Ocean CO_2: Theory and Observations
The Oceanography of CO_2

Part 1: Observing ocean biogeochemistry

1. **Introduction**
2. **Observing surface pCO_2**
3. **Observing column DIC and TA**
4. **Observing pH**

Part 2: Conceptual patterns and mechanisms of ocean biogeochemistry

1. **Air-Sea CO_2 exchange**
2. **Biological processes**

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22.05.2019

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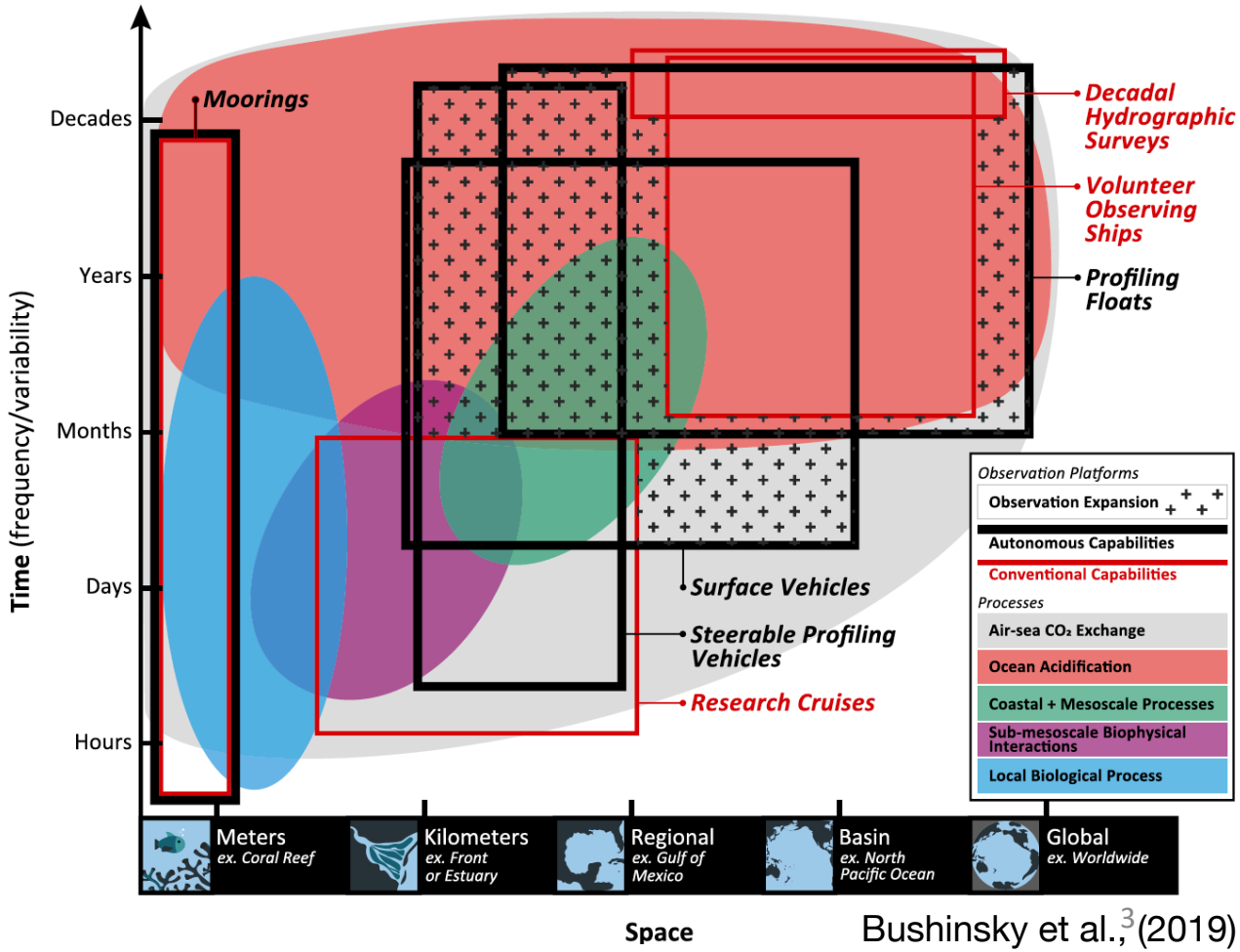
Part 1: Observing ocean biogeochemistry

1. Introduction

The observations platforms currently provide different measurements capabilities, in terms of either parameters measured or spatial/temporal resolution.



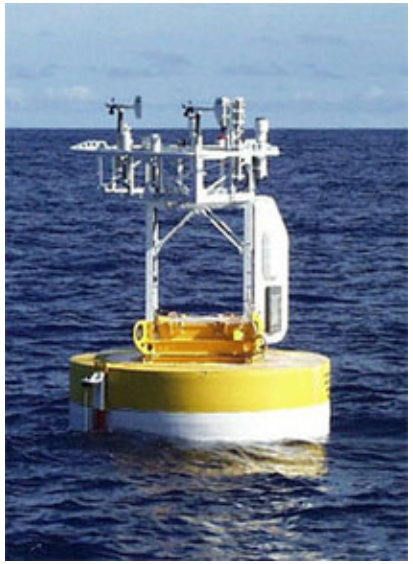
Bushinsky et al.,[3] (2019)

Part 1: Observing ocean biogeochemistry

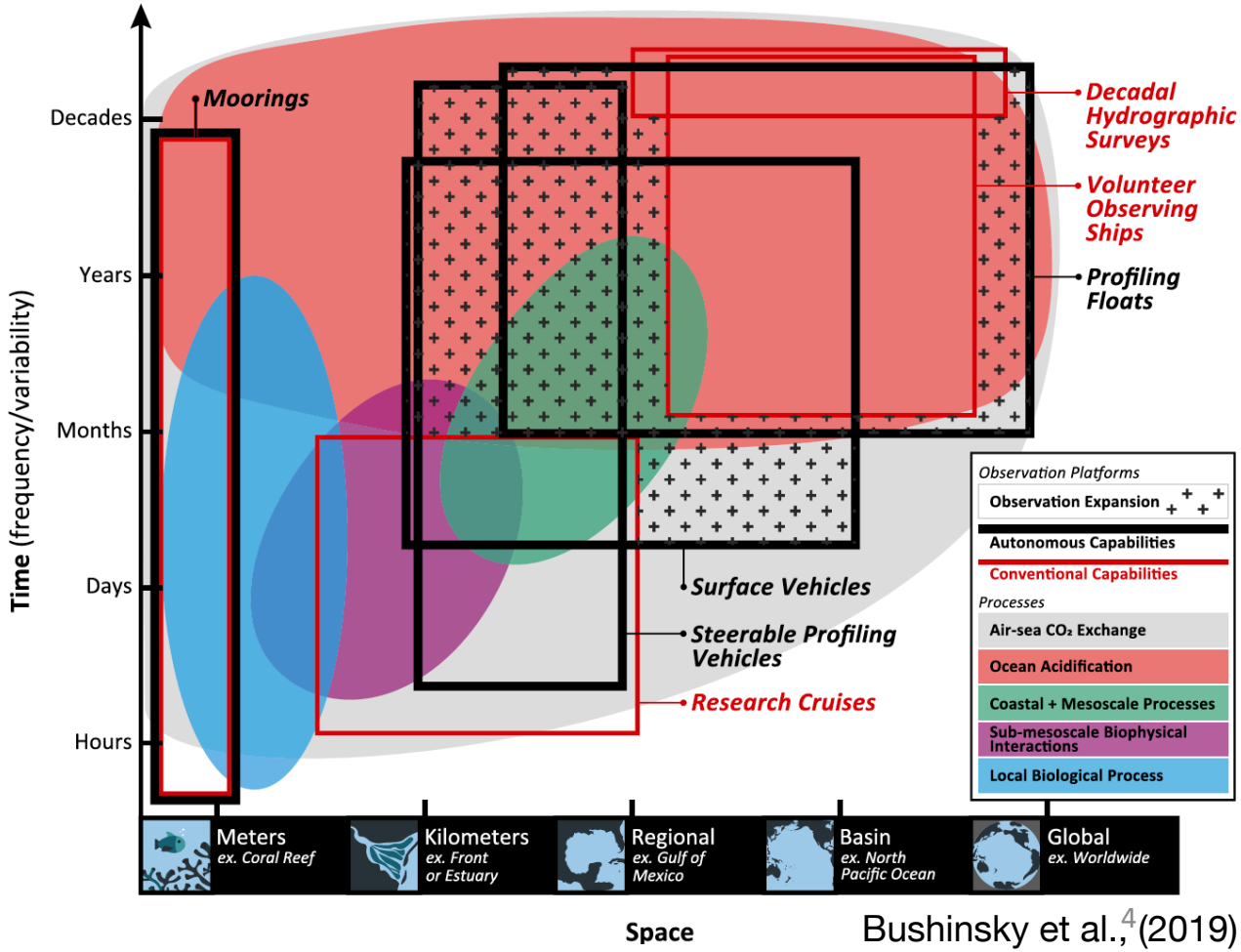
1. Introduction

Moorings

Surface moorings are the oldest platform for autonomous observation of the carbonate system (Bushinksky et al., 2019), particularly the platform Moored Autonomous pCO_2 ($MAPCO_2$) (Sutton et al., 2014).



