PICES 2025, Workshop 4:
Building Framework for Cross-Community Conversation
Between Natural Carbon Cycles and Marine Carbon Dioxide Removal
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Standards for Measurement Methods of Essential Ocean Variables in GOOS

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The Global Ocean Observing System

Essential Ocean Variables

are a minimum set of key variables of physics, biogeochemistry, biology and ecosystem that are critical to understanding ocean change and guiding policy.

https://goosocean.org/whatwedo/framework/essential-ocean-variables/

Physics	Biochemistry	Biology and Ecosystems
Sea state Ocean surface stress Sea ice Sea surface height Sea surface temperature Subsurface temperature Surface currents Subsurface currents Sea surface salinity Subsurface salinity Ocean surface heat flux Ocean bottom pressure Turbulent diapycnal fluxes (*pilot)	Oxygen Nutrients Inorganic carbon Transient tracers Particulate matter Nitrous oxide Stable carbon isotopes Dissolved organic carbon	Phytoplankton biomass and diversity Zooplankton biomass and diversity Fish abundance and distribution Sea turtles abundance and distribution Seabirds abundance and distribution Marine mammal abundance and distribution Coral cover and composition Seagrass cover and composition Macroalgal canopy cover and composition Mangrove cover and composition Microbe biomass and diversity (*pilot) Benthic invertebrate abundance and distribution (*pilot)
Cross-disciplinary (including human impact)		
	Ocean colour Marine debris (*pilot)	Ocean sound

Essential Ocean Variable (EOV): **Inorganic Carbon**

Table 1: EOV Information	
Name of EOV	Inorganic Carbon
Sub-Variables	Dissolved Inorganic Carbon (DIC), Total Alkalinity (TA), Partial pressure of carbon dioxide (pCO_2) and pH. *[At least two of the four Sub-Variables are needed.]*
Derived Products	Saturation state (aragonite, calcite), Dissolved carbonate ion concentration, Air-sea flux of CO_2, Anthropogenic carbon, Change in total carbon
Supporting Variables	Surface and subsurface Temperature, Surface and subsurface Salinity, Ocean vector stress (wind speed), Atmospheric column-averaged dry-air mole fraction of CO2 (xCO_2), Barometric pressure, Oxygen, Calcium concentration, Transient tracers, Oxygen to argon ratio (O_2/Ar)
Responsible GOOS Panel	GOOS Biogeochemistry Panel Contact: ioccp@ioccp.org

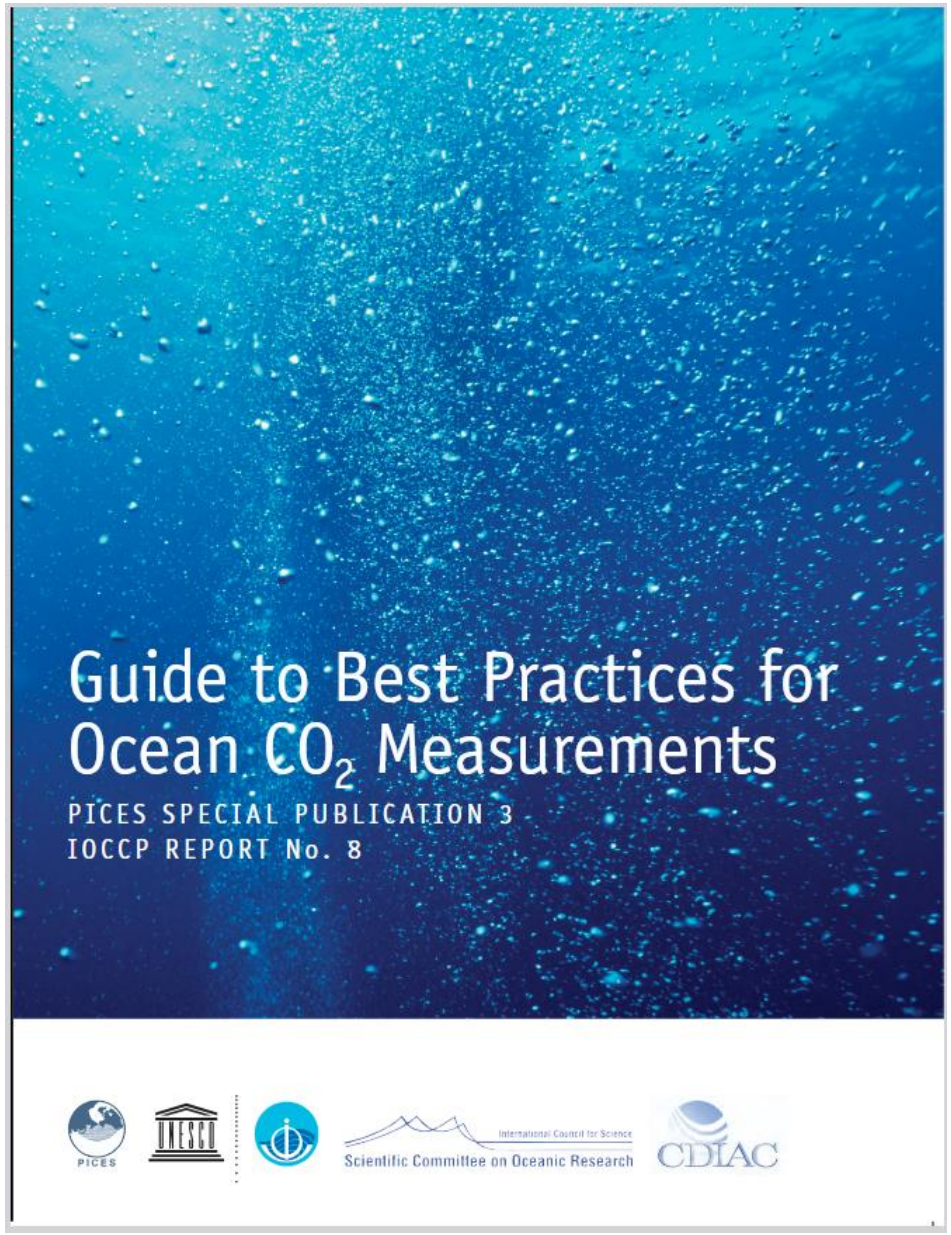
Best Practices

Ocean Best Practices have been an essential component across all areas of the observing system. Best practices have to be comprehensive, findable and used.

