CANAIMOC Workshop

CArbon North Atlantic Irrigation by the Meridional Overturning Circulation

Carbon cycle in the ocean
Methods to estimate anthropogenic carbon

Marcos Fontela, 2021

CCMAR
Centro de Ciências do Mar

*Materials in:
https://github.com/mfontela/CANAIMOC

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  - Methods for Ocean carbon parameters
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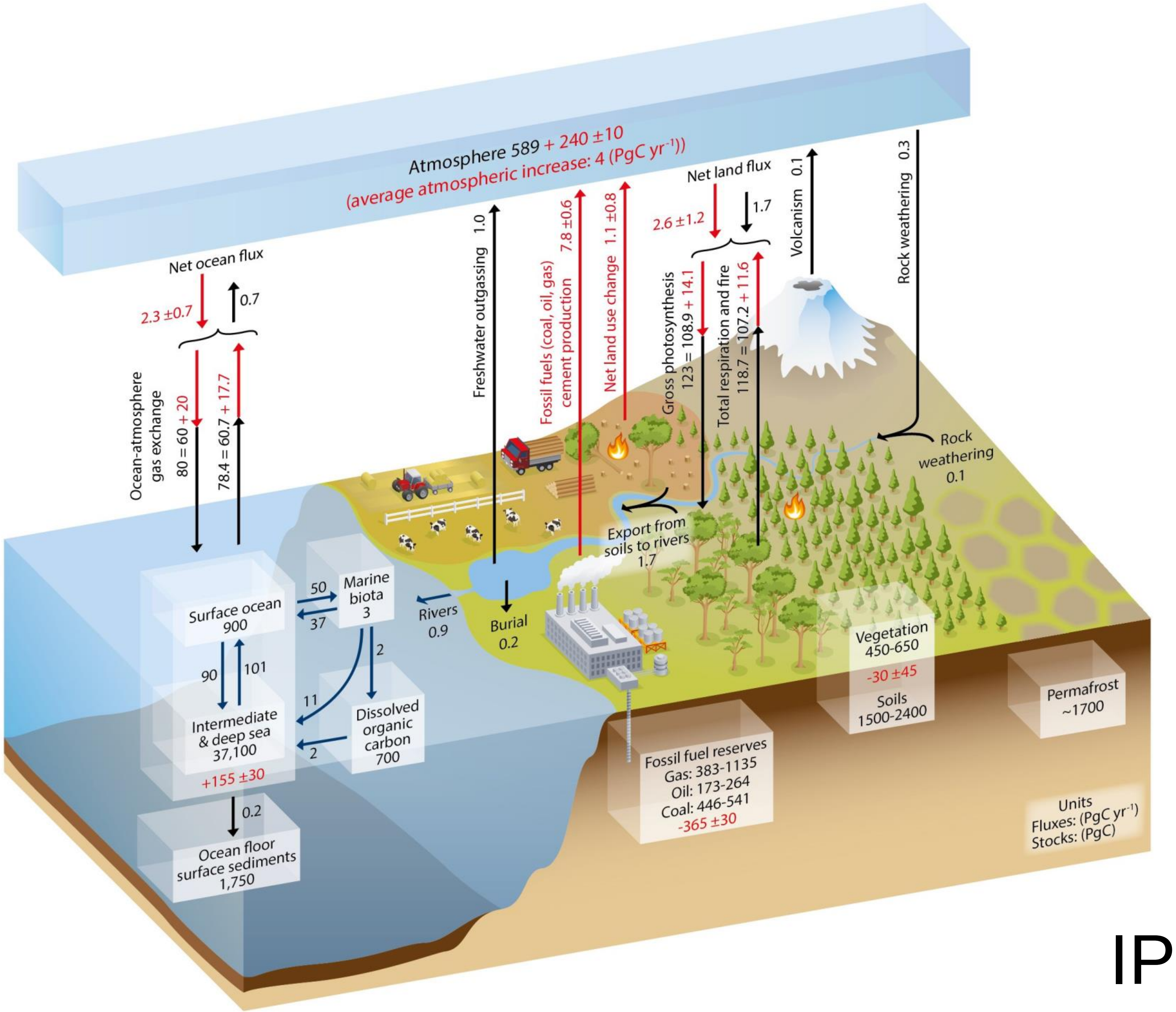
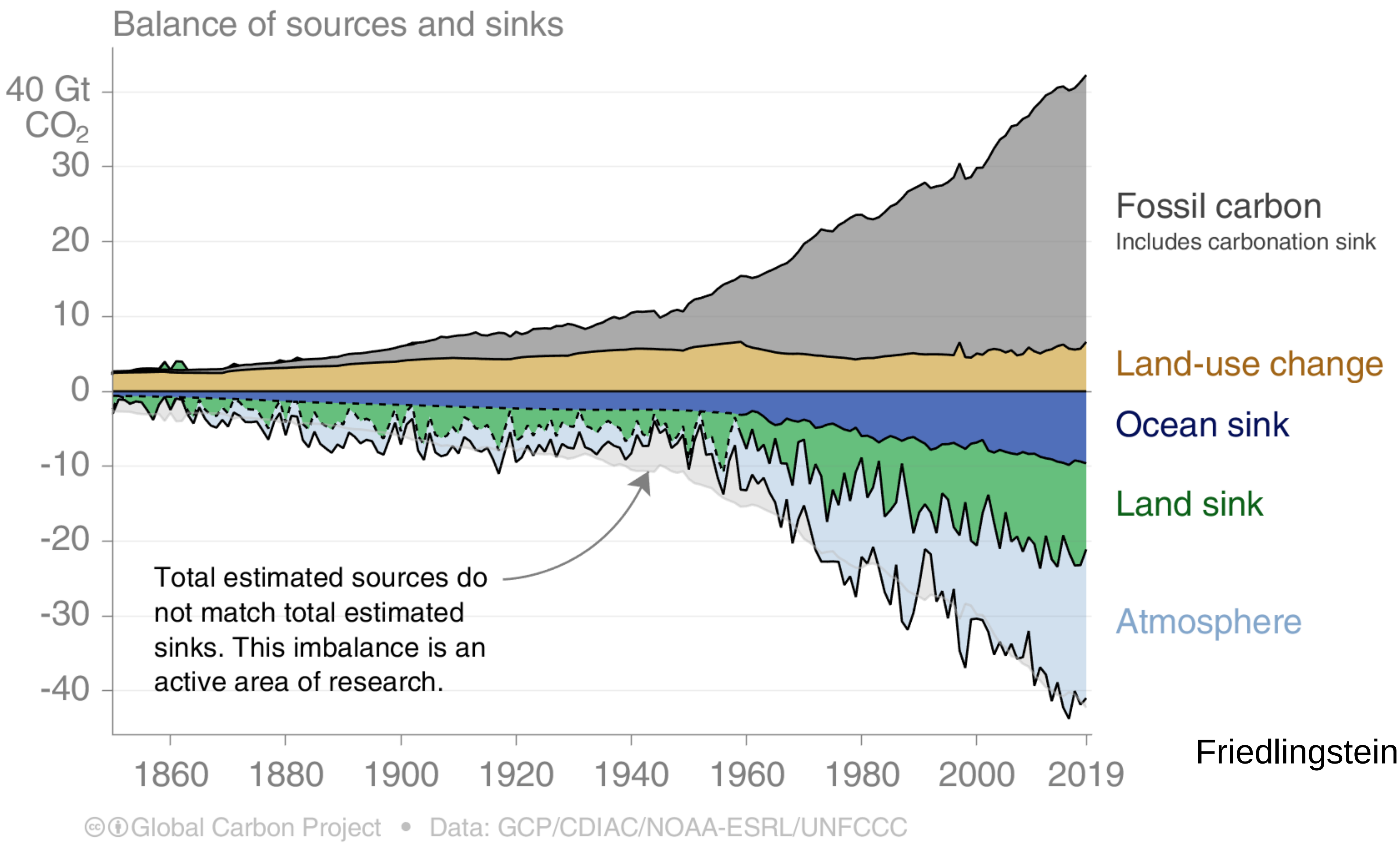
- φC_T^o :
  - Study cases