https://www.pmel.noaa.gov/co2/story/WHOTS



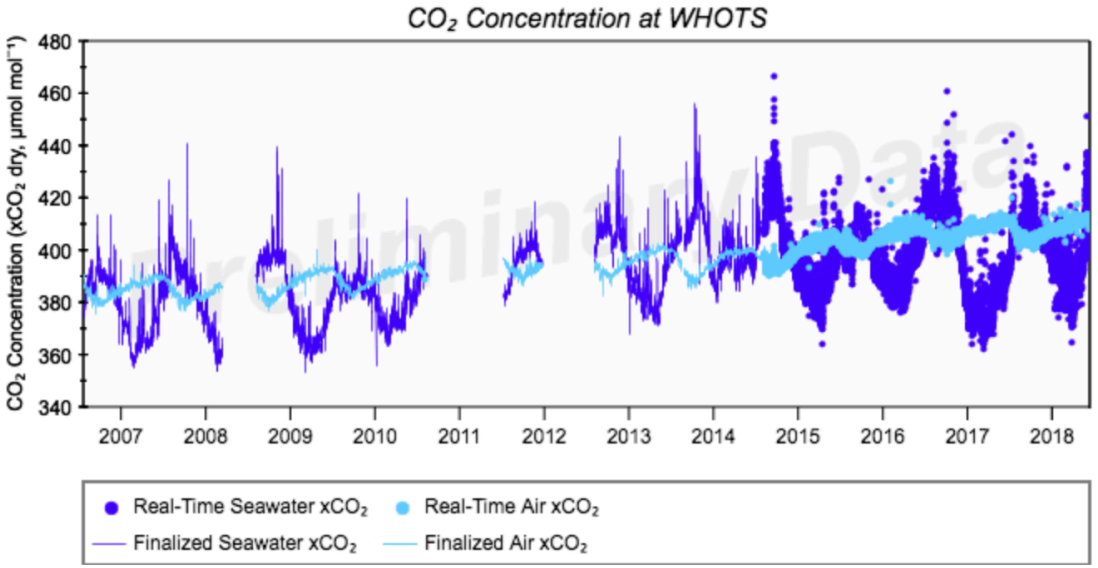
Bushinsky et al.,[4] (2019)

Part 1: Observing ocean biogeochemistry

1. Introduction

Moorings

Spatial and temporal variability is limited with moorings. Mooring observe surface processes but not subsurface processes, which requires frequent *in-situ* calibration and which is not suitable in the open ocean. Associated costs (maintenance in the open ocean and post-pre deployment gas calibration) make it unlikely to have significant increase in the size of mooring arrays.



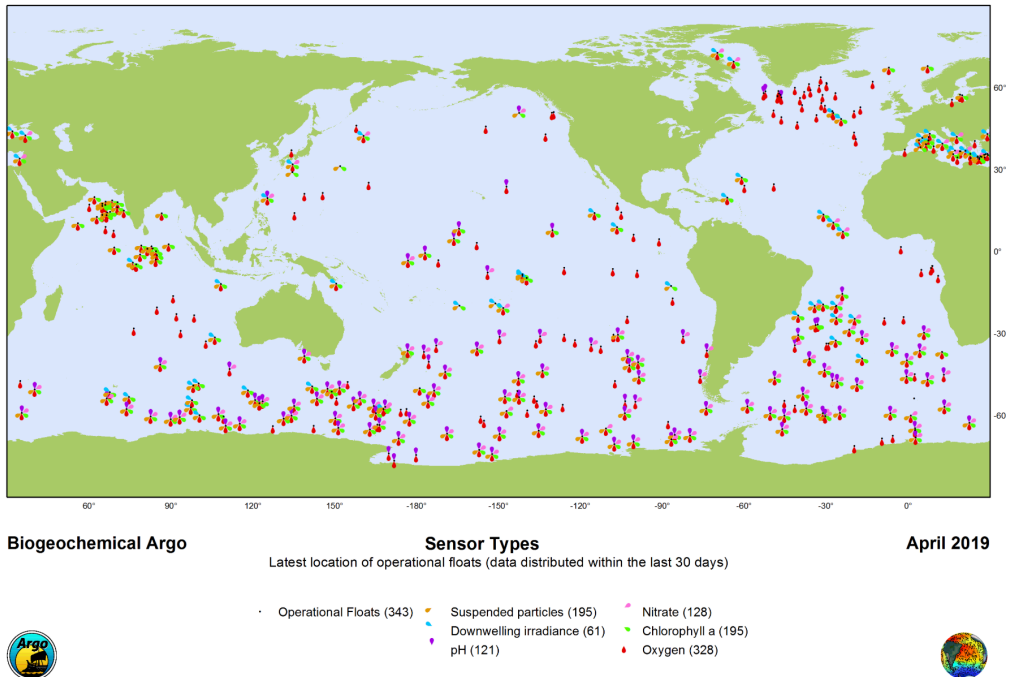
https://www.pmel.noaa.gov/co2/story/WHOTS