Guide to Best Practices for Ocean CO_2 Measurements

Dickson, A.G., Sabine, C.L. and Christian, J.R. [Eds.] 2007

https://www.nodc.noaa.gov/ocads/oceans/Handbook_2007.html



Chapter 4

Recommended **standard operating procedures (SOPs)**

SOP 2 Determination of **total dissolved inorganic carbon** in sea water

SOP 3a Determination of **total alkalinity** in sea water using a closed-cell titration

SOP 3b Determination of **total alkalinity** in sea water using an open-cell titration

SOP 4 Determination of ***p*(CO_2)** in air that is in equilibrium with a discrete sample of sea water

SOP 5 Determination of ***p*(CO_2)** in air that is in equilibrium with a continuous stream of sea water

SOP 6a Determination of the **pH** of sea water using a glass/reference electrode cell

SOP 6b Determination of the **pH** of sea water using the indicator dye m-cresol purple

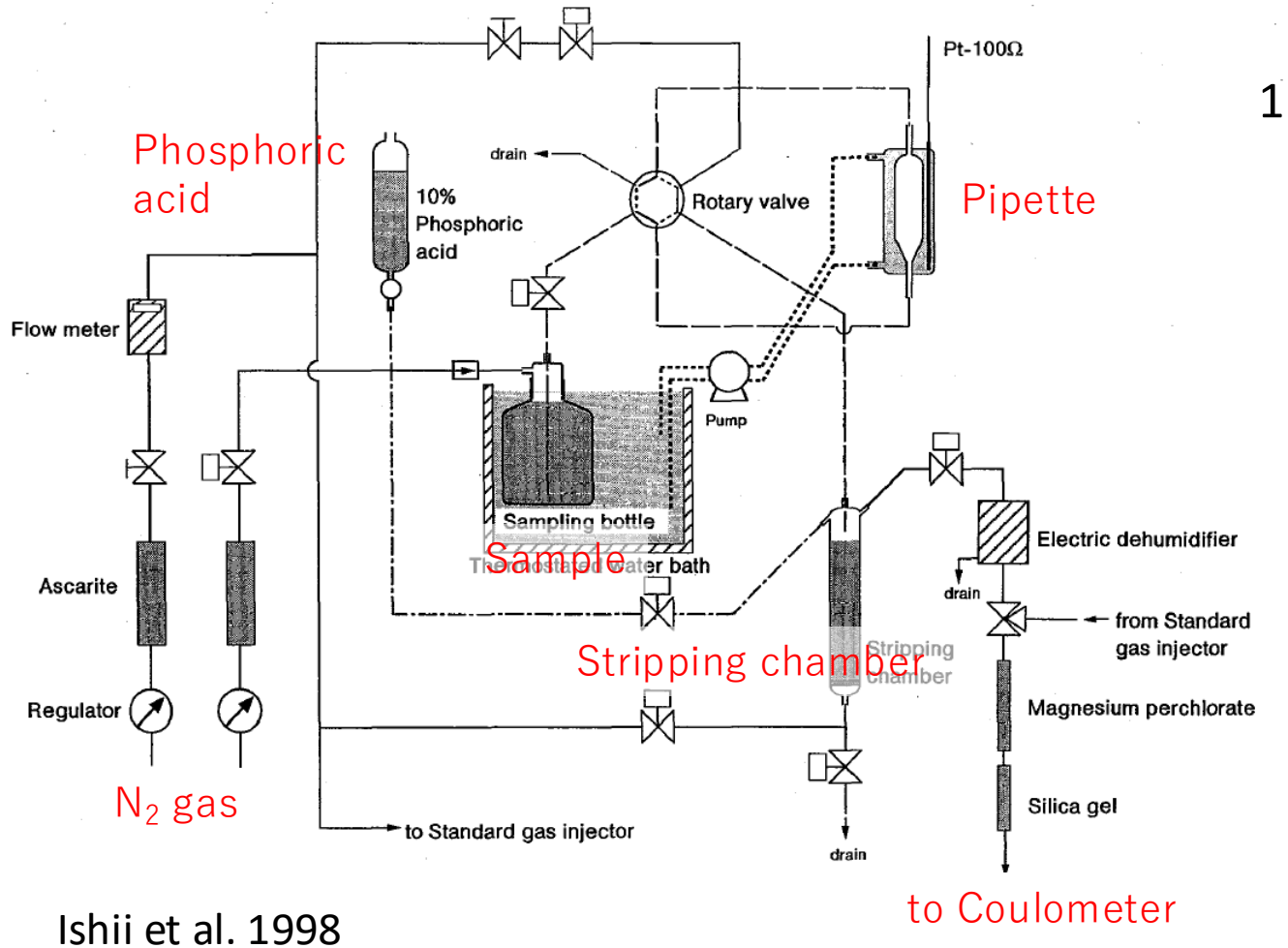
…

…

Determination of **total dissolved inorganic carbon** in sea water by coulometry

(Johnson et al., 1985)