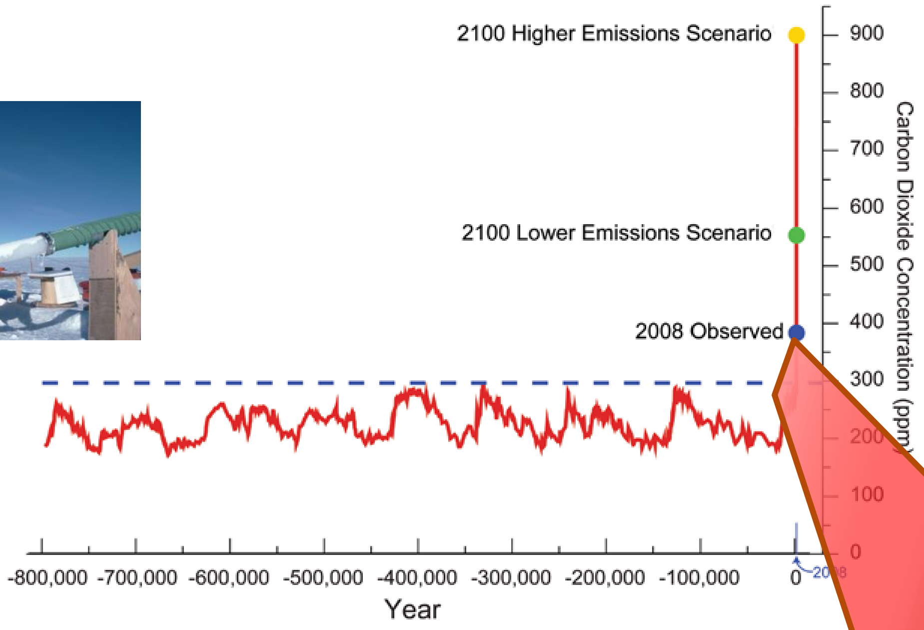
Atmosphere 589 + 240 ±10
(average atmospheric increase: 4 (PgC yr⁻¹))
Net ocean flux
2.3 ±0.7
0.7
Ocean-atmosphere gas exchange
80 = 60 + 20
78.4 = 60.7 + 17.7
Freshwater outgassing 1.0
Fossil fuels (coal, oil, gas) cement production 7.8 ±0.6
Net land use change 1.1 ±0.8
Net land flux
2.6 ±1.2
1.7
Gross photosynthesis 123 = 108.9 + 14.1
Total respiration and fire 118.7 = 107.2 + 11.6
Volcanism 0.1
Rock weathering 0.3
Rock weathering 0.1
Export from soils to rivers 1.7
Surface ocean 900
Marine biota 3
50
37
Rivers 0.9
Burial 0.2
90
101
2
11
Intermediate & deep sea 37,100
+155 ±30
Dissolved organic carbon 700
2
0.2
Ocean floor surface sediments 1,750
Vegetation 450-650
-30 ±45
Soils 1500-2400
Permafrost ~1700
Fossil fuel reserves
Gas: 383-1135
Oil: 173-264
Coal: 446-541
-365 ±30
Units
Fluxes: (PgC yr⁻¹)
Stocks: (PgC)

