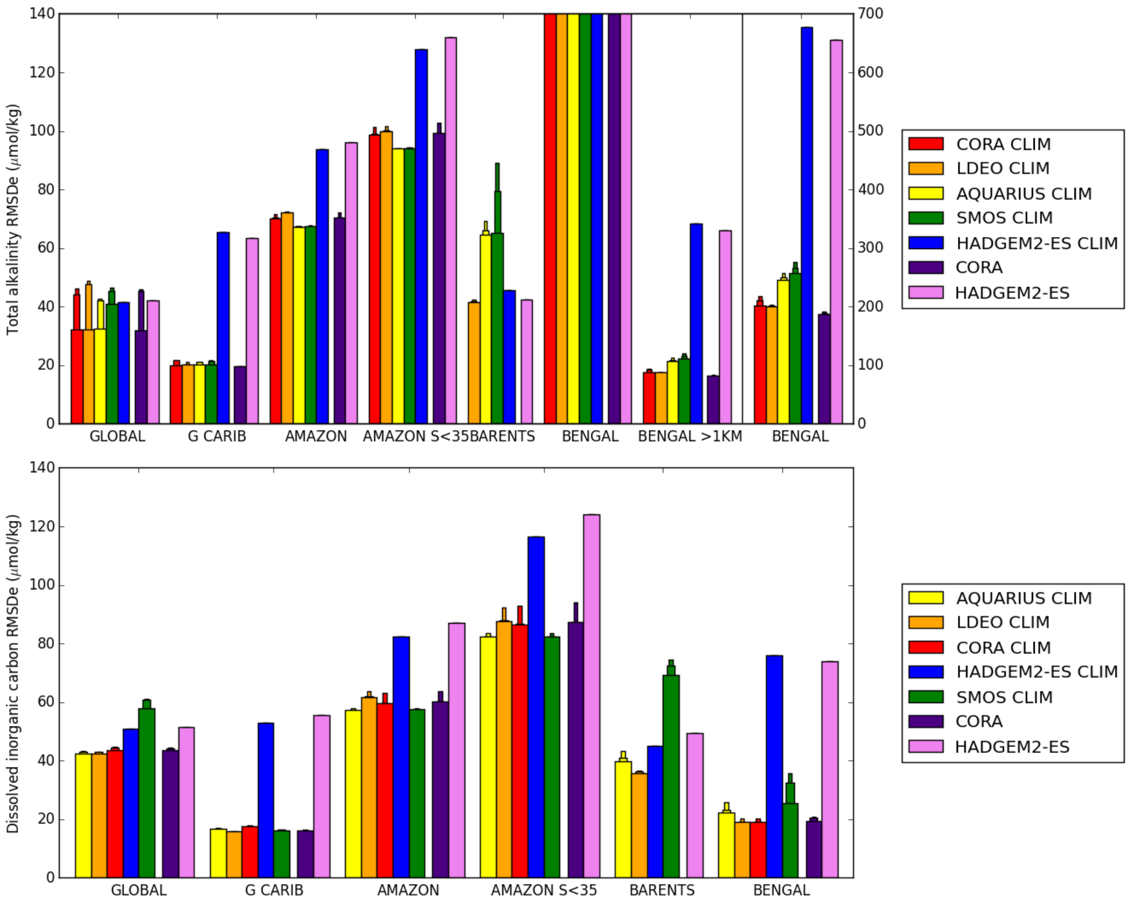
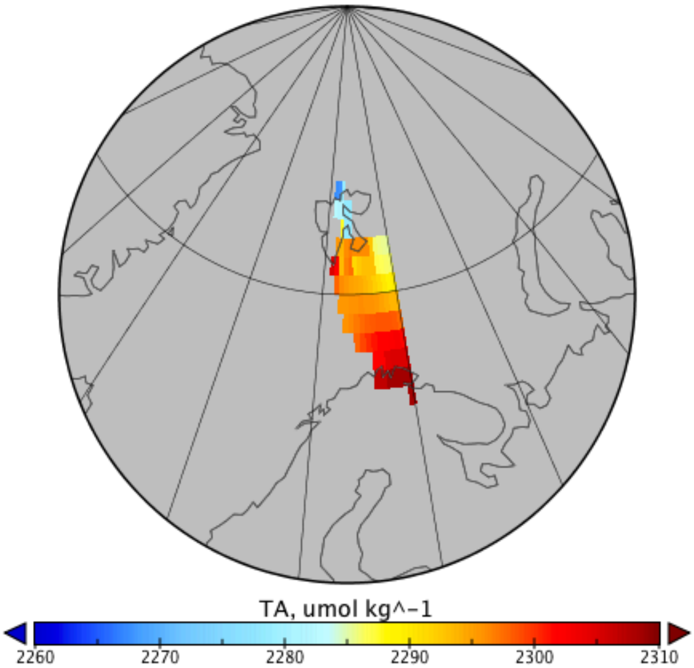
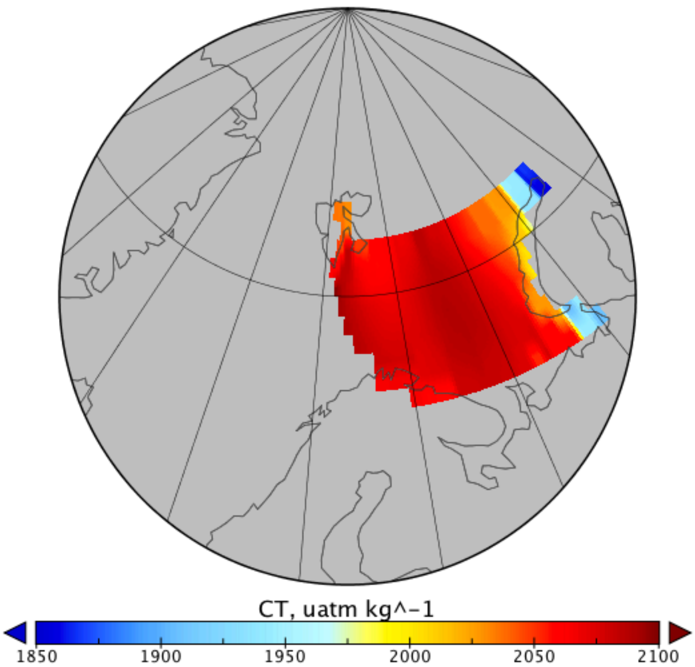