Step 1：Stripping of DIC as gaseous CO_2 into N_2 gas stream

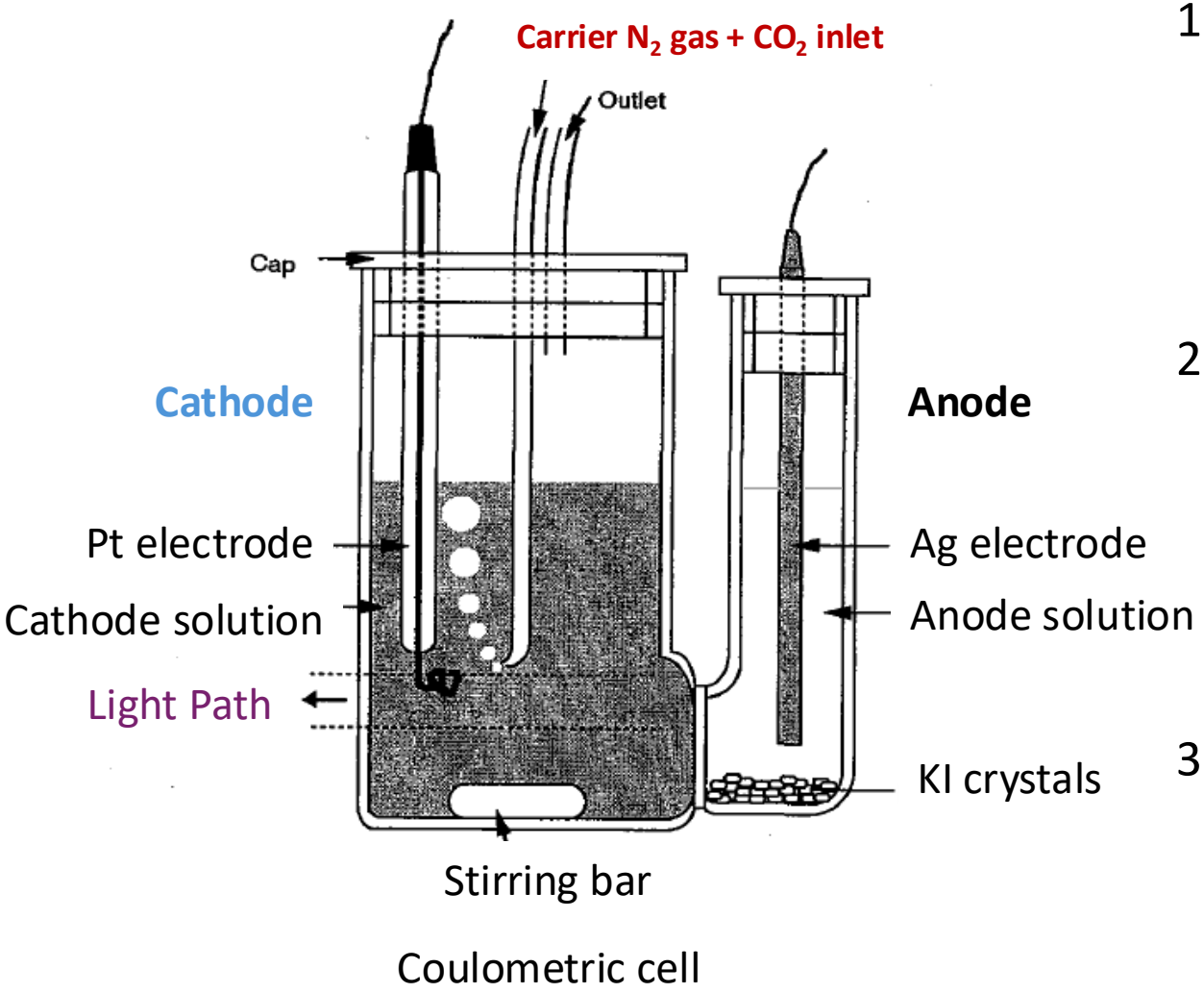


Ishii et al. 1998

1. A portion of sample seawater is taken into a pre-calibrated pipette (~15 cm^3).
2. It is acidified with phosphoric acid in a stripping chamber.
3. The CO_2 evolved in the acidified seawater sample is then quantitatively removed by a stream of N_2 gas.

Determination of total dissolved inorganic carbon in sea water by coulometry

Step 2：Convert CO_2 to a strong acid hydroxycarbamic acid and titrate it by coulometer



Coulometric cell

1. In cathode solution, CO_2 in N_2 stream reacts with 2-amino ethanol to form hydroxycarbamic acid. It acidifies cathode solution and the color of indicator dye (thymol blue) in the solution turns from blue to yellow.
2. Detecting the change in the color by photometry, current flows between the cathode and anode, and hydroxide (OH^-) evolves on Pt electrode together with H_2. It titrates hydroxycarbamic acid until the color of cathode solution returns to the initial blue color.
3. The current that flowed is precisely measured and converted to the titrated amount of hydroxycarbamic acid that is equivalent to the amount of CO_2 supplied by the N_2 stream.

Determination of **total alkalinity** in sea water using an open-cell titration

(Dickson et al., 1981)

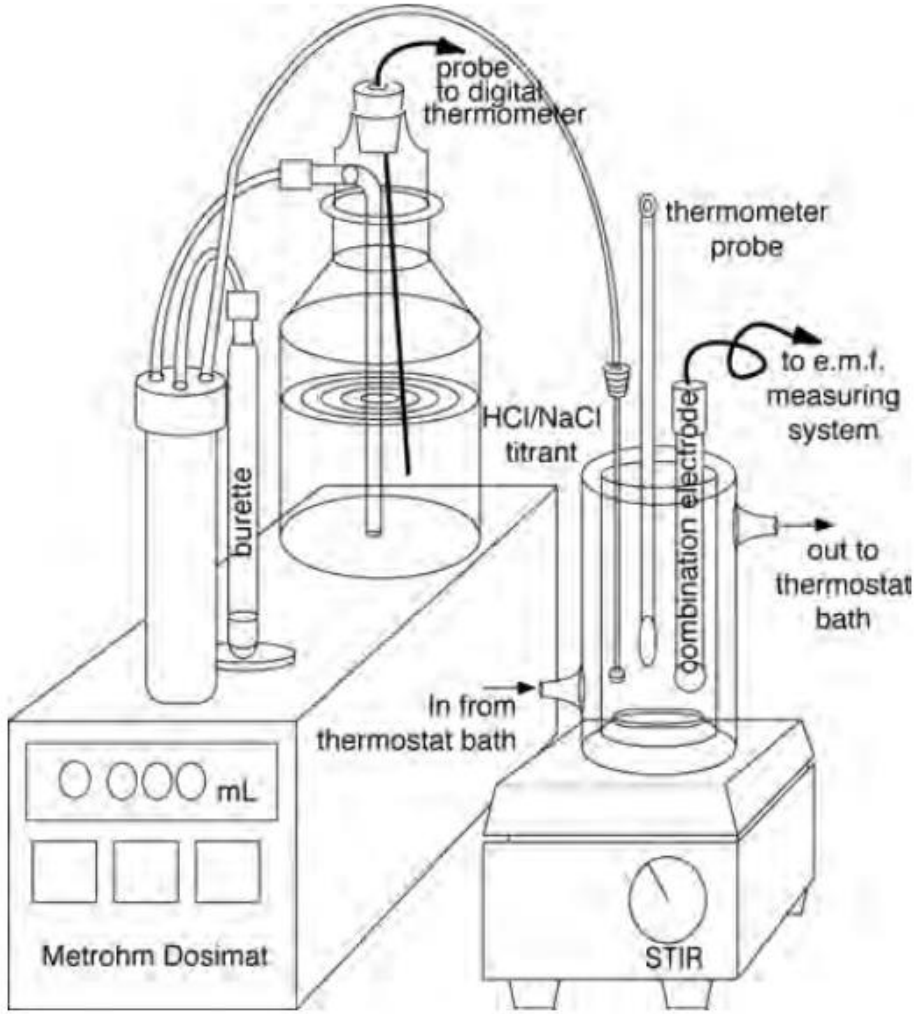


Fig. 1 Open-cell alkalinity measurement set-up.