IPCC AR5

globalcarbonproject.com

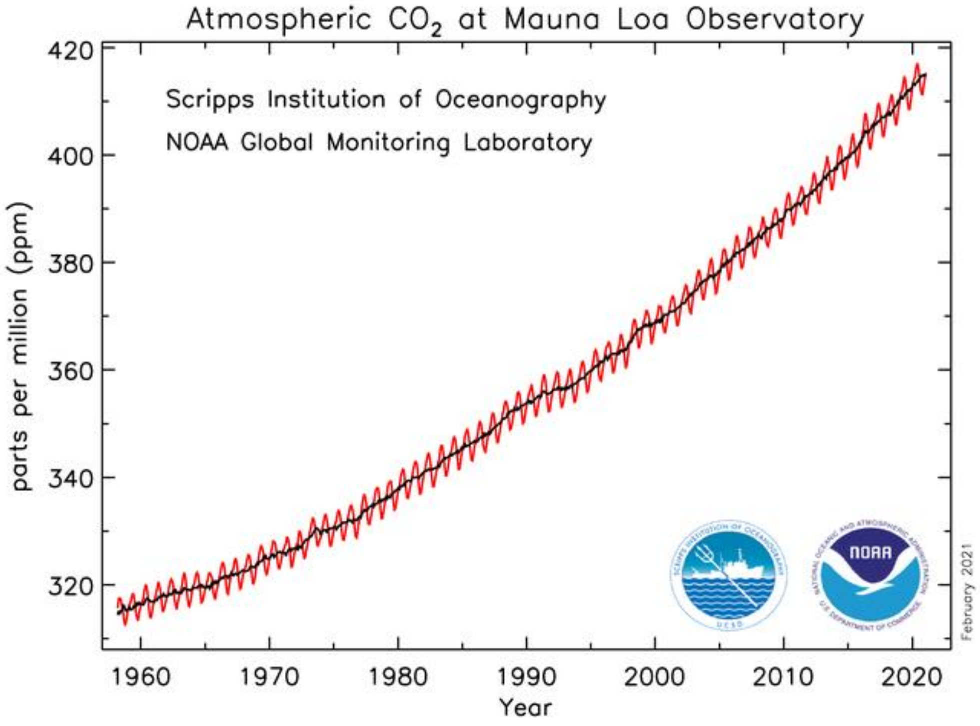


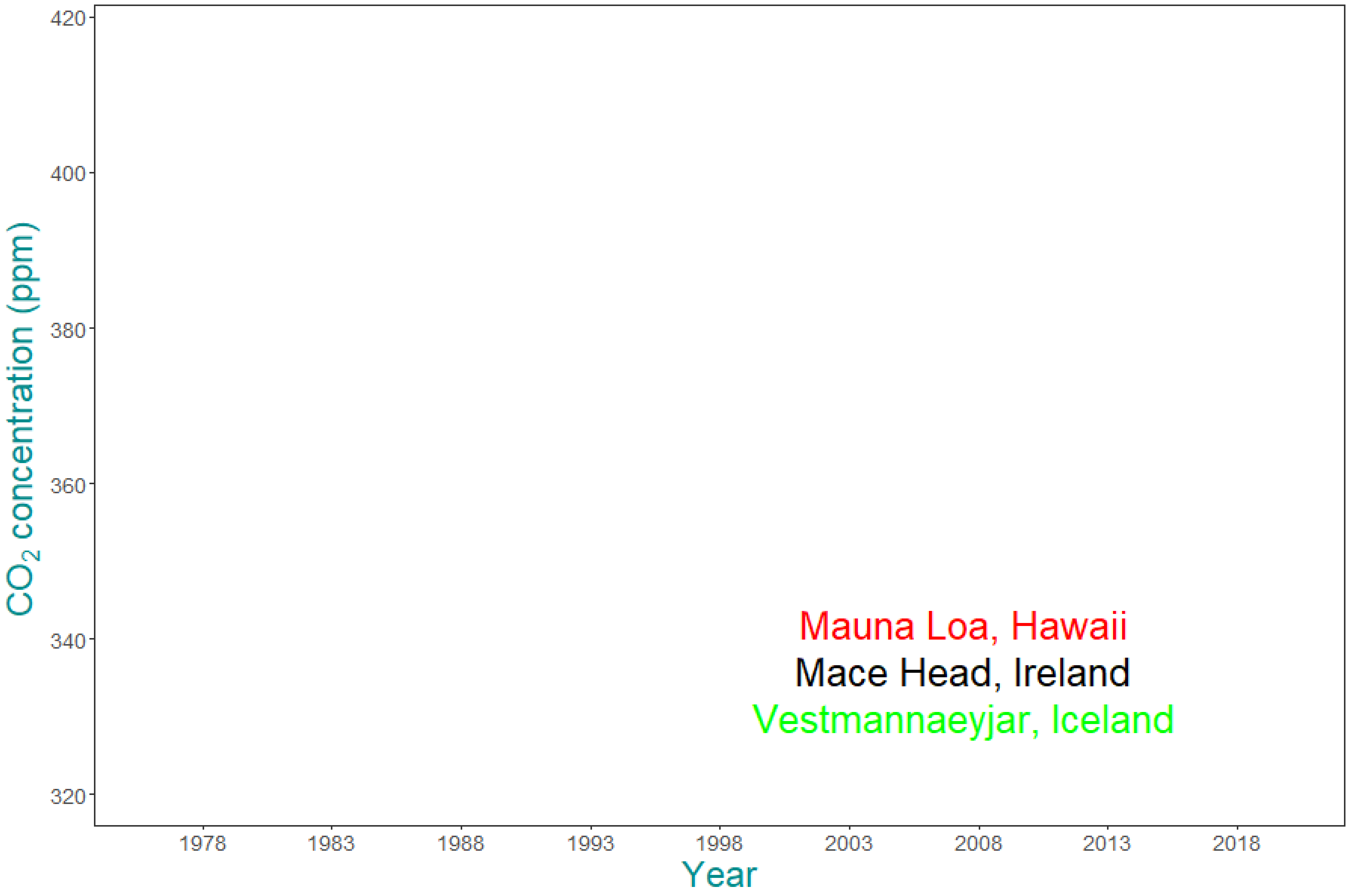
Friedlingstein et al. 2019 ESSD



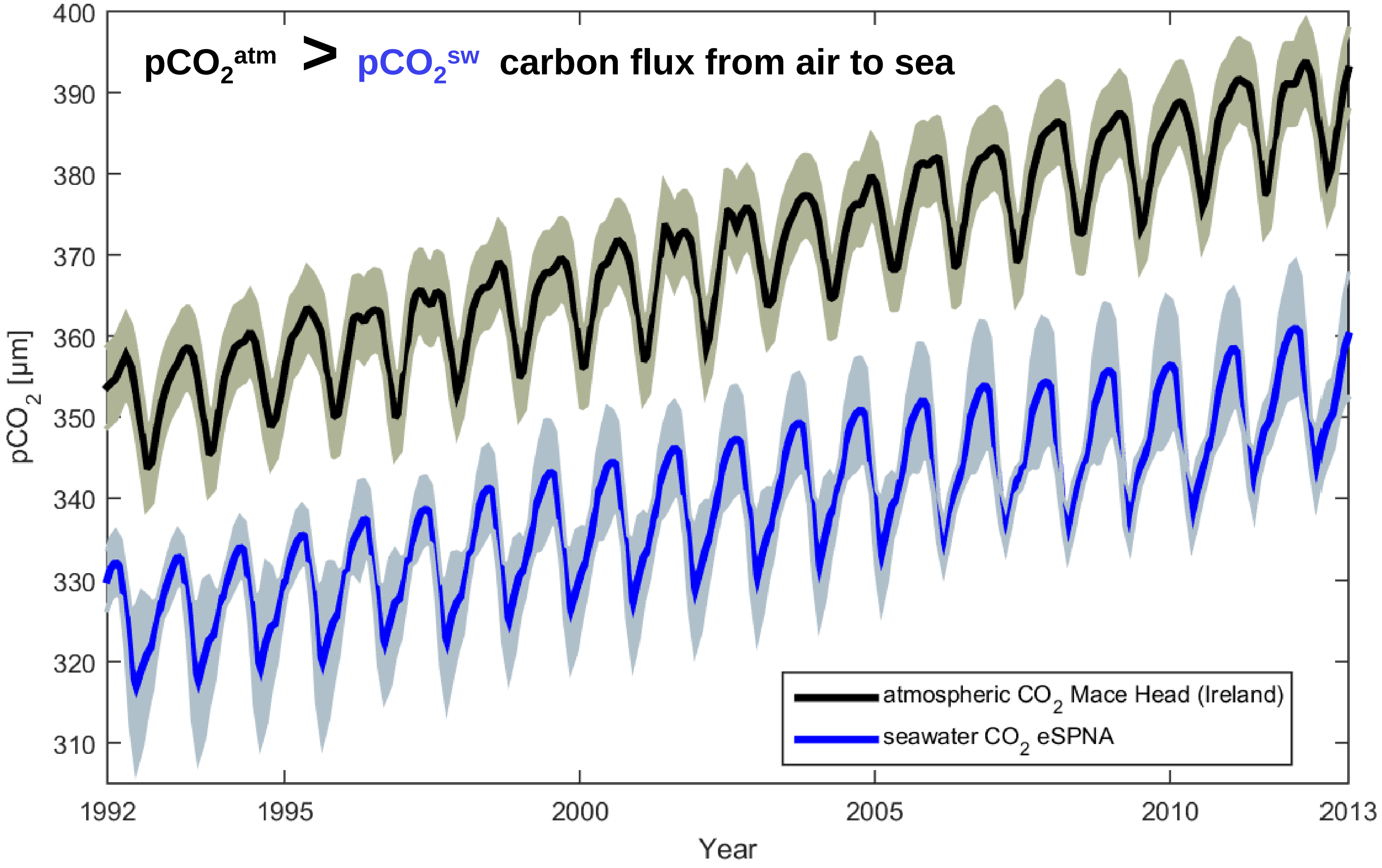
Luthi et al. 2008 Nature

Keeling curve

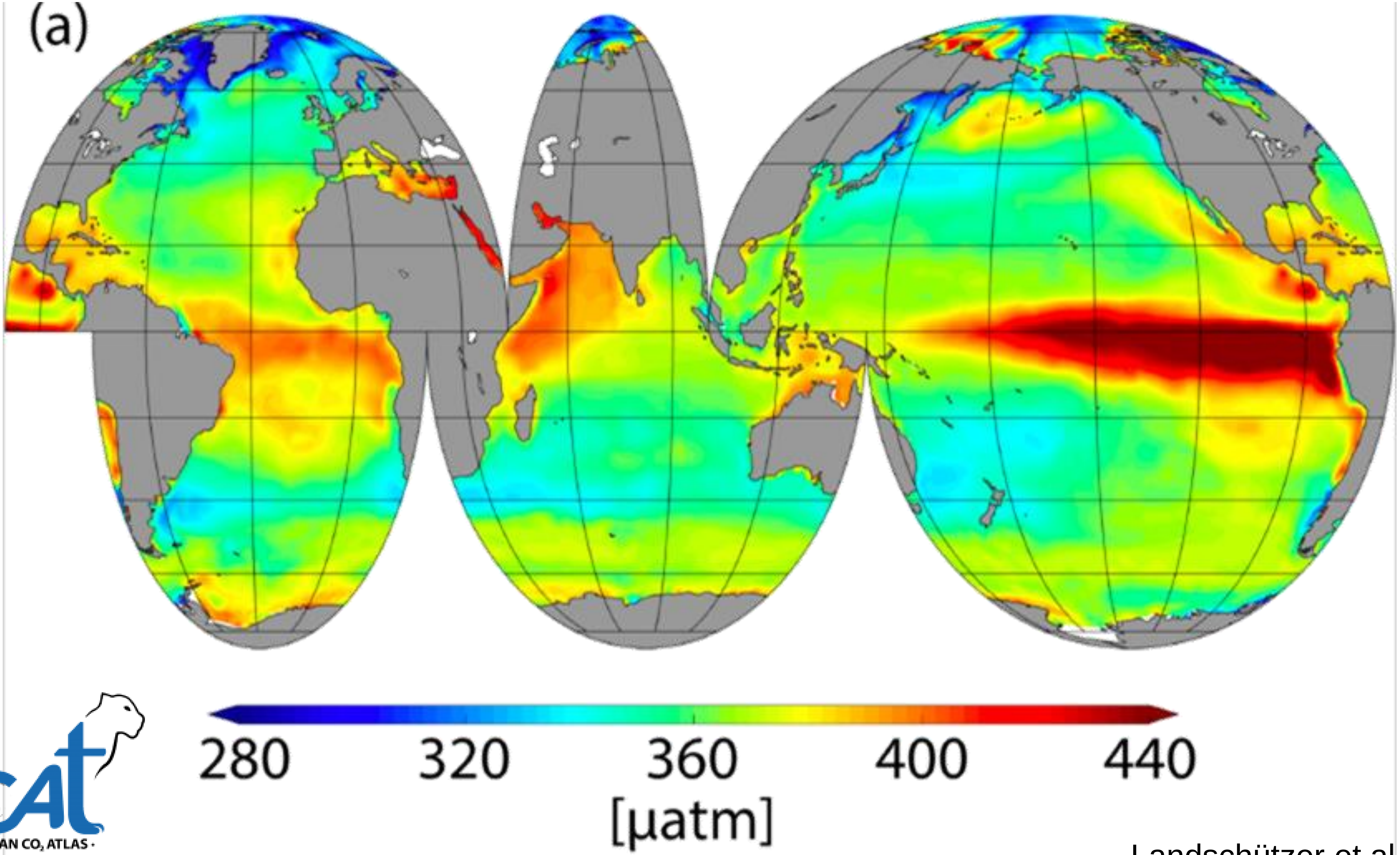




https://www.esrl.noaa.gov/gmd/dv/data/

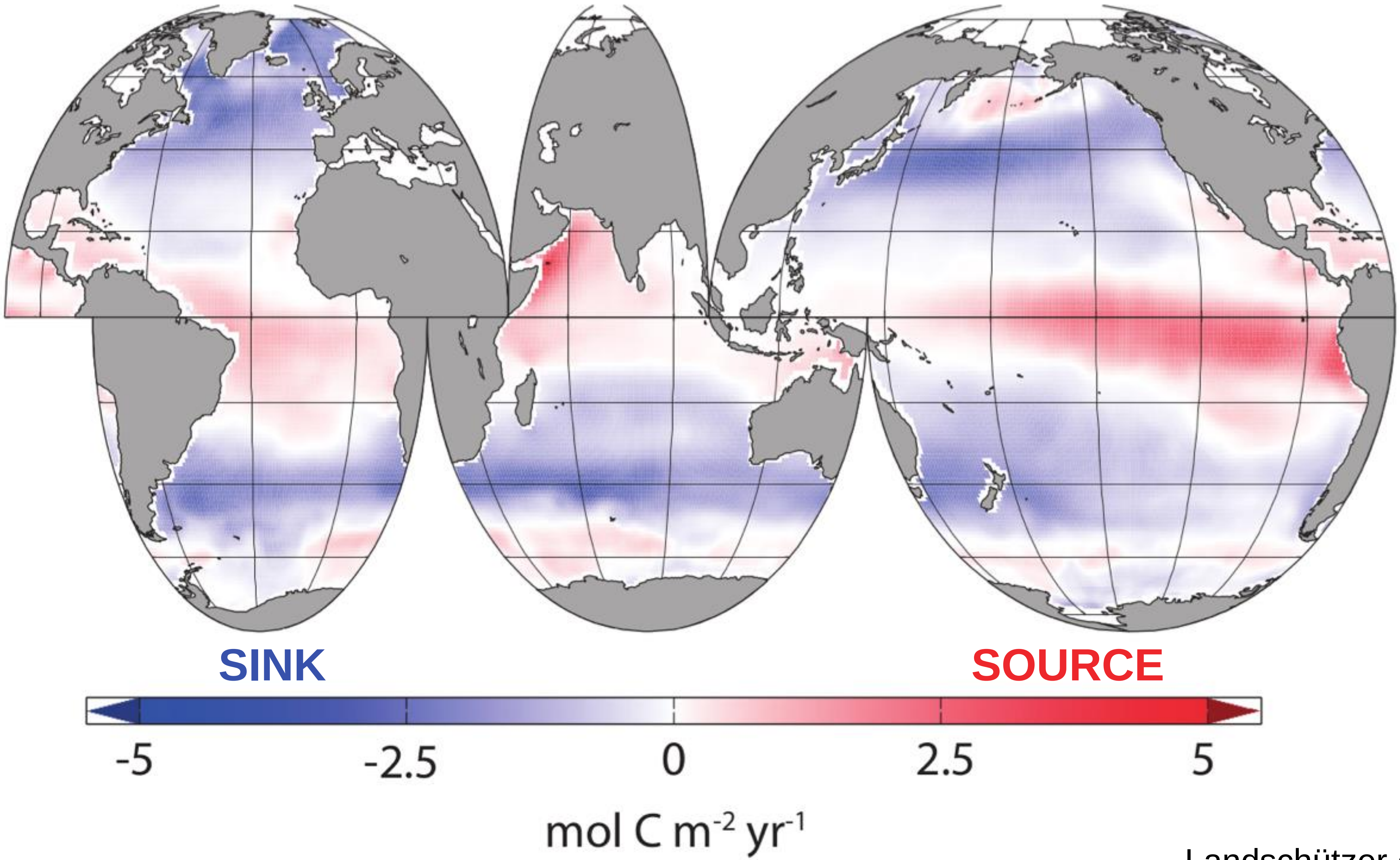


Seawater pCO_2 data from Rödenbeck et al. (2015) BG



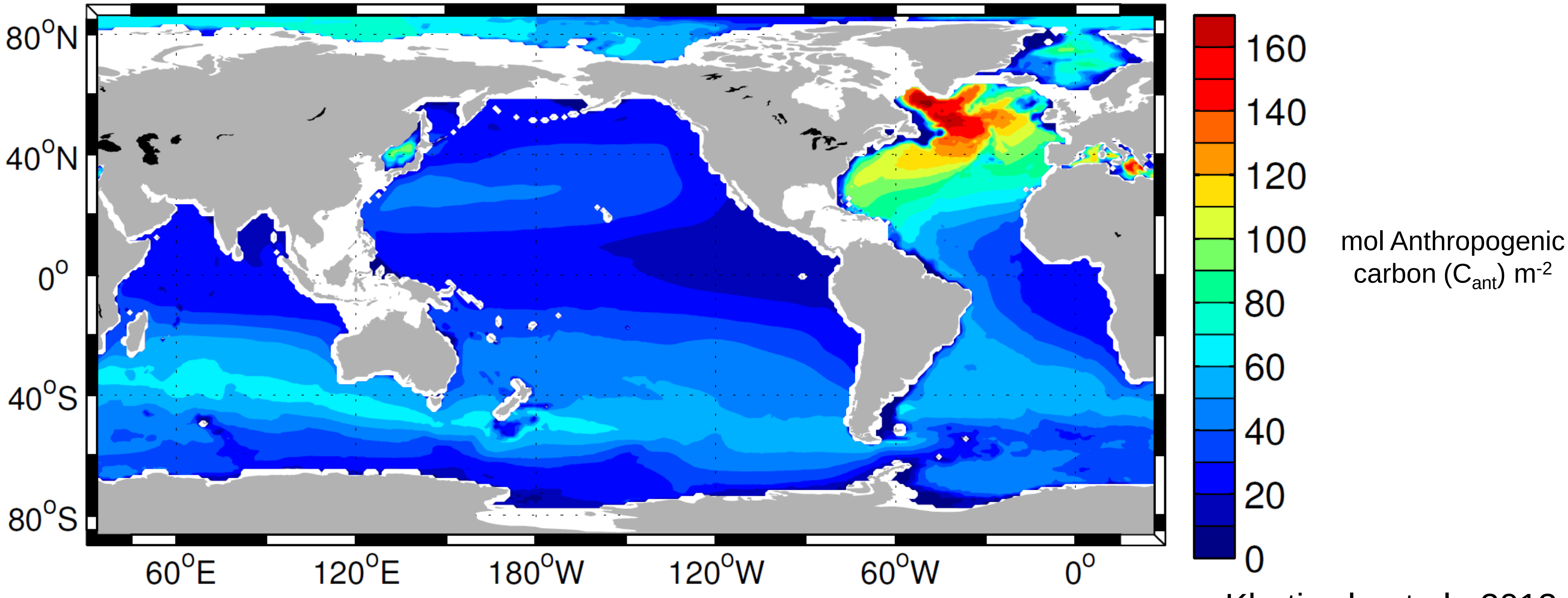
SOCAT · SURFACE OCEAN CO₂ ATLAS ·

Landschützer et al., 2020



Landschützer et al., 2020

HOMOGENEOUS atmosphere versus…



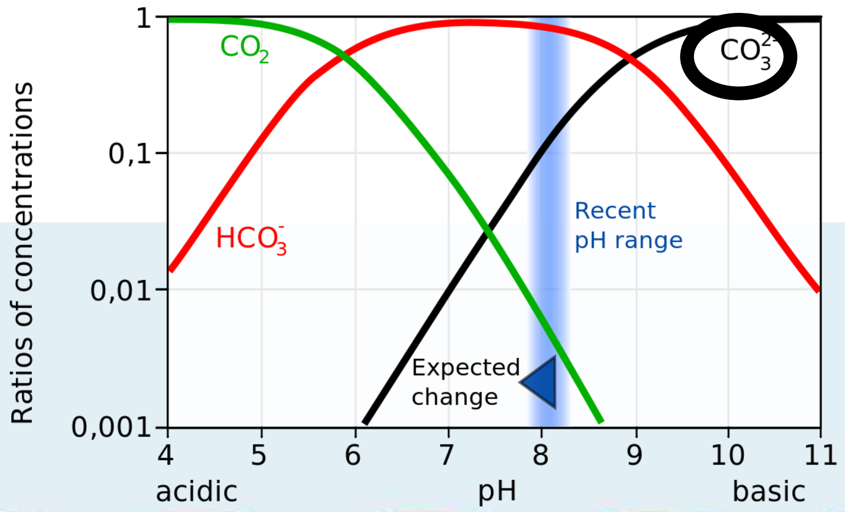