Figure A4.1: The overall A_T (top) C_T (bottom) normalised root mean squared differences across all models (algorithm and input pairing) grouped by region and chosen salinity input. The normalised approach allows the A_T and C_T results between regions to be compared (care should be taken when comparing across regions).



a) A_T (μm kg^{-1})



a) C_T (μm kg^{-1})

Figure A4.2: Example model (empirical algorithm and input pairing) outputs for the Arctic Barents Sea from the Experimental Data Set (EDS) using the best performing model. a) A_T using Takahashi and Sutherland (2013), LDEO salinity climatology and the WOA NO_3 climatology and b) C_T using Lee (2000), LDEO salinity, ESA CCI SST climatology and the WOA NO_3 climatology.

12. Annex 5 – partial pressure of CO_2 (pCO_2) round-robin inter-comparison results

The pCO_2 inter-comparison was very limited due to the existence of only one empirical pCO_2 algorithm. The plot below shows the overall results. Essentially the global normalised root mean square difference is > 50 µatm, which is much larger than the expected variability and larger than the accepted total uncertainty of in situ measurements (e.g. within SOCAT the accepted uncertainty in low cost pCO_2 instruments is ±10 µatm). Whereas the regional results are more promising giving a normalised root mean square difference of 14-20 µatm. These results are captured in figure A5.1 below.

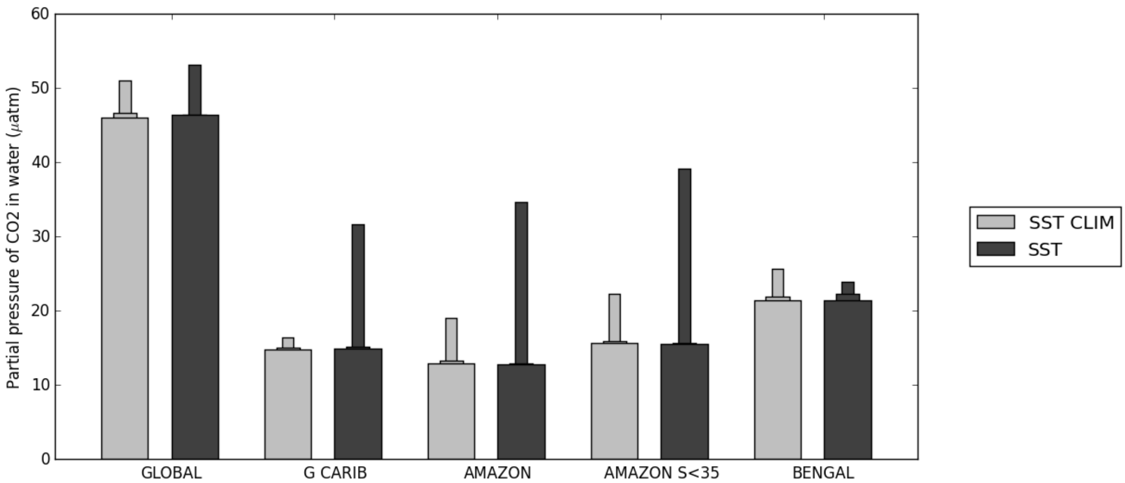


Figure A5.1: The normalised root mean squared differences for the pCO_2 algorithm assessed grouped by region and chosen sea surface temperature input. The normalised approach allows the results between regions to be compared (care should be taken when comparing across regions).