Potentiometric titration using high-performance piston burette

Determination of total alkalinity in sea water by spectrophotometry

(Breland and Byrne, 1993)

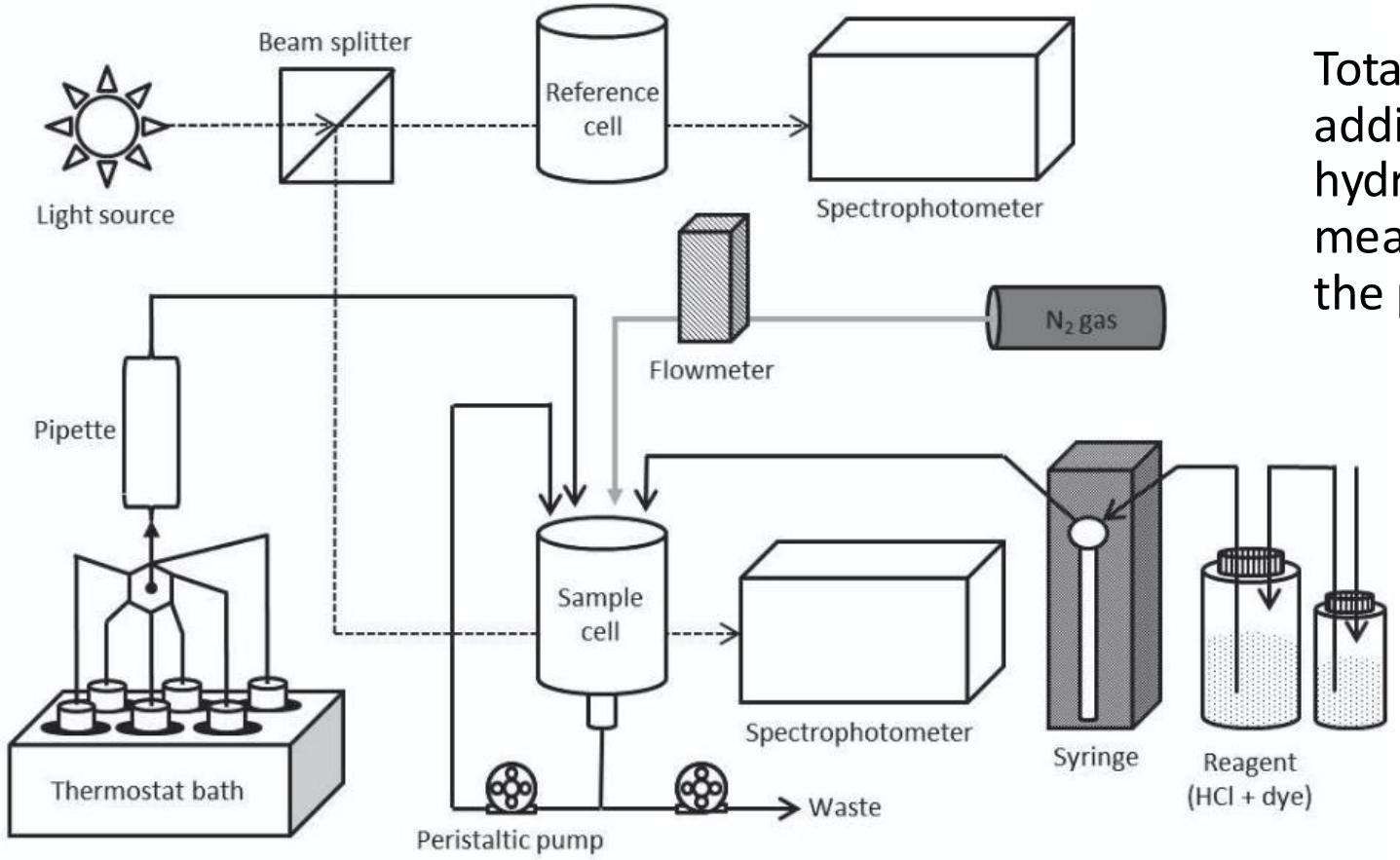


Figure 1. Schematic diagram of an apparatus for spectrophotometric total alkalinity determination in sea water.

Total alkalinity can also be determined by adding an accurately measured amount of hydrochloric acid to an accurately measured seawater sample and measuring the pH accurately by spectrophotometry.

file:///C:/Users/Masao%20Ishii/Downloads/2025-11-04-1829.pdf

GLODAPv2.2023

A data product of internally consistent ocean biogeochemical observations.
It provides access to quality controlled surface to bottom ocean biogeochemical data, with an emphasis on seawater inorganic carbon.

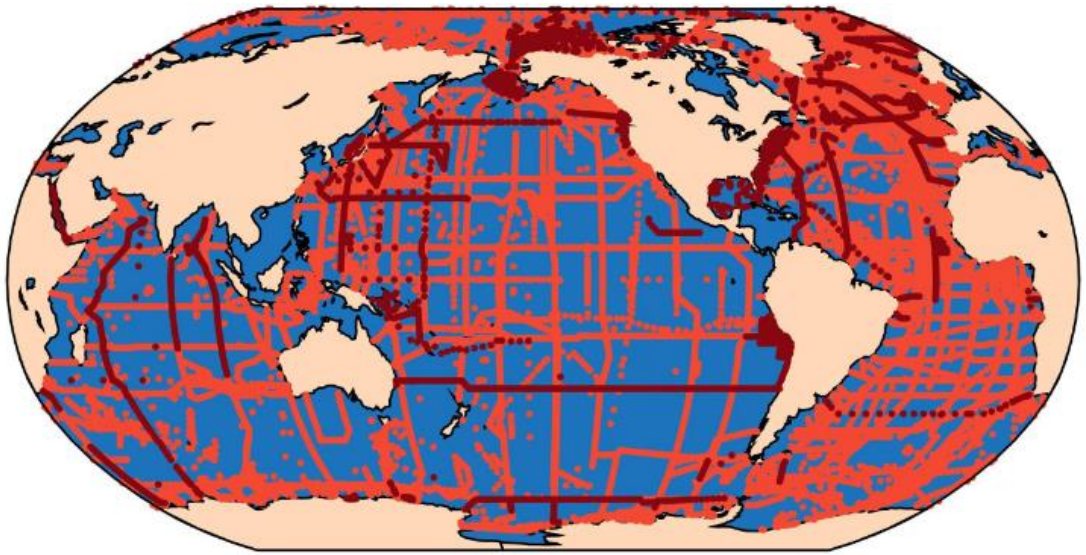
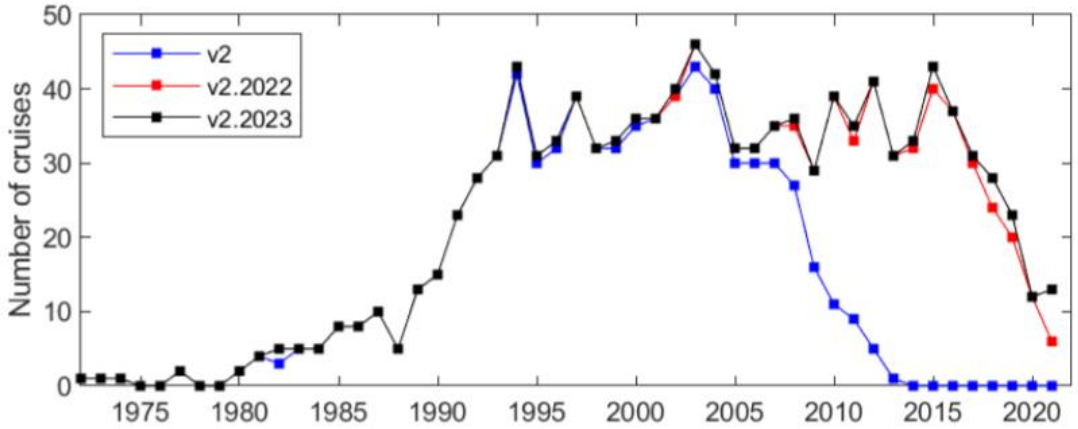


Figure 1. Station locations of all stations in GLODAPv2.2023.