Khatiwala et al., 2013

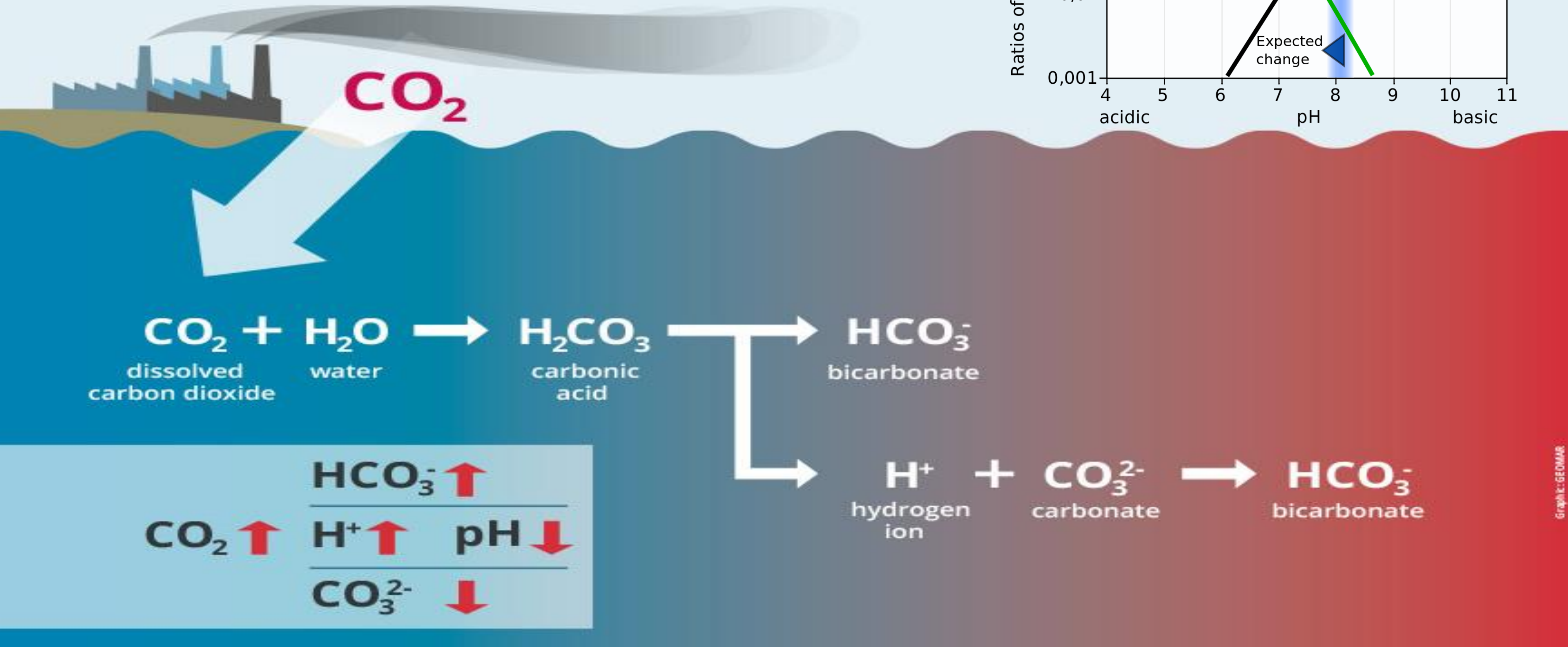
HETEROGENEOUS ocean!

OCEAN ACIDIFICATION:

The other CO_2 problem, the evil twin of Climate Change…

$[CO_3^{2-}]$ = carbonate





- Carbon cycle
  - Methods for Ocean carbon parameters:

DIC	**ALK**
pH	**pCO_2**

"If you know two of these parameters you can compute all the others with a given Tª, salinity and pressure"

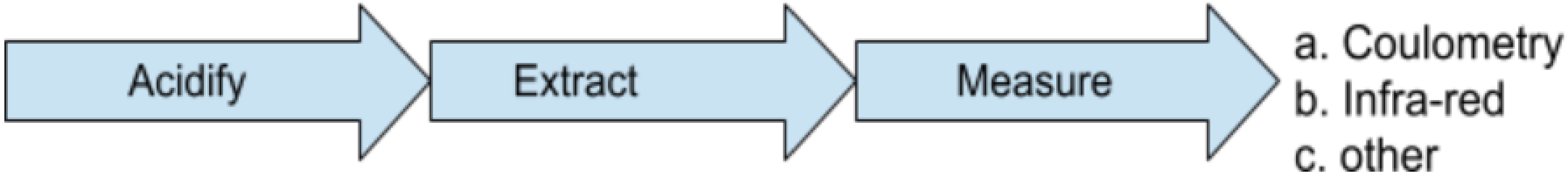
- Carbon cycle
  - Methods for Ocean carbon parameters:

DIC

Dissolved inorganic carbon (DIC or CT) is **the sum of the concentrations** of all inorganic carbon species.