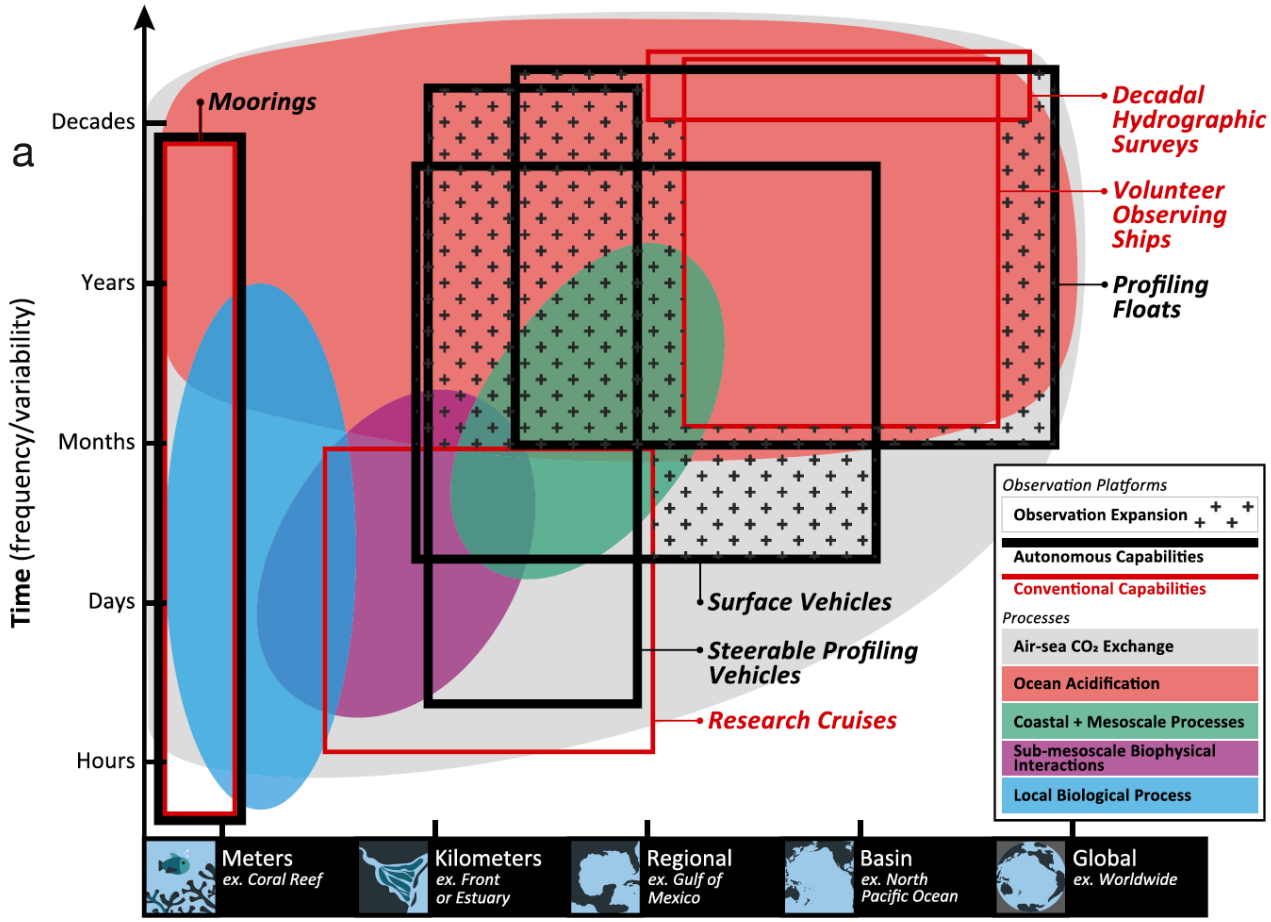
Part 1: Observing ocean biogeochemistry

1. Introduction

Profiling floats

Profiling floats are the only autonomous observational platform that has been demonstrated to be scalable to a global level, and are particularly suited to study basin-wide to global processes on seasonal to interannual scales (Bushinsky et al. 2019).





Bushinsky et al., (2019)

Part 1: Observing ocean biogeochemistry

1. Introduction

Profiling floats

Biogeochemical floats include oxygen, nitrate, and bio-optical measurements for chlorophyll a fluorescence and particle backscatter. Integrating pCO_2 sensors is still under the prototype phase (Bushinksky et al., 2019).

Autonomous sensors for key oceanic biogeochemical variables

Variable	Sensor Type	Accuracy/Precision	Reference
Oxygen (1,3,4)	Lifetime optode	1% of surface O_2 / 0.2 µmol kg^{-1}	[Körtzinger et al., 2004] [Johnson et al., 2015] [Bittig et al., 2015]
Nitrate (1,4)	Ultraviolet absorbance	1 µmol kg^{-1} / 0.1 µmol kg^{-1}	[Johnson et al., 2013]
pH (1,4)	Ion Sensitive Field Effect Transistor	0.01 pH / 0.0005 pH	[Johnson et al., 2016]
Chlorophyll *a* (2,3,4)	Fluorescence	Max (30%,0.03 mg Chl*a* m^{-3}) / 0.025 mg Chl*a* m^{-3}	[Boss et al., 2008]
	Radiometer	Max (24%,0.03 mg Chl*a* m^{-3}) / 0.025 mg Chl*a* m^{-3}	[Xing et al., 2011]
Suspended particles (3)	Optical backscatter	Suspended particles: Max (50%, 1.5 µg kg^{-1}) / 1 µg kg^{-1}	[Boss et al., 2015]
		Backscattering coefficient: Max (10%, $10^{-5} m^{-1}$) / 4 x10^{-6} m^{-1}	[Sullivan et al., 2013]
		POC : Max (30%, 20 mg m^{-3}) / 10 mg m^{-3}	[Cetinic et al., 2012]
		PC: Max (30%, 6 mg m^{-3}) / 3 mg m^{-3}	[Graff et al., 2015]
Downwelling irradiance (3,4)	Radiometer	PAR: Max (3%, 5 µmol photons m^{-2} s^{-1}) / 1 µmol photons m^{-2} s^{-1}	[Manufacturer web site]
		Spectral: Max (3%, 5 X10^{-3} µW cm^{-2} nm^{-1}) / 2.5 X 10^{-3} µW cm^{-2} nm^{-1}	

http://biogeochemical-argo.org

Part 1: Observing ocean biogeochemistry

1. Introduction

Profiling floats

Project Info:

Acronym:	SOCCO BIO-ARGO
Title:	Understanding the biogeochemical response to physical drivers in the Southern Ocean using bio-optics
Started in:	2012
Area of interest:	Southern Ocean
Website:	http://socco.org.za/research/#Bio

Principal investigators:

- Sandy Thomalla, SOCCO, CSIR, SA
- Stewart Bernard, CSIR, SA

Share:

SOCCO BIO-ARGO

SEE IT ON THE MAP

Follow Profiling floats.

KEY VARIABLES

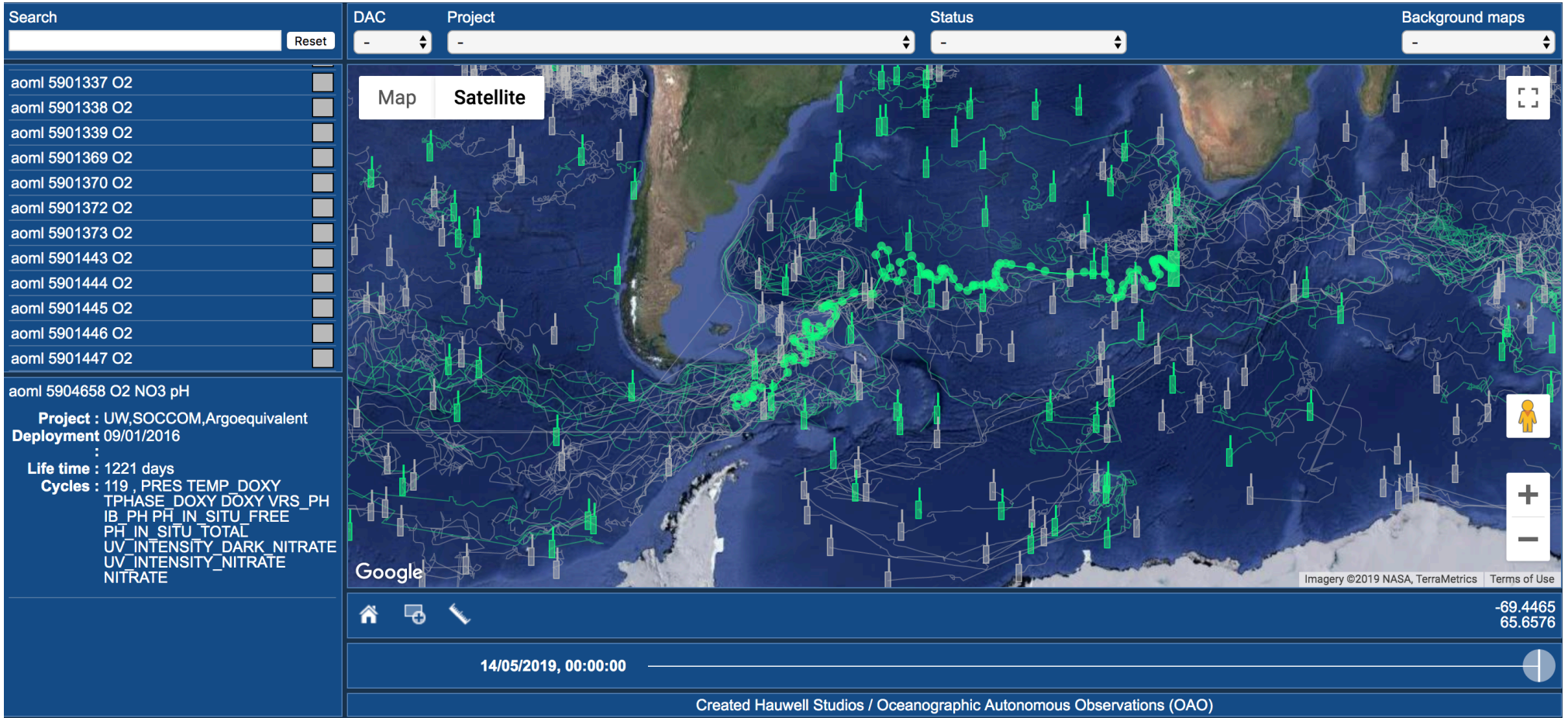
O_2, Chl*a*, Suspended particles, Downwelling irradiance