Data are available at
https://www.nodc.noaa.gov/ocads/oceans/GLODAPv2_2023

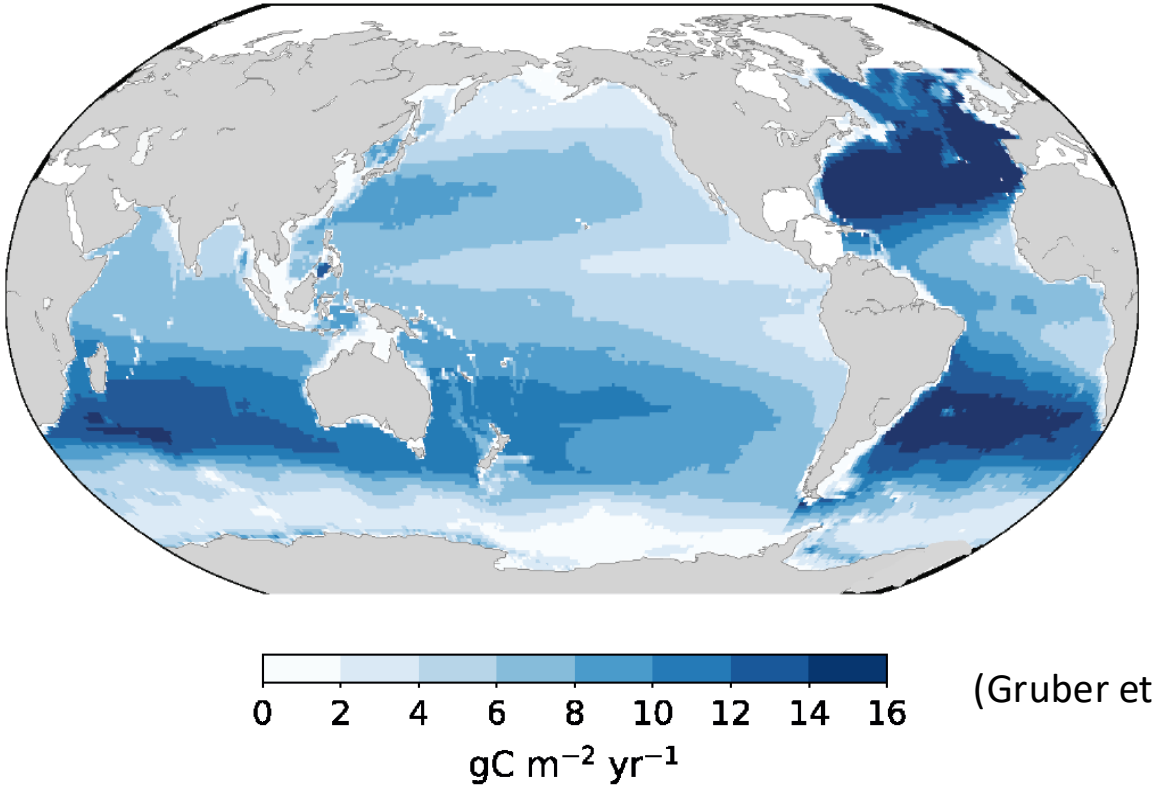


A total of 1108 cruises in v2.2023

- Includes more than 1.4 million water samples
- The data for the 13 core variables (salinity, oxygen, nitrate, silicate, phosphate, DIC, TA, pH, CFC-11, CFC-12, CFC-113,CCl4 and SF6) have undergone extensive quality control, especially systematic evaluation of bias.