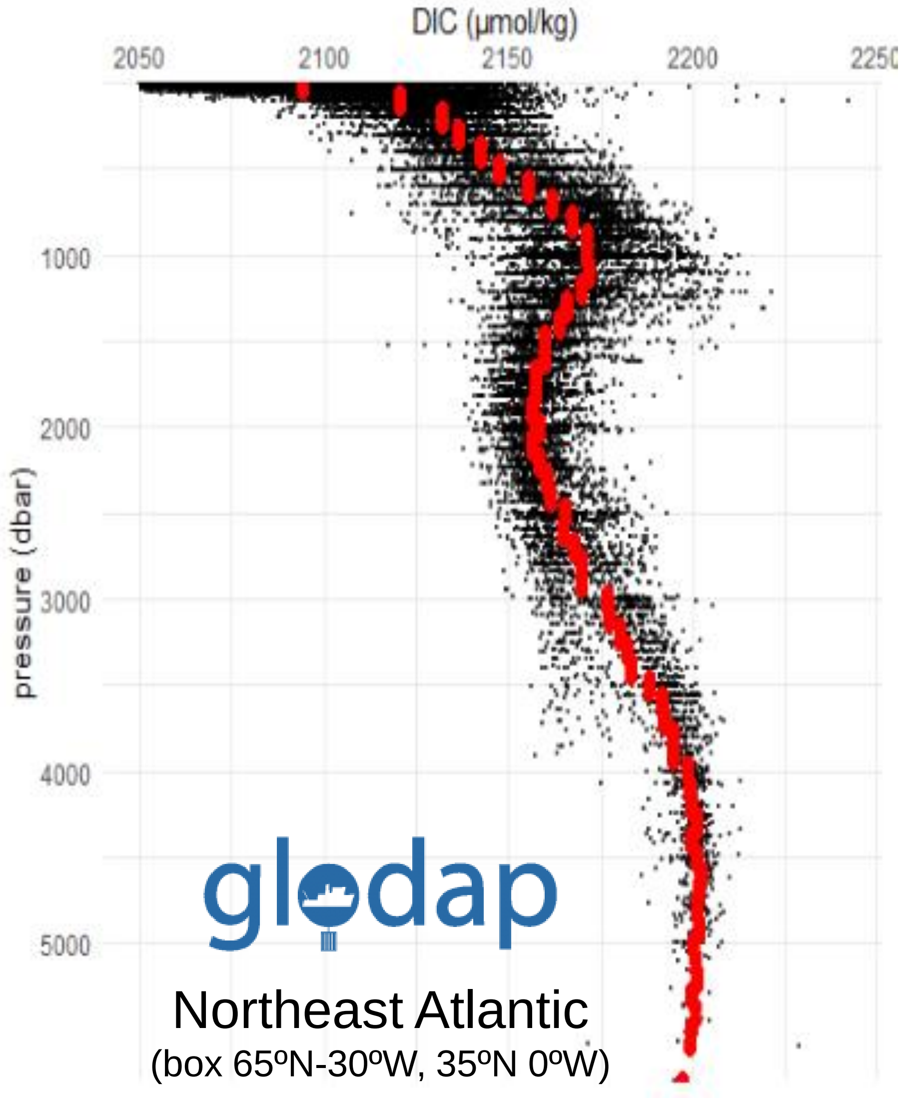
$$DIC = [CO_2]+[HCO_3^-]+[CO_3^=]$$

(1:90:9)



- Carbon cycle
  - ➢ Methods for Ocean carbon parameters:

DIC



- Carbon cycle
    - Methods for Ocean carbon parameters:

ALK

The excess of proton acceptors over proton donors with respect to a certain zero level of protons (Dickson, 1981):

$$\boxed{A_T \cong \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right]} \left[\cancel{B(OH)_4^-}\right] + \left[\cancel{OH^-}\right] + \left[\cancel{HPO_4^{2-}}\right] + 2\left[\cancel{PO_4^{3-}}\right] + \left[\cancel{SiO(OH)_3^-}\right]$$

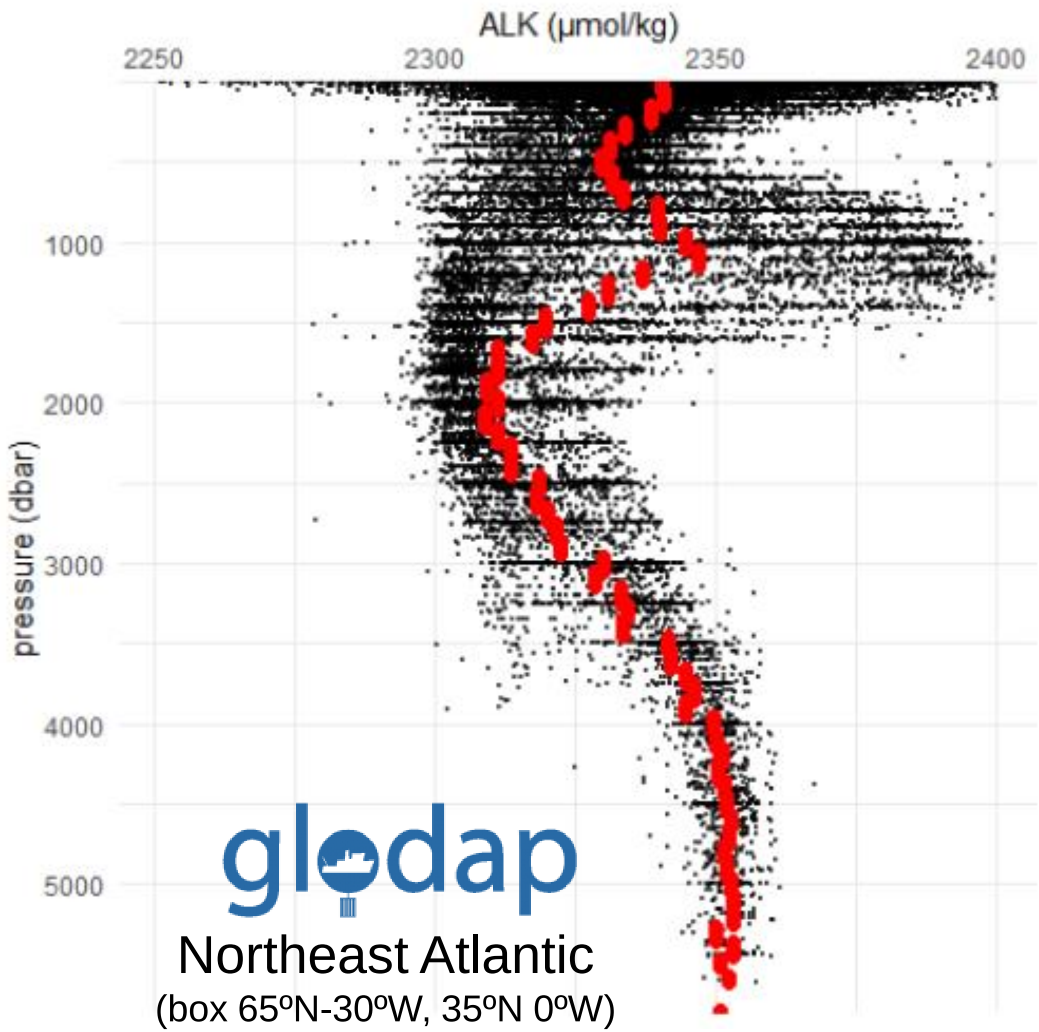
$$+ \left[\cancel{NH_3}\right] + \left[\cancel{HS^-}\right] - \left[\cancel{H^+}\right]_F - \left[\cancel{HSO_4^-}\right] - \left[\cancel{HS}\right] - \left[\cancel{HSO_4^-}\right] \ldots$$

Measurement techniques:

1. Acidimetric titration

- Carbon cycle
  - Methods for Ocean carbon parameters:

ALK



Northeast Atlantic
(box 65ºN-30ºW, 35ºN 0ºW)

- Carbon cycle
  - Methods for Ocean carbon parameters:

pH

defined as the negative of the base 10 logarithm of the hydrogen ion ($[H^+]$) concentration