Part 1: Observing ocean biogeochemistry

1. Introduction

Profiling floats

http://www.oao.obs-vlfr.fr/mapsg/en/

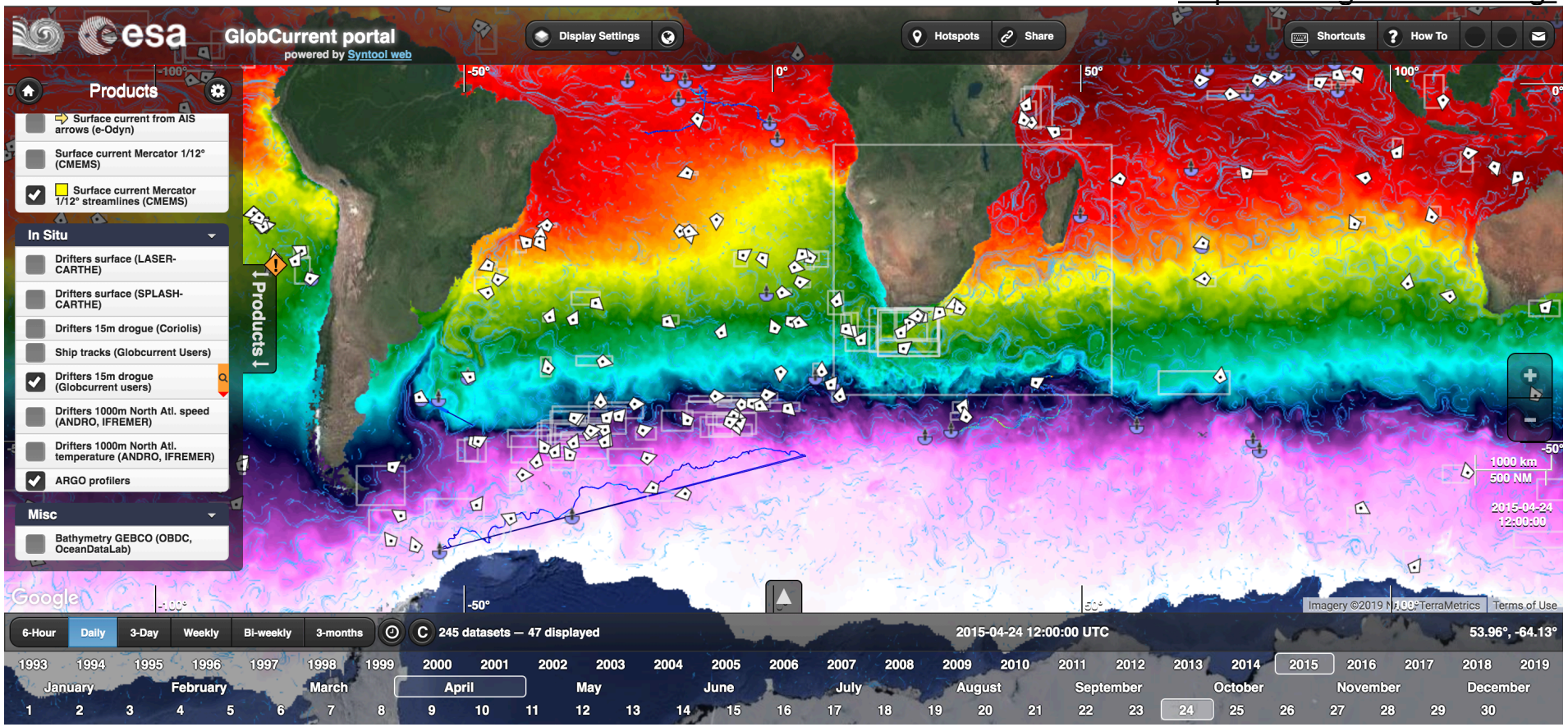


Part 1: Observing ocean biogeochemistry

1. Introduction

Profiling floats

http://www.globcurrent.org/

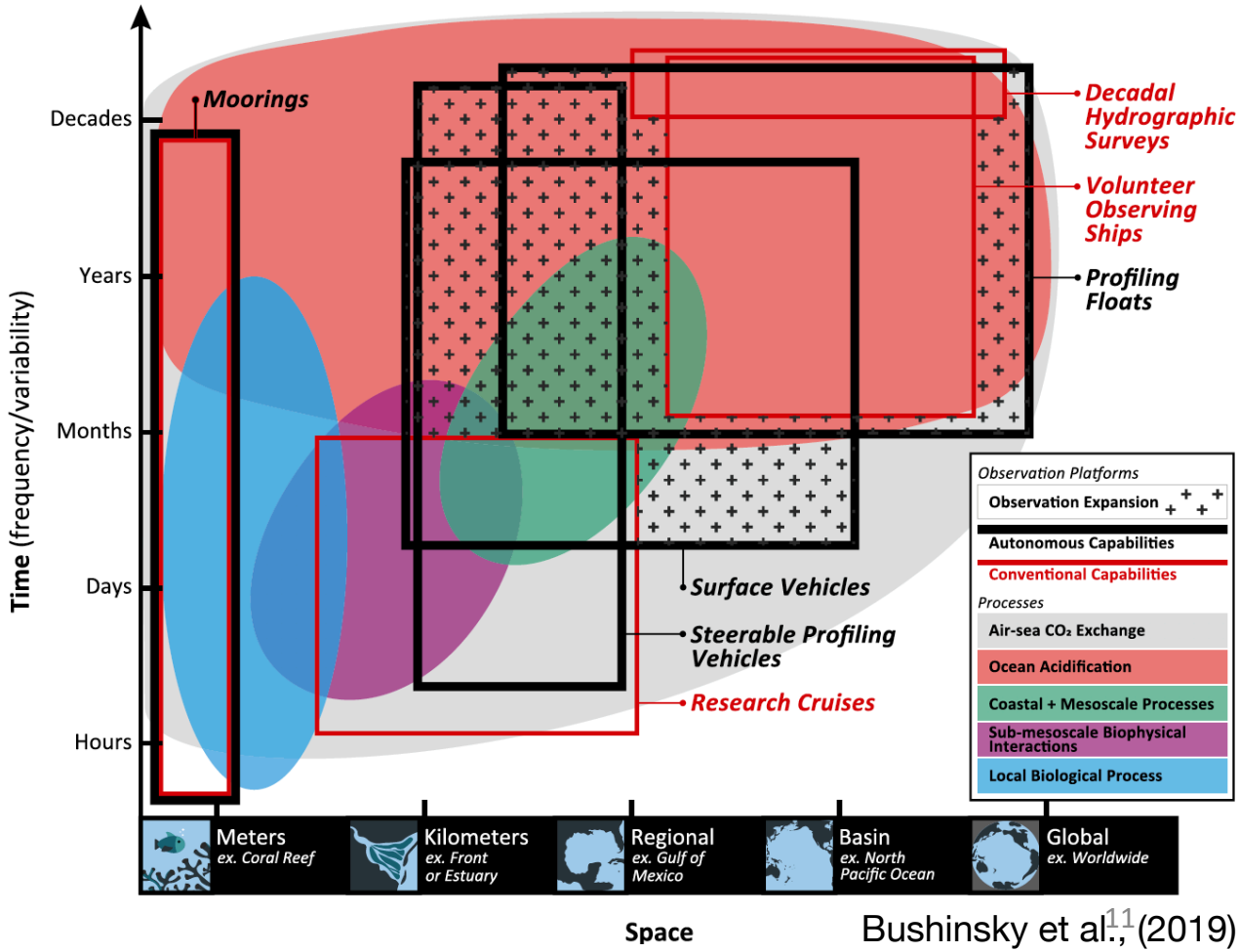


Part 1: Observing ocean biogeochemistry

1. Introduction

Ships (Hydrological section and VOS)

Essential platforms to monitor the change in biogeochemical variables in the ocean interior (unlike profiling floats that currently reach up to 2000m depth, hydrographic sections reach the bottom of the ocean), when the sections is repeated (ideally yearly). Yet hydrographic sections are typically biased toward summer due to optimum weather conditions.