Accumulation of anthropogenic carbon in the ocean interior

— Rate of change in anthropogenic CO_2 inventory (1994 – 2017) —

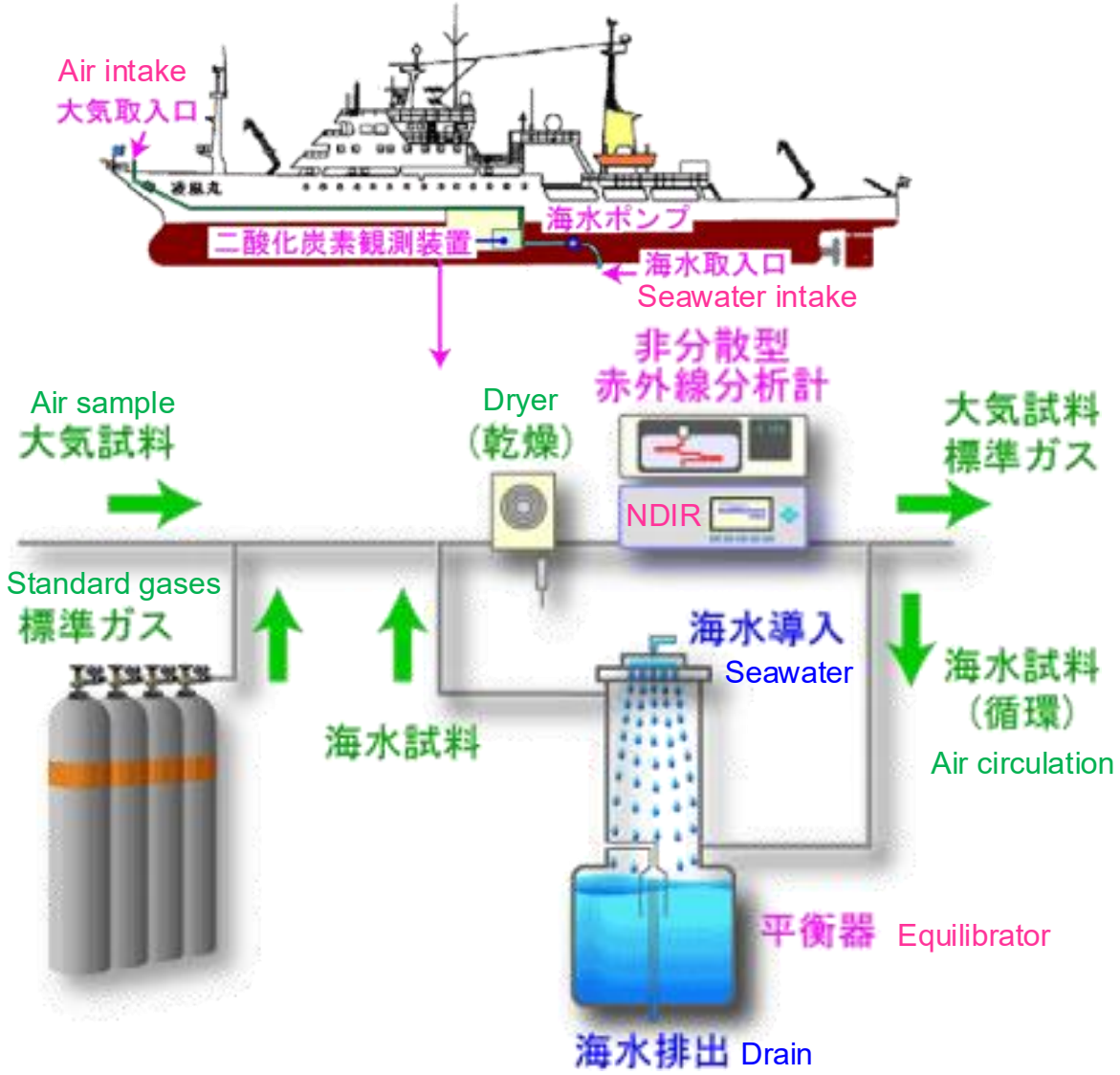


Pacific (44°S–62°N): 0.91 ±0.18 PgC yr^{-1}

Global: 2.6 ±0.3 PgC yr^{-1}

(Gruber et al., 2019; Canadell et al., 2021)

Underway determination of partial pressure of CO_2 in sea water in surface layer



https://www.data.jma.go.jp/kaiyou/shindan/index.html

An aliquot of air is equilibrated with a large excess of seawater in the "equilibrator" and its CO_2 mixing ratio (concentration) is measured using non-dispersive infra-red (NDIR) gas analyzer.

The CO_2 mixing ratio (x_{CO2}) measured is converted to partial pressure of CO_2 by taking total atmospheric pressure (P) and water vapor pressure (p_{H2O}) into account:

$$pCO_2 = x_{CO2} \cdot (P - p_{H2O})$$

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SOCAT v2025

Data sets of quality-controlled, in situ surface ocean $p(CO)_2$ measurements with an estimated uncertainty of better than 5 µatm collected between 1957 and 2024.

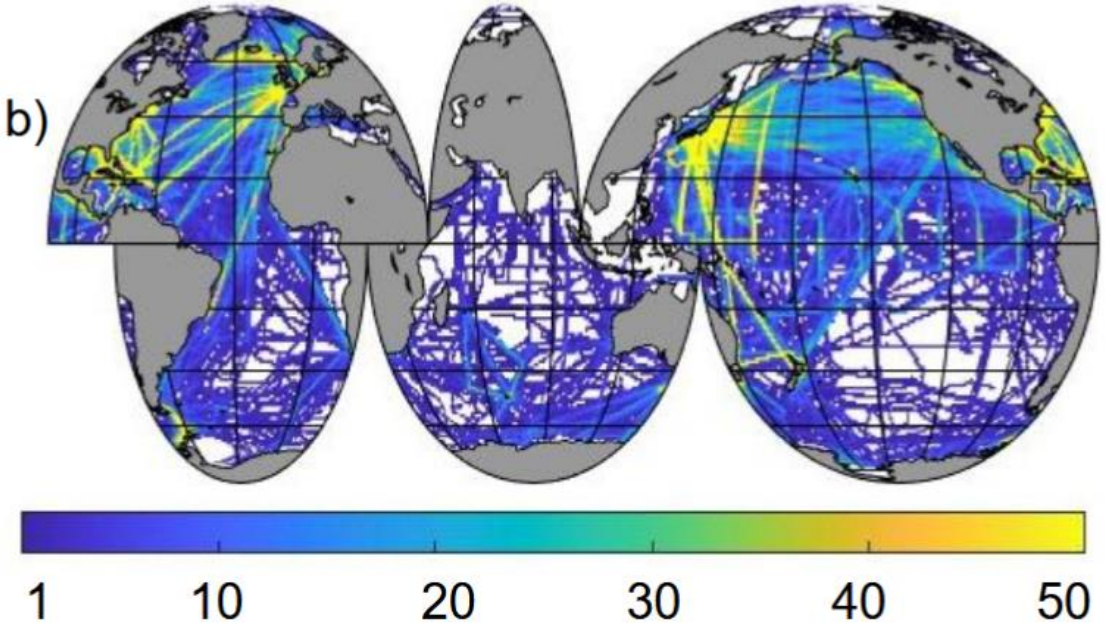


Figure 1. Number of individual months with 1° x 1° gridded fCO2 from 1970 to 2024.