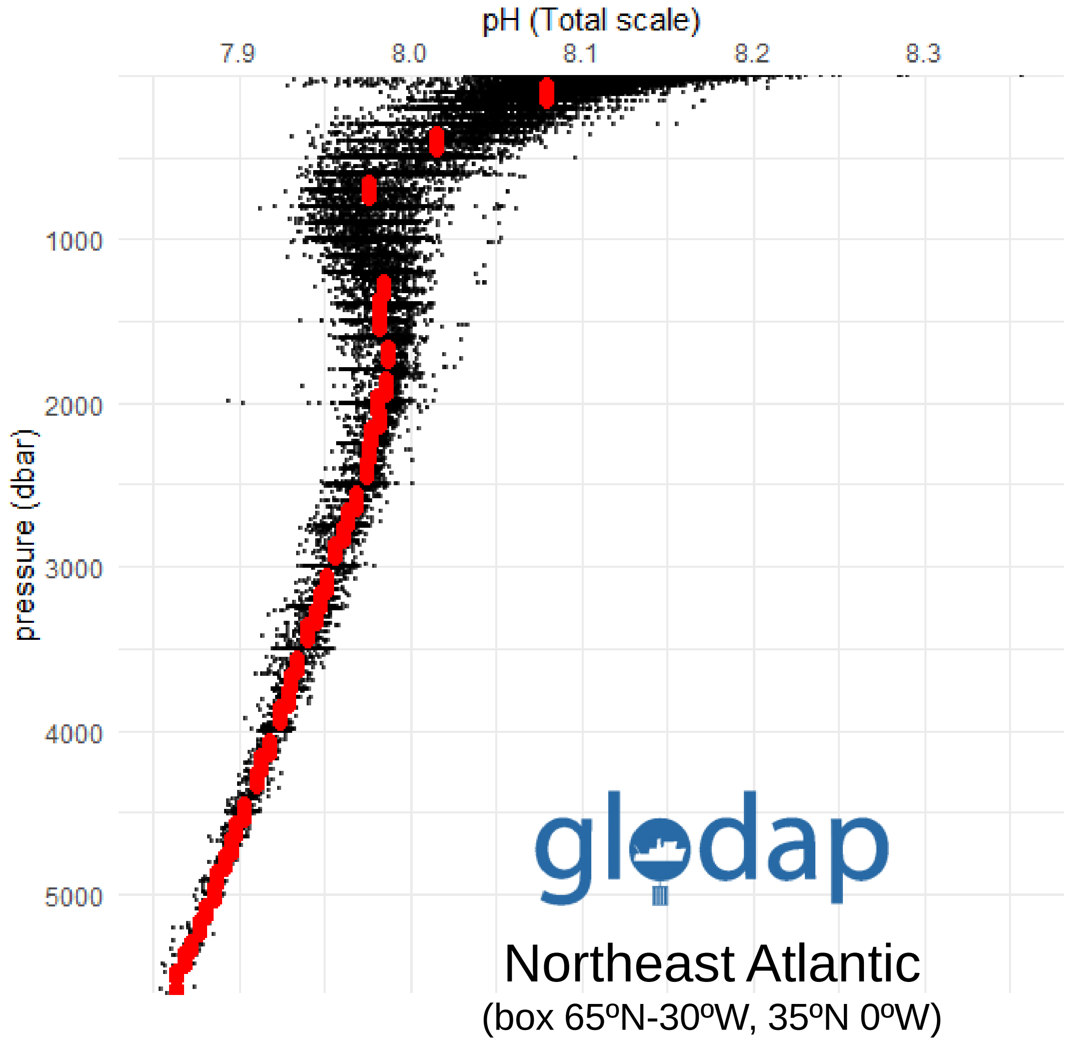
$$pH = -\log_{10}[H^+]$$

Measurement techniques:

1. Potentiometric technique using a glass/reference electrode cell
2. Spectrophotometric with indicator dye *m*-cresol pruple

- Carbon cycle
  - ➢ Methods for Ocean carbon parameters:

pH



- Carbon cycle
  - Methods for Ocean carbon parameters:

$\boxed{\mathbf{pCO_2}}$

The product of the mole fraction of CO_2 (xCO_2) in the equilibrated gas phase and the total pressure of equilibration (p):

$$p(CO_2) = x(CO_2) \cdot p$$

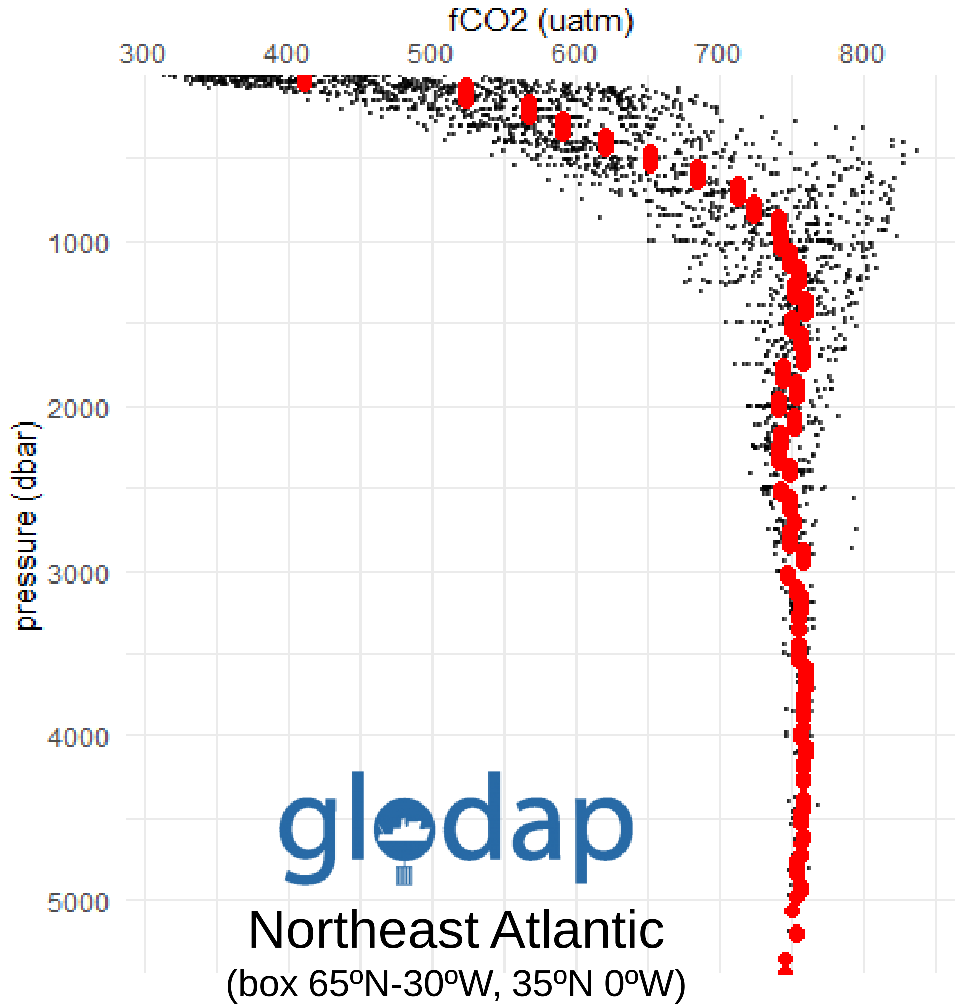
A temperature-dependent property

Measurement techniques:
1. from discrete samples in air equilibrium
2. From continuous stream in air equilibrium

$\Rightarrow$ Non-dispersive infrared absorption detector

- Carbon cycle
  - Methods for Ocean carbon parameters:

pCO_2



- Carbon cycle
  - ➢ Methods for Ocean carbon parameters
    - ❖ Study cases: *seacarb*

Table 1. Carbonate system software packages.

Package	Language	Version	Reference
CO2SYS[a]	QBasic	1.05	Lewis and Wallace (1998)
CO2SYS[b]	Excel	24	Pelletier et al. (2007)
CO2SYS[a]	Excel	2.1	Pierrot et al. (2006)
CO2SYS[a]	MATLAB	1.1	van Heuven et al. (2011)
CO2calc[c]	Visual Basic	1.3.0	Robbins et al. (2010)
csys[d]	MATLAB	04–2014	Zeebe and Wolf-Gladrow (2001)
ODV[e]	C++	4.5.0	Schlitzer (2002)
mocsy[f]	Fortran 95	2.0	Orr and Epitalon (2015)
seacarb[g]	R	3.0.6	Gattuso et al. (2015)
swco2[h]	Excel	2	Hunter (2007); Mosley et al. (2010)
swco2[h]	Visual Basic	2	Hunter (2007)

[a] http://cdiac.ornl.gov/oceans/co2rprt.html
[b] http://www.ecy.wa.gov/programs/eap/models.html
[c] http://pubs.usgs.gov/of/2010/1280/
[d] http://www.soest.hawaii.edu
[e] http://odv.awi.de/
[f] http://ocmip5.ipsl.jussieu.fr/mocsy
[g] http://cran.r-project.org/package=seacarb
[h] http://neon.otago.ac.nz/research/mfc/people/keith_hunter/software/swco2/

PyCO2SYS: marine carbonate system calculations in Python

Humphreys, Matthew P.; Gregor, Luke; Pierrot, Denis; van Heuven, Steven M. A. C.; Lewis, Ernie R.; Wallace, Douglas W. R.