Bushinsky et al., (2019)

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Part 1: Observing ocean biogeochemistry

2. Observing surface pCO_2

How is surface ocean pCO_2 obtained*?

Surface pCO_2 can be deduced via:

(1) Discrete seawater sample (deducting pCO_2 from the other carbonate parameters)
(2) pCO_2 sensors
(3) Underway systems

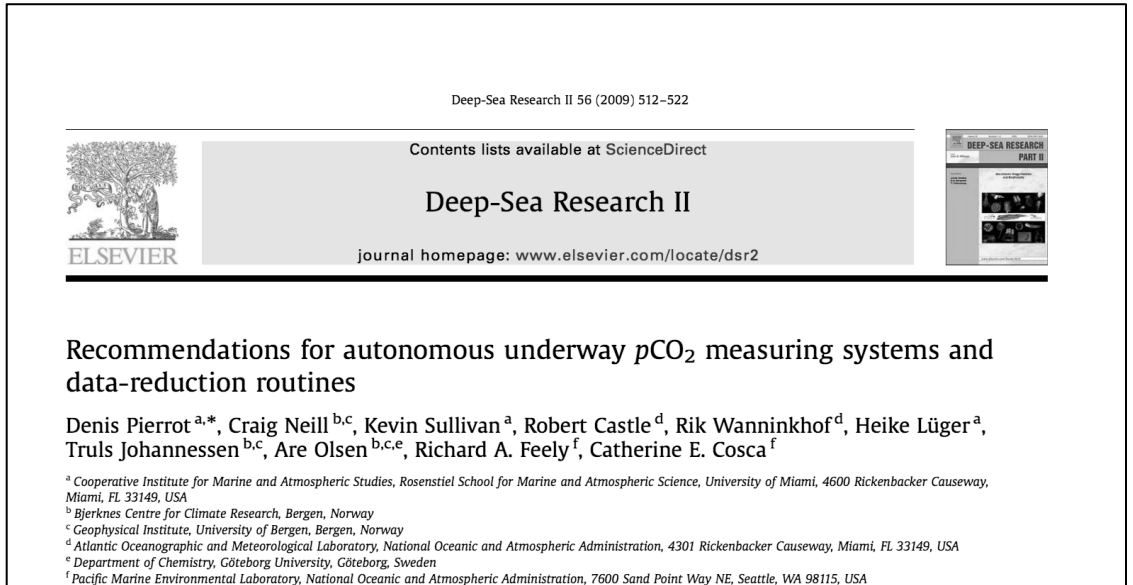
* Importantly note that pCO_2 is not a measured property. It is deduced from the measured xCO_2 (mixing ratio).

Part 1: Observing ocean biogeochemistry

2. Observing surface pCO_2

How is surface ocean pCO_2 obtained?

Underway pCO_2 systems allow to produce high quality and comparable data sets, and are designated to operate autonomously with just maintenance work in port.



Deep-Sea Research II 56 (2009) 512–522

Contents lists available at ScienceDirect

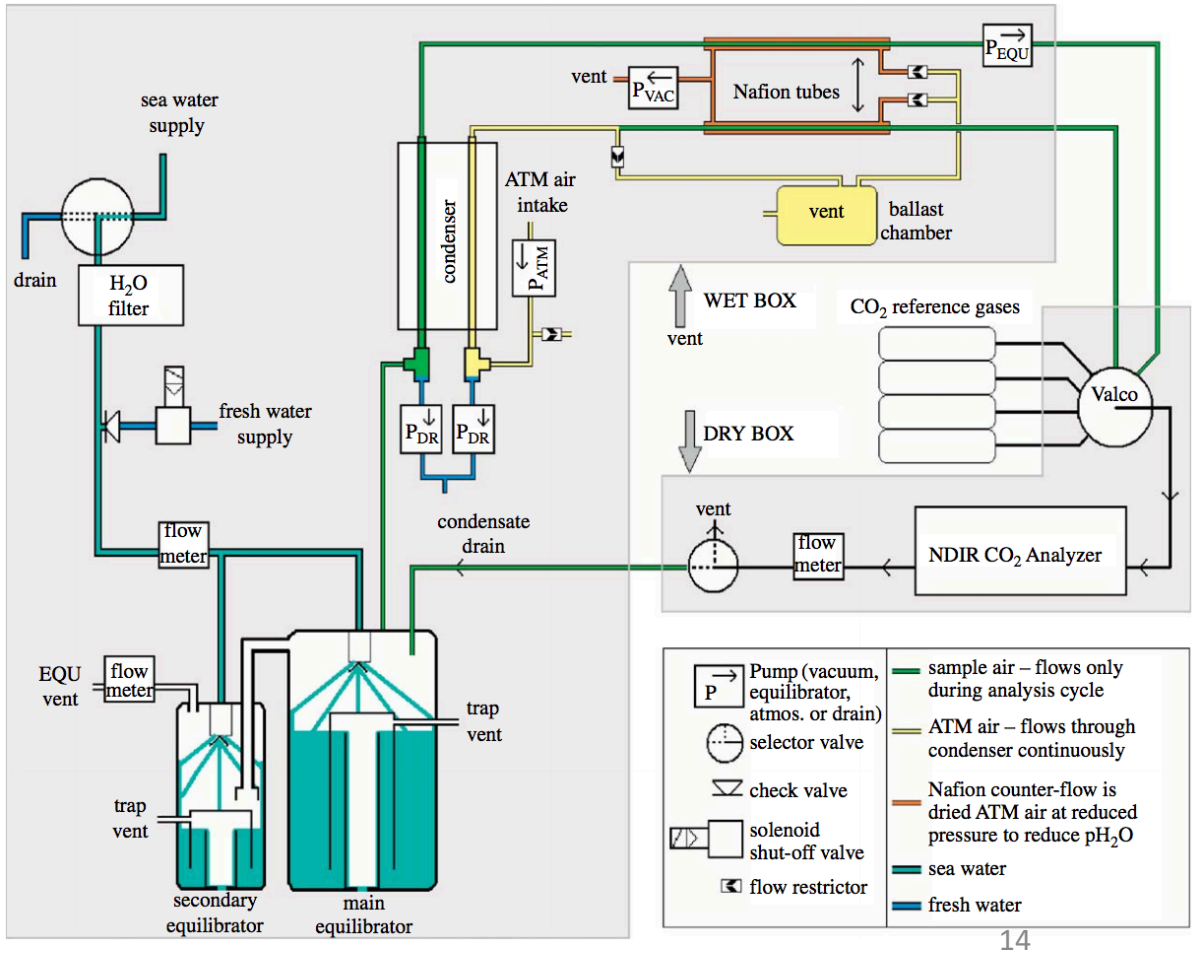
Deep-Sea Research II

journal homepage: www.elsevier.com/locate/dsr2

Recommendations for autonomous underway pCO_2 measuring systems and data-reduction routines

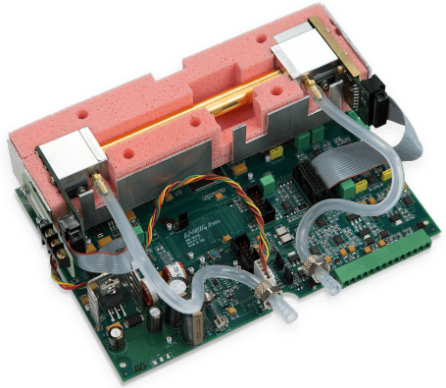
Denis Pierrot [a,*], Craig Neill [b,c], Kevin Sullivan [a], Robert Castle [d], Rik Wanninkhof [d], Heike Lüger [a], Truls Johannessen [b,c], Are Olsen [b,c,e], Richard A. Feely [f], Catherine E. Cosca [f]

[a] Cooperative Institute for Marine and Atmospheric Studies, Rosenstiel School for Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, FL 33149, USA
[b] Bjerknes Centre for Climate Research, Bergen, Norway
[c] Geophysical Institute, University of Bergen, Bergen, Norway
[d] Atlantic Oceanographic and Meteorological Laboratory, National Oceanic and Atmospheric Administration, 4301 Rickenbacker Causeway, Miami, FL 33149, USA
[e] Department of Chemistry, Göteborg University, Göteborg, Sweden
[f] Pacific Marine Environmental Laboratory, National Oceanic and Atmospheric Administration, 7600 Sand Point Way NE, Seattle, WA 98115, USA