Data are available at www.socat.info

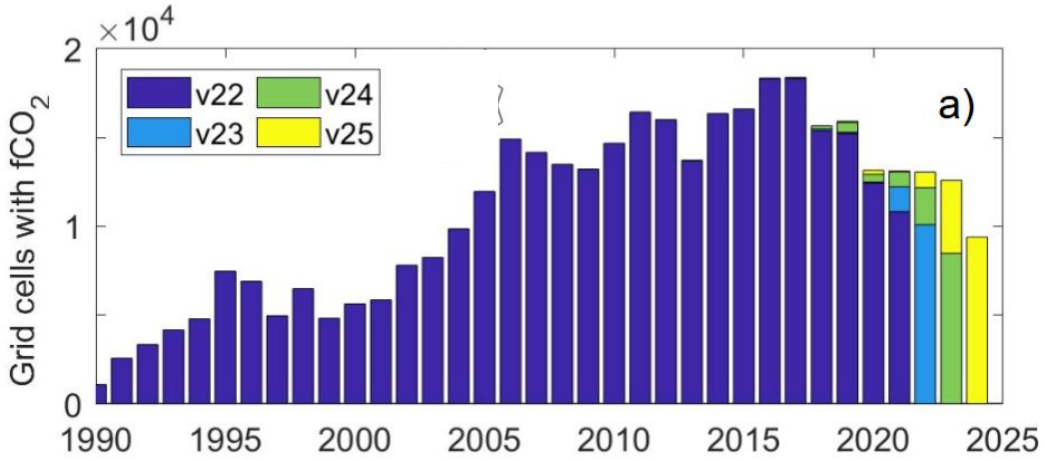
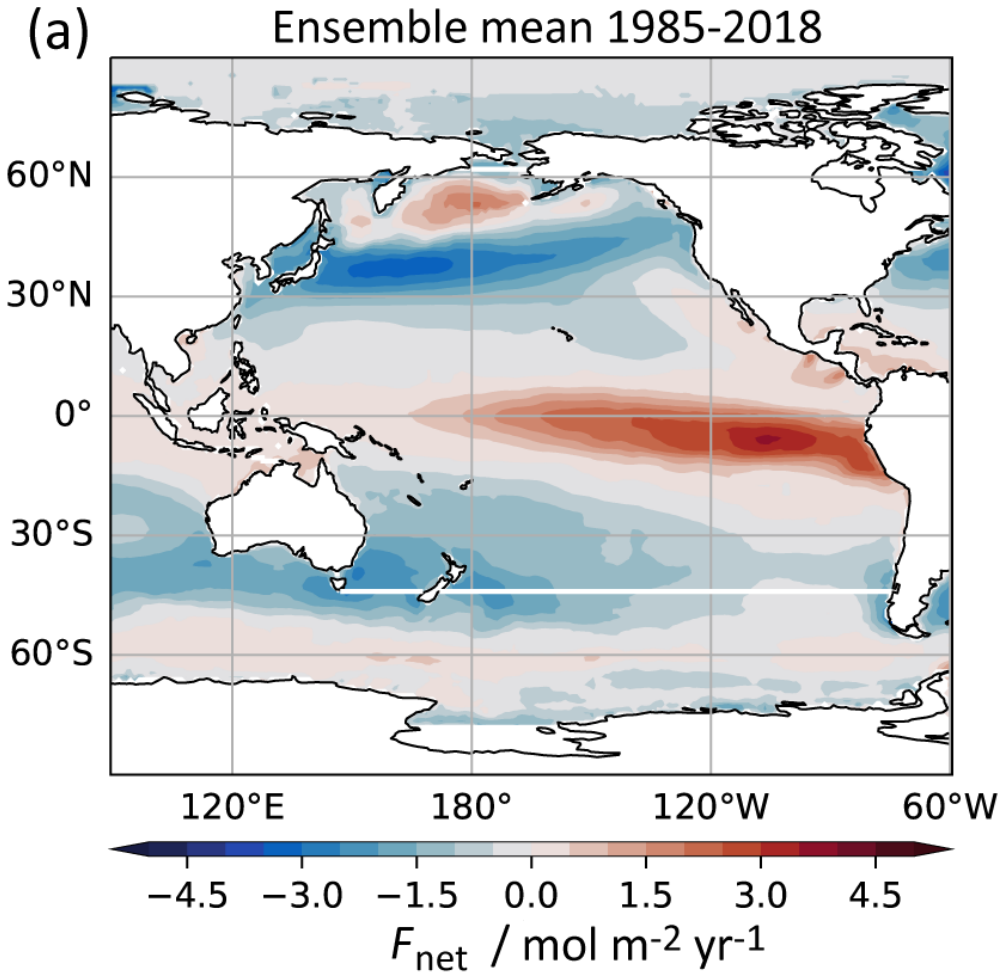


Figure 2. Number of monthly, 1° x 1° grid cells with pCO_2 by year.

- Includes 41.4 million measurements in v.2025.

Net CO_2 fluxes in the Pacific (44°S – 62°N; 1985 - 2018)

Eight pCO_2 observation-based gap-filling products



- ✓ Topical Pacific：Strong CO_2 source.
- ✓ Western N. Pacific mid-latitude： Strong CO_2 sink.

Pacific 44°S–62°N: -0.41 ±0.12 PgC yr^{-1}

Global: -1.7 ±0.2 PgC yr^{-1}

Ishii et al., 2025

Comparative trends in observation- and model-based estimates for the ocean CO_2 uptake