13. Annex 6 Round robin intercomparison data and methods

Round-robin comparison and datasets

Five case study regions were used in a round-robin comparison of the algorithms: the global ocean, the Greater Caribbean region (GCR) (14°N to 30°N, 90°W to 60°W), the Amazon Plume region (APR) (2°S to 30°N, 70°W to 20°W), the Bay of Bengal region (BBR) (5°N to 24°N, 78°E to 96°E, using the Bay of Bengal International Hydrographic Office Sea Area [IHO, 1953]) and the Arctic Barents Sea. These case studies were chosen as areas that are potentially challenging for this assessment and are discussed in more detail in Land et al. (2015).

Each algorithm (C_T, A_T, pCO_2) was tested using input data for each forcing factor (SSS, SST, and/or NO_3) from a range of data sources and combined in the round-robin comparison. The data sources were:

1) satellite observed data from the Soil Moisture and Ocean Salinity (SMOS) satellite [SSS], the Aquarius satellite [SSS], and the Climate Change Initiative (CCI) [SST];
2) *In situ* re-analysis data from the Coriolis Ocean Re-Analysis (CORA v4.0) database [SSS, SST];
3) climatology data from the Lamont Doherty Earth Observatory (LDEO) datasets [SSS, SST] and the World Ocean Atlas (WOA) dataset [NO_3]; and
4) output from the HadGEM2-ES global climate model (Jones et al., 2011).

All data were binned spatially to a 1°x1° grid and temporally to monthly intervals. The multi-year CORA, satellite and model data were also combined to form monthly climatologies (henceforth referred to as climatological data). In the case of SMOS and Aquarius, nearly all the *in situ* carbonate data (used here for validation) were collected before the satellites were launched, hence only climatological data were used for these sensors (for SMOS data from years 2010-2013, and Aquarius years 2011-2013.

The binned output from each algorithm, herein referred to as 'model output', was compared to *in situ* binned data of the same carbonate parameter. Data from the Global Data Analysis Project (GLODAP) (Key et al., 2004) and the CARbon dioxide IN the Atlantic (CARINA) Project [CARINA Group, 2009a, 2009b, 2010] were the primary datasets used with some additional regional data. In all cases of *in situ* data, the mean of the top 10 m water depth was used.

Statistics

Nominal state-of-the-art errors of 0.5% were applied to *in situ* A_T and C_T (Bockman and Dickson, 2015), and the stated algorithm uncertainties were propagated through to the algorithm outputs. Uncertainties in the forcing factors (SST, SSS, NO_3 and model A_T and C_T) were not included, since for many input datasets these are unknown. *In situ* and algorithm squared uncertainties were added, and weighted statistics were calculated, with each data point weighted by the inverse of this sum. As a check, un-weighted statistics were also calculated, and were very similar to the weighted statistics.

Weighted model mean ($\overline{x}_m$), standard deviation (σ_m) and *in situ* carbonate data mean ($\overline{x}_d$) and standard deviation (σ_d) were output for each assessment, as well as weighted root-mean-square-difference (RMSD), normalized standard deviation ($\sigma^* = \sigma_m/\sigma_d$), bias ($B = \overline{x}_m - \overline{x}_d$), weighted point-to-point correlation (R) and t-test for the difference between model and data.

References

Land, P. E., J. D. Shutler, H. S. Findlay, G. Girard-Ardhuin, N. Reul, J.-F. Piolle, B. Chapron, Y. Quilfen, J. Salisbury, D. Vandemark, R. G. J. Bellerby, P. Bhadury, and R. Sabia, (2015), Salinity from space unlocks satellite-based monitoring of ocean acidification, Environ. Sci. Tech., 49, 1987-1994, doi:10.102/es504849s.

Jones, C. D., J. K. Hughes, N. Bellouin, S. C. Hardiman, G. S. Jones, J. Knight, S. Liddicoat, F. M. O'Connor, R. J. Andres, C. Bell, K.-O. Boo, A. Bozzo, N. Butchart, P. Cadule, K.D. Corbin, M. Doutriaux-Boucher, P. Friedlingstein, J. Gornall, L. Gray, P. R. Halloran, G. Hurtt, W. J. Ingram, J.-F. Lamarque, R. M. Law, M. Meinshausen, S. Osprey, E. J. Palin, L. Parsons Chini, T. Raddatz, M. G. Sanderson, A. A. Sellar, A. Schurer, P. Valdes, N. Wood, S. Woodward, M. Yoshioka, and M. Zerroukat, (2011), The HadGEM2-ES implementation of CMIP5 centennial simulations, Geosci. Model Dev., 4, 543-570, doi:10.5194/gmd-4-543-2011.

Key, R. M., A. Kozyr, C. L. Sabine, K. Lee, R. Wanninkhof, J. L. Bullister, R. A. Feely, F. J. Millero, C. Mordy, and T. H. Peng, (2004), A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP), Global Biogeochem. Cycles, 18(4).