Part 1: Observing ocean biogeochemistry

2. Observing surface pCO_2

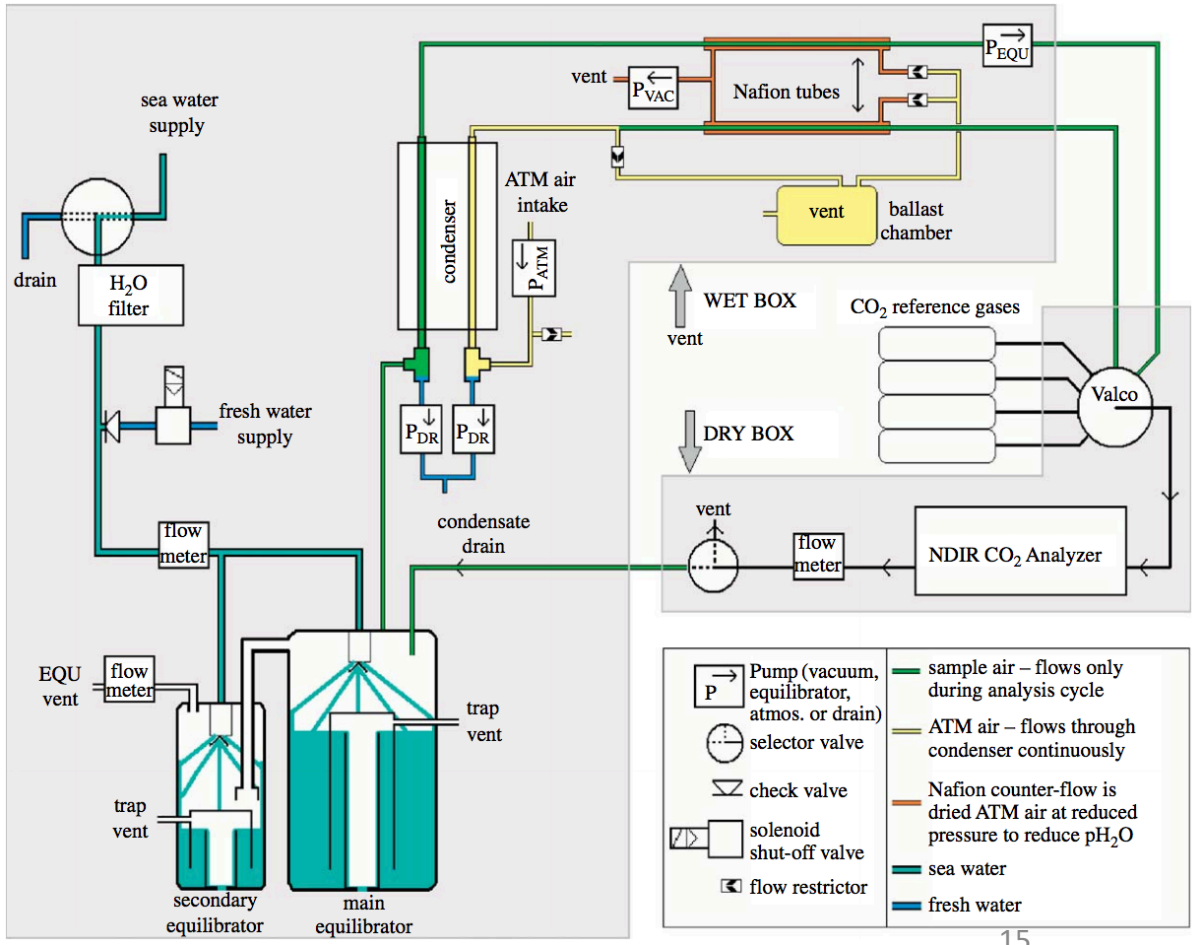


How is surface ocean pCO_2 obtained?

The system broadly works as follow:
(1) Seawater is pumped at the bottom of the ship (about 7m depth) and reaches the equilibrator (showerhead).
(2) The CO_2 in seawater equilibrates with the headspace gas in the chamber.
(3) The equilibrated CO_2 is dried (remaining water vapour is removed) and pumped through a non-dispersive infrared analyser.
(4) The analyser measures the air's CO_2 mole fraction (xCO_2) instantaneously, and then returned to the equilibrator thus forming a closed loop.

Periodically, atmospheric air is also pumped through the analyser, measuring its CO_2 mole fraction to quantify the gas headspace's concentration. The infrared analyser is calibrated with CO_2 standard gases at regular intervals.

Sims et al., A measurement system for vertical seawater profiles close to the air-sea interface, Ocean Science, (2017)



Pierrot et al., (2009)

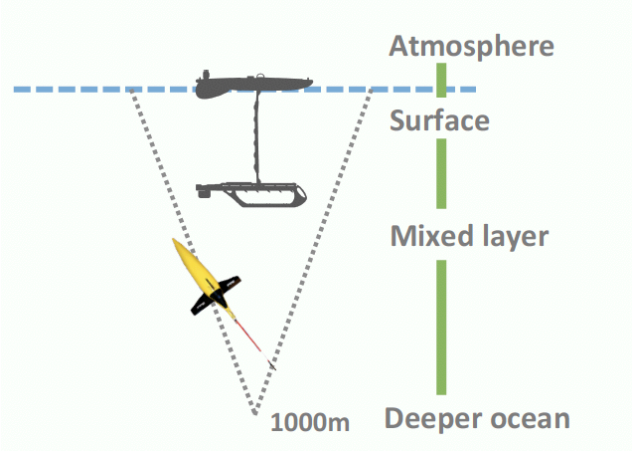
Part 1: Observing ocean biogeochemistry

2. Observing surface pCO_2

What are the platforms that measure surface ocean pCO_2?

Over the past decades, surface ocean CO_2 observations have been collected through the development of autonomous instrumentation on board research vessels and Voluntary Observing Ships (i.e. commercial ships), on moorings and more recently on autonomous vehicles (Monteiro et al., 2015).

The sustained CO_2 observing are the results of broad international efforts.



Nicholson & Du Plessis Gliders Lecture

Part 1: Observing ocean biogeochemistry

2. Observing surface pCO_2

How are the observations gathered for easy public use?

The Surface Ocean CO2 Atlas (**SOCAT**) grids global pCO2 data from 1972 to 2017 (version 6).
https://www.socat.info/

Earth Syst. Sci. Data, 8, 383–413, 2016
www.earth-syst-sci-data.net/8/383/2016/
doi:10.5194/essd-8-383-2016

Open Access Earth System Science Data

A multi-decade record of high-quality *f*CO_2 data in version 3 of the Surface Ocean CO_2 Atlas (SOCAT)

Dorothee C. E. Bakker[1], Benjamin Pfeil[2,3], Camilla S. Landa[2,3], Nicolas Metzl[4], Kevin M. O'Brien[5,6], Are Olsen[2,3], Karl Smith[5,6], Cathy Cosca[5], Sumiko Harasawa[7], Stephen D. Jones[2,3], Shin-ichiro Nakaoka[7], Yukihiro Nojiri[7], Ute Schuster[8], Tobias Steinhoff[9], Colm Sweeney[10,11], Taro Takahashi[12], Bronte Tilbrook[13,14], Chisato Wada[7], Rik Wanninkhof[15], Simone R. Alin[5], Carlos F. Balestrini[16], Leticia Barbero[15,17], Nicholas R. Bates[18,19], Alejandro A. Bianchi[16], Frédéric Bonou[20], Jacqueline Boutin[4], Yann Bozec[21], Eugene F. Burger[5], Wei-Jun Cai[22], Robert D. Castle[15], Liqi Chen[23,24], Melissa Chierici[25,26], Kim Currie[27], Wiley Evans[5,28,29], Charles Featherstone[15], Richard A. Feely[5], Agneta Fransson[30], Catherine Goyet[31,32],