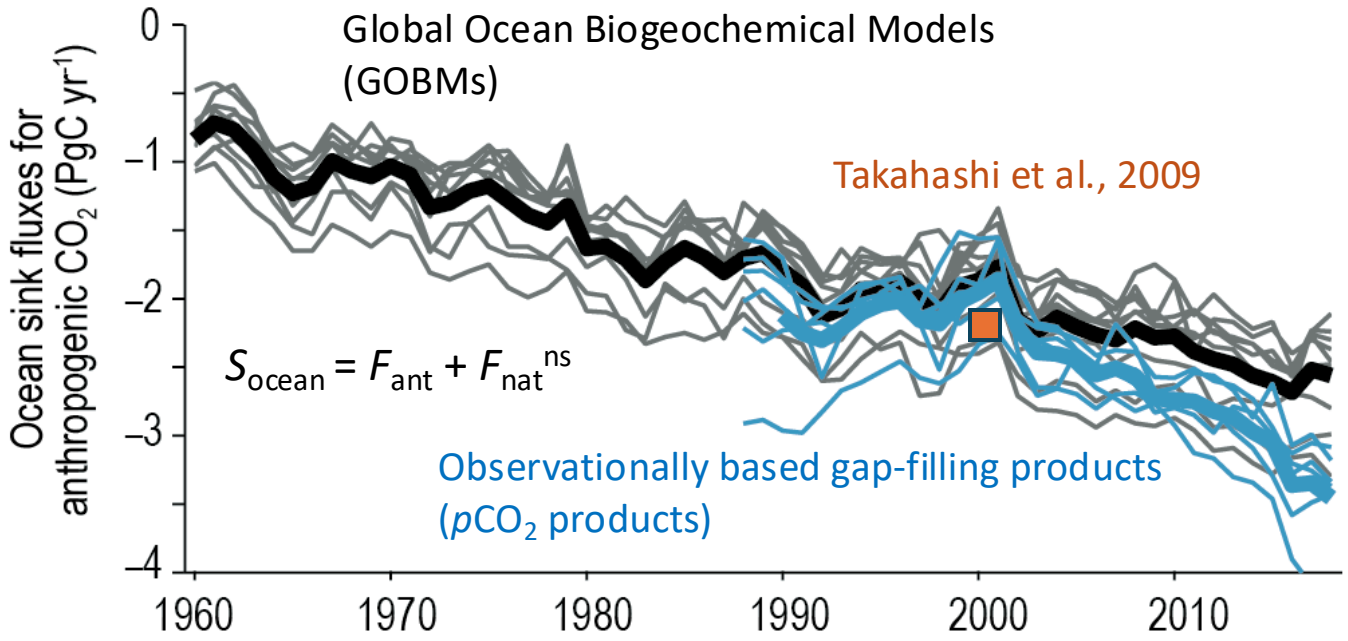


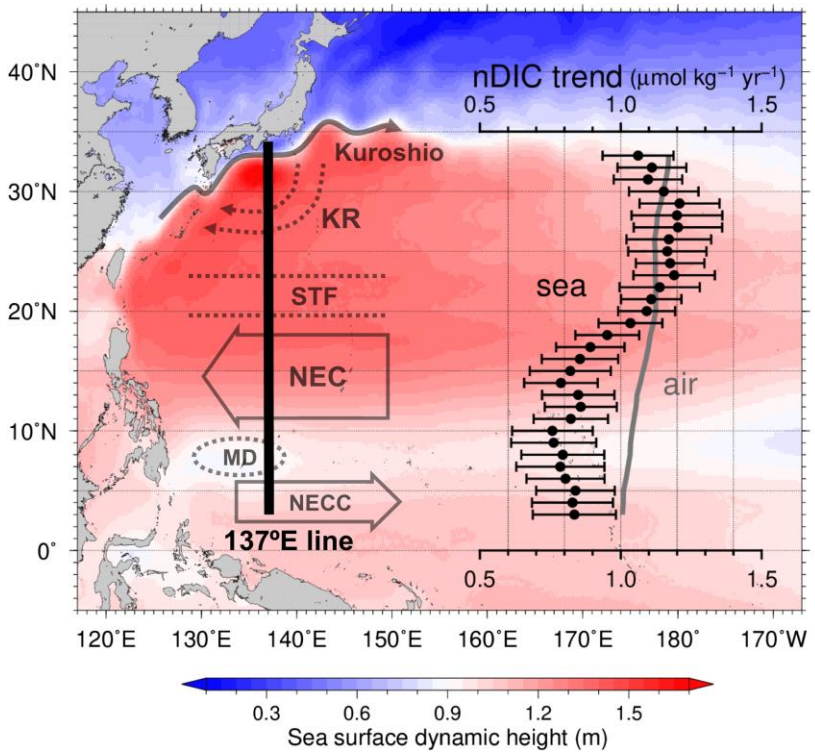
Figure 5.8 (a) | Multi-decadal trends in the annual ocean sink of CO_2.

Observationally based products have been corrected for pre-industrial sea-to-air fluxes (0.62 PgC yr^{-1}) based on the average of estimates from Jacobson et al. (2007) and Resplandy et al. (2018).

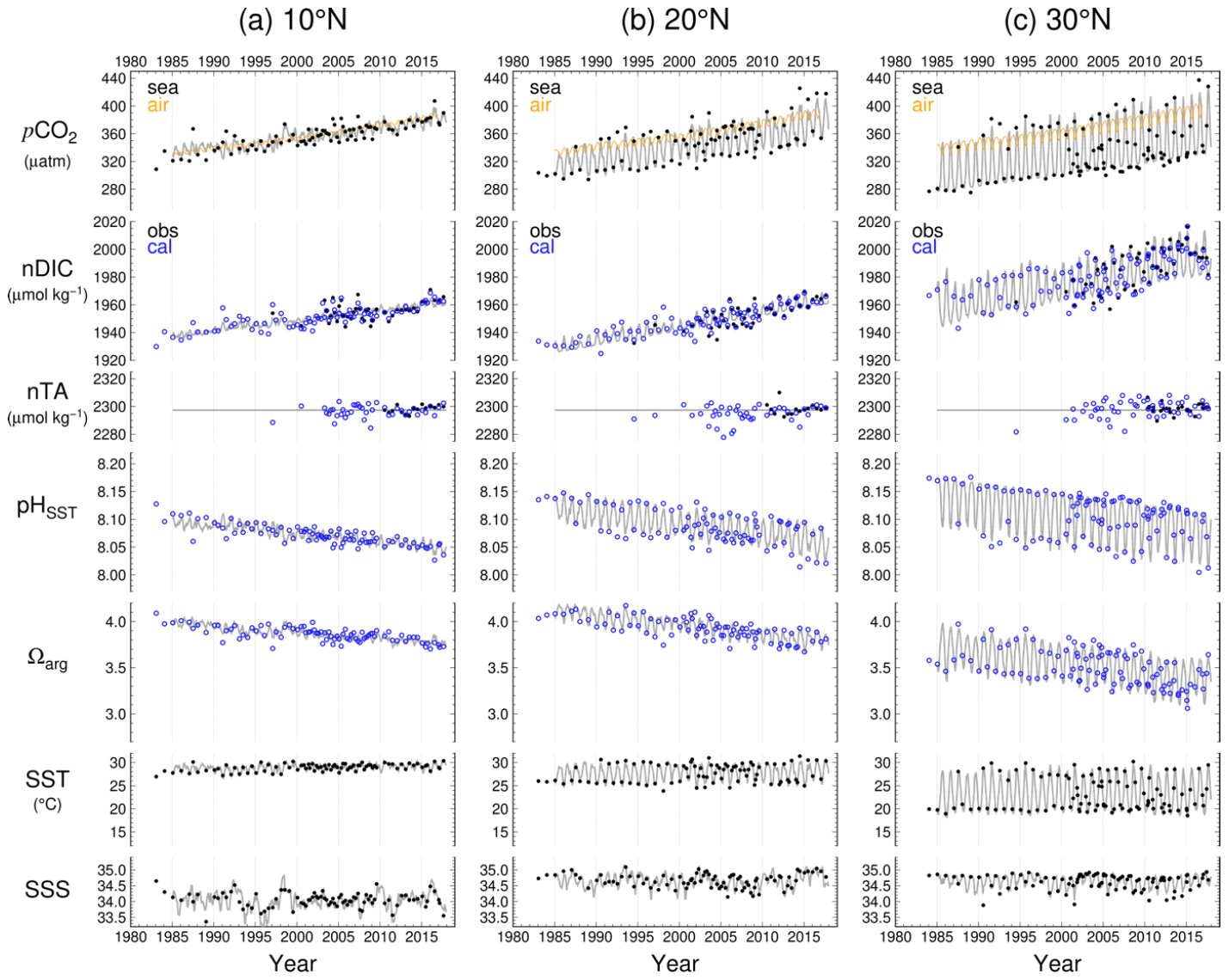
(Canadell et al., 2021: IPCC AR6 WG1, Ch.5)

- ✓ As anthropogenic CO_2 emissions increase, CO_2 uptake by the ocean also increases, but the ratio has not changed significantly.
- ✓ After 2000, the pCO_2 data products show larger changes in anthropogenic CO_2 uptake.

Trends of CO_2 increase in surface layers at 137°E repeat line



- In the northern subtropics, nDIC is increasing at a rate inferred from atmospheric CO_2 increase and Revelle factor.
- In the tropics, nDIC is increasing at a rate **slower** than that inferred from atmospheric CO_2 increase and Revelle factor.



Ono et al., 2019

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