PyCO2SYS is a Python toolbox for solving the marine carbonate system and calculating related seawater properties. Its core is a Python implementation of CO2SYS for MATLAB. Documentation is available at PyCO2SYS.rtfd.io.

https://github.com/mvdh7/PyCO2SYS

https://github.com/mvdh7/PyCO2SYS-examples

Orr, J. C., Epitalon, J. M. & Gattuso, J. P. Comparison of ten packages that compute ocean carbonate chemistry. *Biogeosciences* **12**, (2015). (link)

seacarb

Gattuso, J.-P., Epitalon, J.-M., Lavigne, H., Orr, J., 2020. seacarb: Seawater Carbonate Chemistry.

```
> library(seacarb)
```

KEY FUNCTION: *carb(…)*

```
> carb(flag, var1, var2, S=35, T=25, Patm=1, P=0,
Pt=0, Sit=0,k1k2="x", kf="x", ks="d", pHscale="T", b="u74",
gas="potential", warn="y", eos="eos80", long, lat)
```

> carb(**flag**, var1, var2,
S=Salinity, T=Temperature,
Patm=1, P=Pressure **in bar**,
Pt=Total phosphate mol/kg, Sit=Total Silicate mol/kg,
k1k2="x", kf="x", ks="d", pHscale="T", b="u74", gas="potential",
warn="y", eos="eos80", long, lat)

flag = 1 pH and CO_2 given
flag = 2 CO_2 and HCO_3 given
flag = 3 CO_2 and CO_3 given
flag = 4 CO_2 and ALK given
flag = 5 CO_2 and DIC given
flag = 6 pH and HCO_3 given
flag = 7 pH and CO_3 given
flag = 8 pH and ALK given

flag = 9 pH and DIC given
flag = 10 HCO_3 and CO_3 given
flag = 11 HCO_3 and ALK given
flag = 12 HCO_3 and DIC given
flag = 13 CO_3 and ALK given
flag = 14 CO_3 and DIC given
flag = 15 ALK and DIC given

flag = 21 pCO_2 and pH given
flag = 22 pCO_2 and HCO_3 given
flag = 23 pCO_2 and CO_3 given
flag = 24 pCO_2 and ALK given
flag = 25 pCO_2 and DIC given

```
> carb(flag, var1, var2,
        S=Salinity, T=Temperature,
        Patm=1, P=Pressure in bar,
        Pt=Total phosphate mol/kg, Sit=Total Silicate mol/kg,
        k1k2="x", kf="x", ks="d", pHscale="T", b="u74", gas="potential",
        warn="y", eos="eos80", long=1.e20, lat=1.e20)
```

	var1		var2	
flag = 8	pH	and	ALK	given
flag = 9	pH	and	DIC	given
flag = 15	ALK	and	DIC	given

NOTE: the order is important!

> carb(**flag**, var1, var2,
S=Salinity, T=Temperature,
Patm=1, P=Pressure **in bar**,
Pt=Total phosphate mol/kg, Sit=Total Silicate mol/kg,
k1k2="x", kf="x", ks="d", pHscale="T", b="u74", gas="potential",
warn="y", eos="eos80", long=1.e20, lat=1.e20)

flag = 8	pH	and	ALK	given
flag = 9	pH	and	DIC	given
flag = 15	ALK	and	DIC	given

var1
var2

Units: mol/kg always **expect pH (no units) and pCO_2 (µatm)**

NOTE UNITS! is important!

Summary *(for a intro level)*

These are your carbon data

```
> carb(flag, var1, var2,
      S=Salinity, T=Temperature,
      Patm=1, P=Pressure in bar,
      Pt=Total phosphate mol/kg, Sit=Total Silicate mol/kg,
      k1k2="x", kf="x", ks="d", pHscale="T", b="u74", gas="potential",
      warn="y", eos="eos80", long, lat)
```

Almost sure you also have this data

You can let Nutrient info in blank

…and forget about this

(unless you like to go into detail, of course!)

These are your carbon data

> carb(**flag, var1, var2**,
S=Salinity, T=Temperature, Patm=1, P=Pressure **in bar**)

*HTML "CANAIMOC.html" done with the Rmarkdown file "CANAIMOC.Rmd" in:

https://github.com/mfontela/CANAIMOC

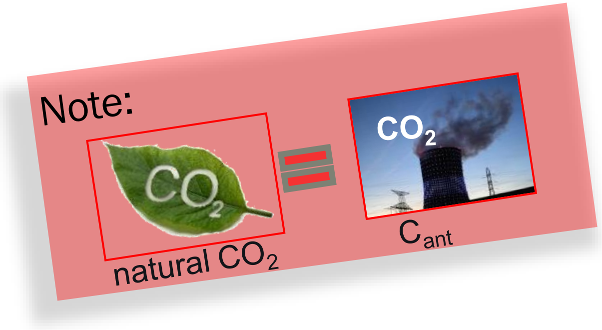
Also available online here:
https://mfontela.github.io/web/CANAIMOC.html

Index

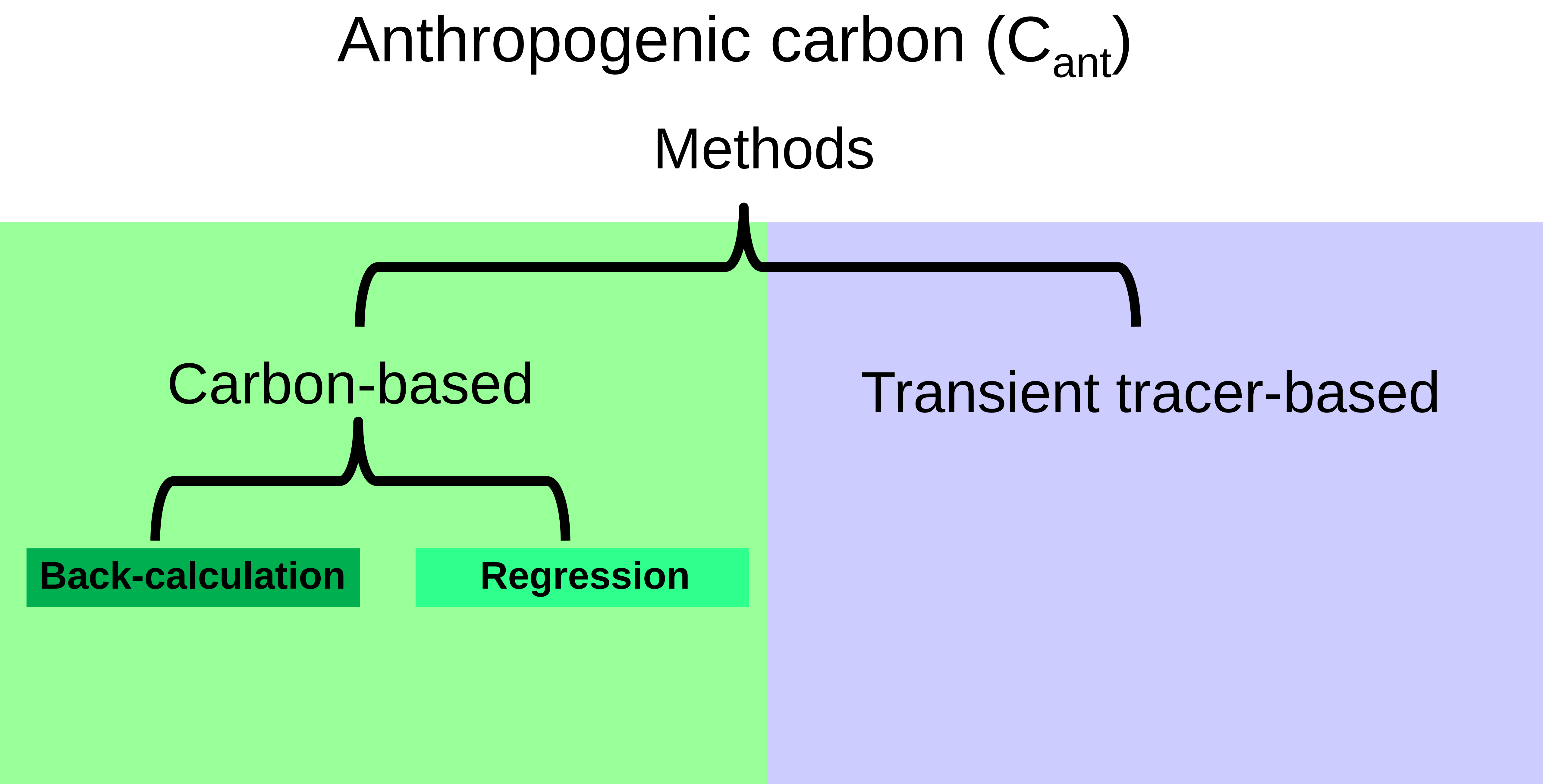
- Carbon cycle
  - ➢ Intro
  - ➢ Methods for Ocean carbon parameters
    - ❖ Study cases: seacarb, CO2SYS
- Anthropogenic carbon (C_{ant})
  - ➢ Intro
  - ➢ Methods: carbon-based vs transient tracers-based
    - Biogeochemical back-calculation φC_T^o method:
      - ❖ Study cases

- Anthropogenic carbon
  - Intro

$$\mathbf{DIC = DIC_{nat} + C_{ant}}$$



- C_{ant} is **not a directly measurable quantity**. It has to be estimated using indirect means.
- The anthropogenic signal in the ocean is only **a few percent (3-4%)** of DIC
- Carbon in the ocean participates in rather complex **in situ biogeochemistry processes**.
- C_{ant} distribution in the ocean is highly **heterogeneous**.