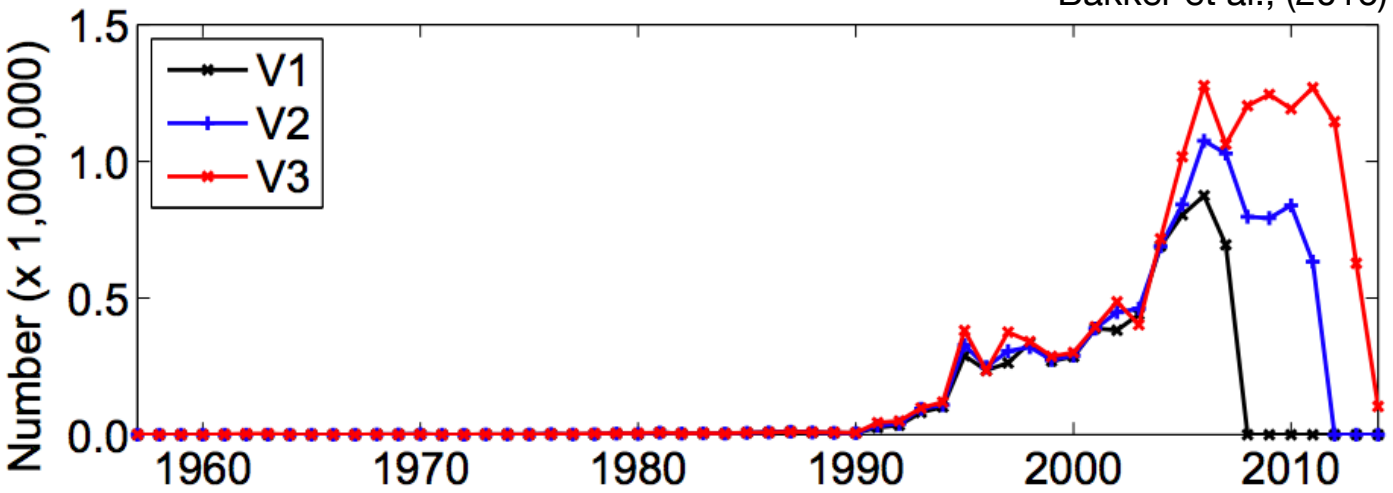
Part 1: Observing ocean biogeochemistry

2. Observing surface pCO_2

How are the observations gathered for easy public use?

The SOCAT database was created to gather the substantial number of measurements, and whose version 4 records from **1.9 million measurements from the 1990s to 8.4 million from the 2000s** (Pfeil et al., 2013; Bakker et al., 2016). The monthly gridded version gathers uniformly quality controlled $fCO_{2\text{-ocean}}$ observations since 1970 into a regular 1°x1° monthly grid (Pfeil et al., 2013). The SOCAT product is updated every year.

Bakker et al., (2016)

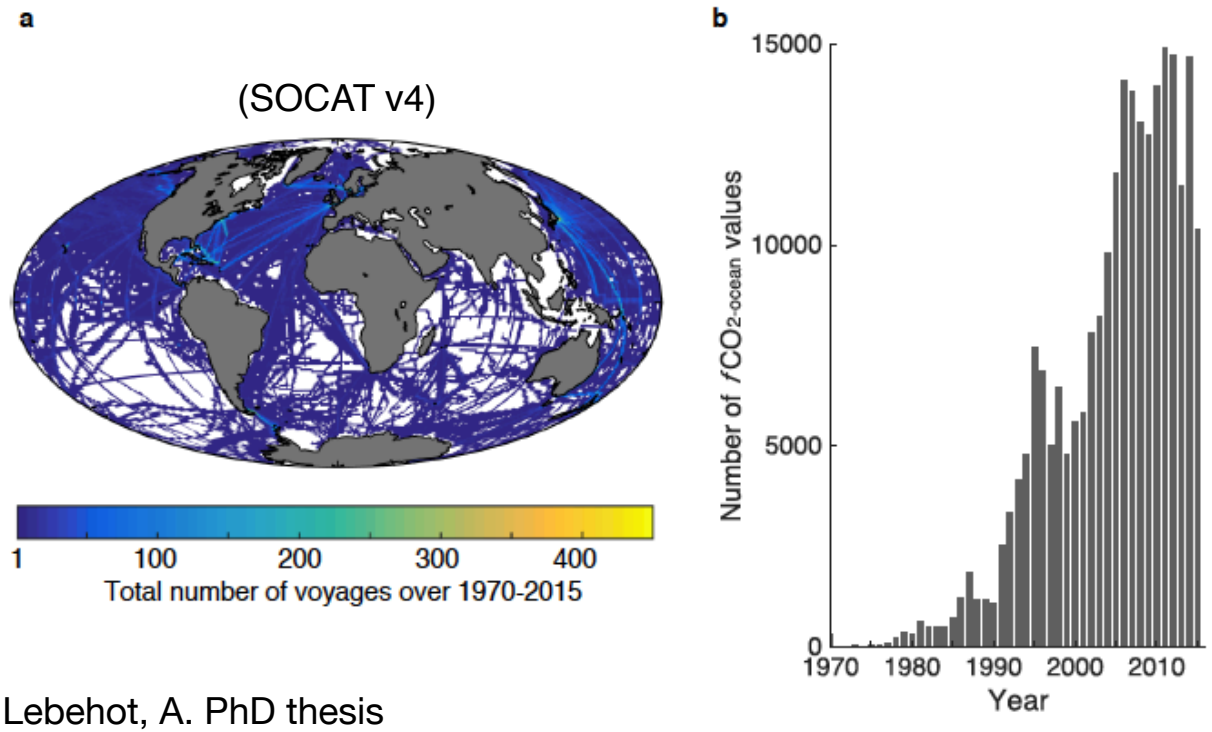


Part 1: Observing ocean biogeochemistry

2. Observing surface pCO_2

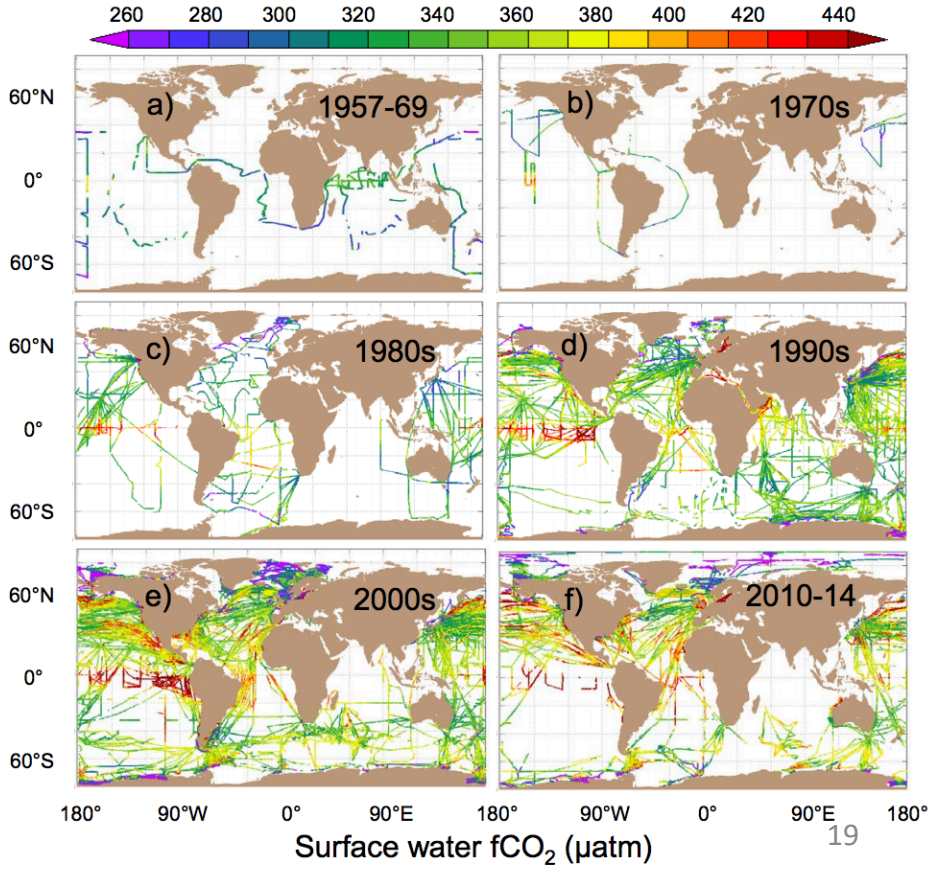
How are the observations gathered for easy public use?

SOCAT provides a time-varying but not interpolated product (voyage weighted means).



Lebehot, A. PhD thesis

Bakker et al., (2016)



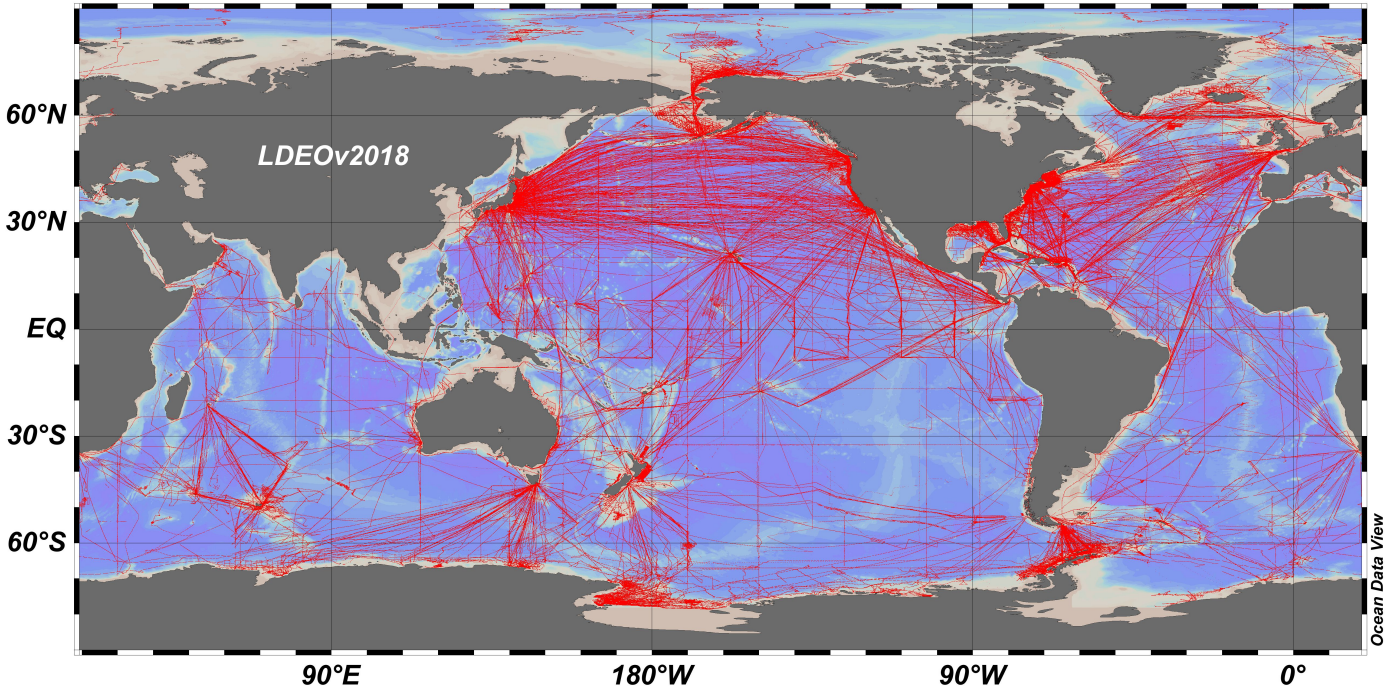
Part 1: Observing ocean biogeochemistry

2. Observing surface pCO_2

How are the observations gathered for easy public use?

The Lamont-Doherty Earth Observatory (**LDEO**) provides a synthesis of pCO_2 observations from 1957 to 2016.

The LDEO database provides, in a non-gridded format, global $pCO_{2\text{-ocean}}$ observations available for each date with measurements (taken from semi-continuous underway $pCO_{2\text{-ocean}}$ systems and deduced from discrete bottled data) (Takahashi et al., 2017).



https://www.nodc.noaa.gov/ocads/oceans/LDEO_Underway_Database/
https://www.ldeo.columbia.edu/res/pi/CO2/

Part 1: Observing ocean biogeochemistry

2. Observing surface pCO_2

How are the observations gathered for easy public use?

While the **SOCAT** and **LDEO** products mostly contain similar original sources of data, their treatment and quality control differ and as such, are treated as **independent product**s (Bakker et al., 2016). Example, Laruelle et al., (2017) that used LDEO to test their interpolated empirical product:

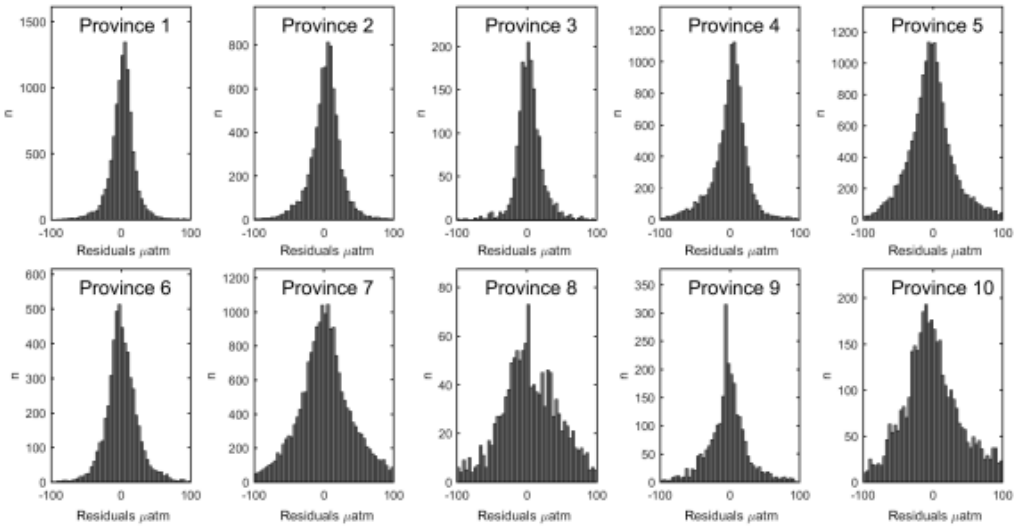


Figure 6. Histograms reporting the distribution of residuals between observed (LDEO*) and computed (SOM_FFN) pCO_2 in each biogeochemical province.

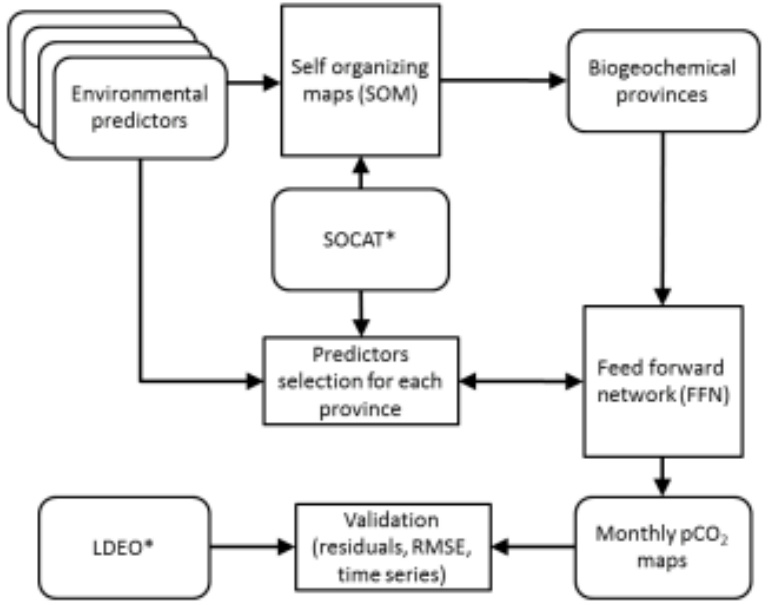


Figure 1. Schematic scheme of the different steps involved in the SOM-FFN artificial neural network calculations leading to continuous monthly pCO_2 maps over the 1998–2015 period.