Anthropogenic carbon (C_{ant})
Methods
Carbon-based
Transient tracer-based
Back-calculation
Regression

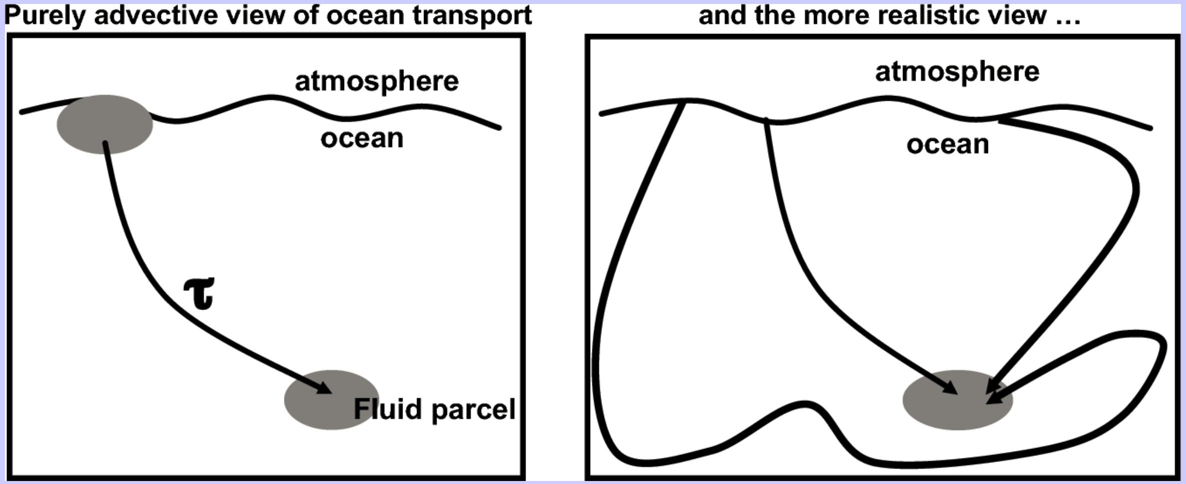
Methods

Transient tracer-based

- TTD: Transient tracer distribution (Waugh et al., 2006)
- GF: Green function (Khatiwala et al., 2009)

- OCIM: Ocean Circulation Inverse Model (DeVries, 2014)

(a bit in-between methods: also an inversión method but with $\Delta^{14}C$ as constraint)



CAVEAT: mean air-sea equilibrium times of transient tracers different to CO_2

Methods

Carbon-based

Back-calculation

Regression

- **multiple linear regressions** on a number of biogeochemical variables
- Assumption: **no temporal trends in the independent variables** and the relationship between dependent and independent variables stays the same.
- Weakness: you need **at least two observations** at approximately the same location for different periods.

Methods

Carbon-based

Back-calculation

Regression

- MLR (Wallace, 1995)
- eMLR (Friis et al., 2005)
- eMLR(C*) (Clement & Gruber, 2018)

Regression

➢eMLR(C*) (Clement & Gruber, 2018)

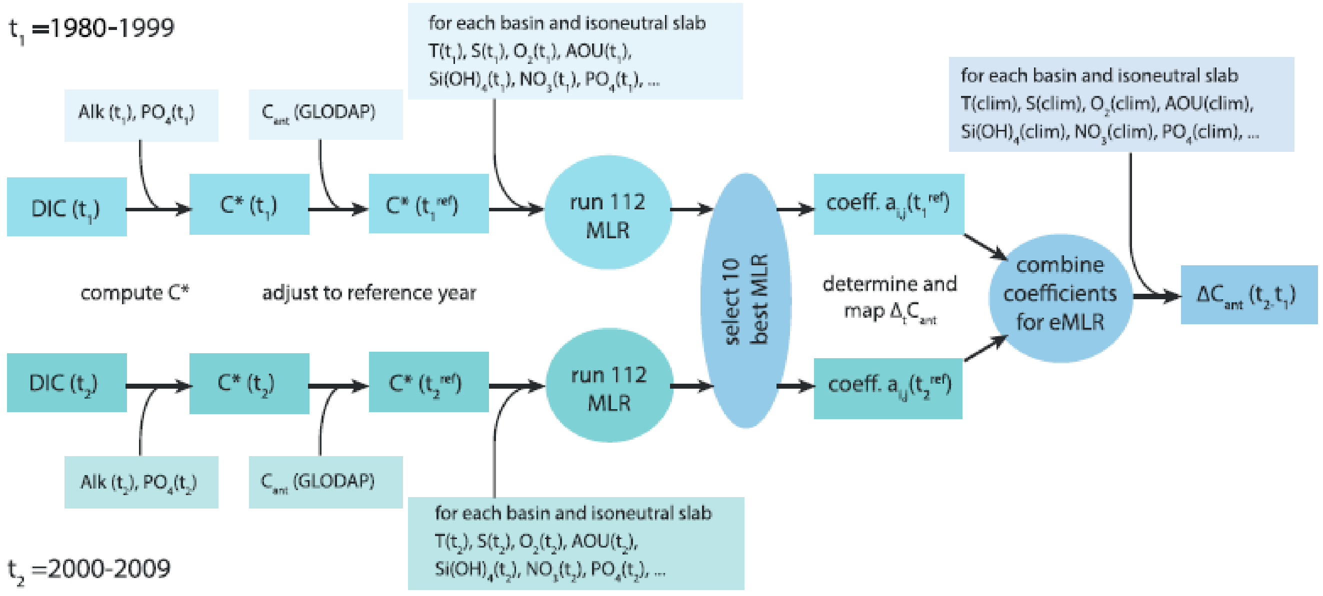
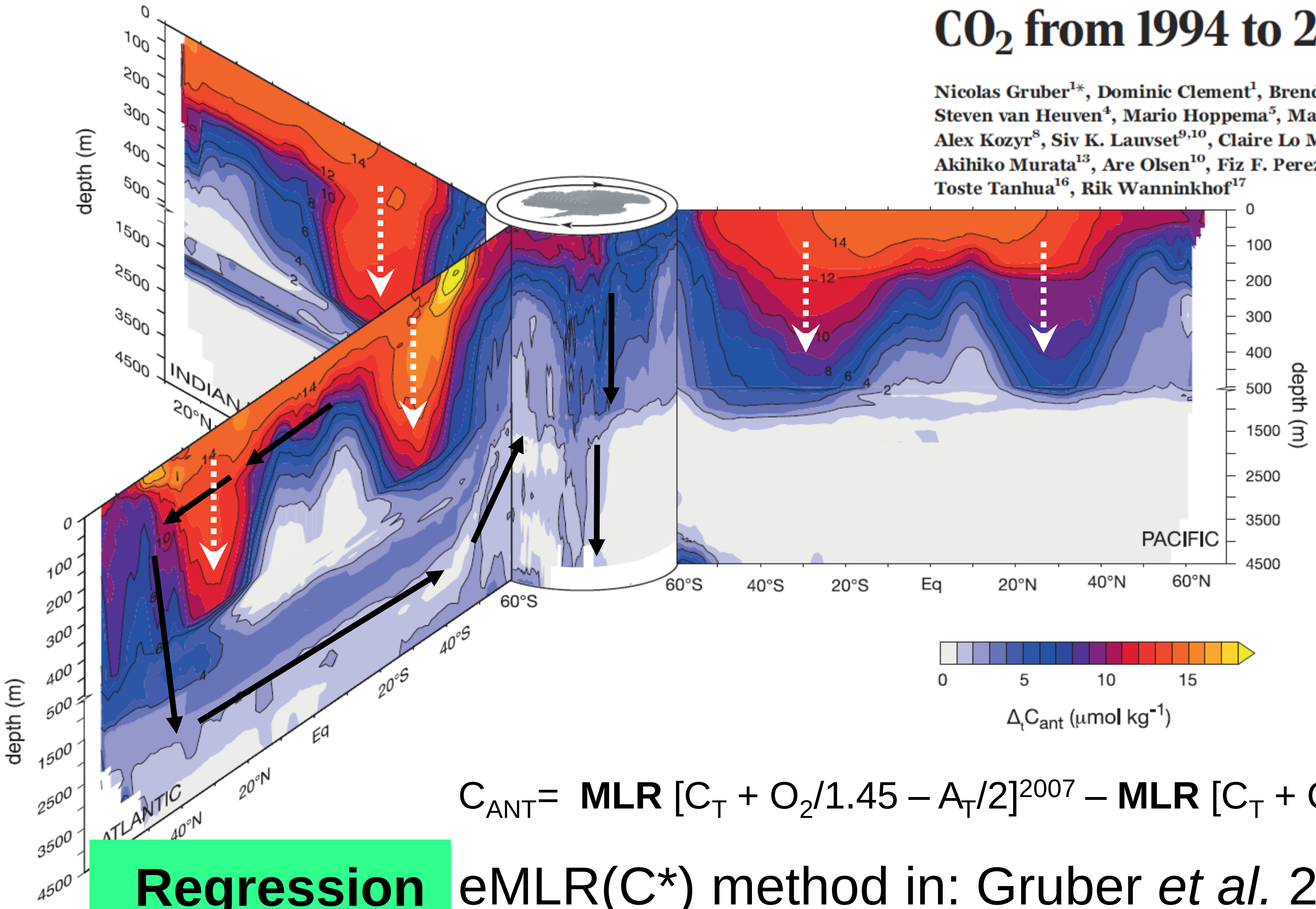


Figure 2. Flowchart of the eMLR(C*) method to determine the decadal increase in the oceanic content of anthropogenic CO_2, that is, $\Delta C_{ant}(t_2 - t_1)$. Also shown are the required input data in each of the four major steps. In the first step, C^* is computed from the measured DIC, Alk, and PO_4. In the second step, C^* is adjusted to a common reference year for each of the two periods, that is, t_i^{ref}. In the third step, separate multiple linear regressions are run for each time period, using all possible combinations. The best 10 regression models are selected for each isoneutral surface based on their fit to the data and combined to form the eMLR. In the fourth and final step, the eMLR models are combined with global gridded climatological distributions of the predictors to map $\Delta C_{ant}(t_2 - t_1)$ globally below 150 m.

The oceanic sink for anthropogenic CO_2 from 1994 to 2007

Nicolas Gruber[1*], Dominic Clement[1], Brendan R. Carter[2,3], Richard A. Feely[2], Steven van Heuven[4], Mario Hoppema[5], Masao Ishii[6], Robert M. Key[7], Alex Kozyr[8], Siv K. Lauvset[9,10], Claire Lo Monaco[11], Jeremy T. Mathis[12], Akihiko Murata[13], Are Olsen[10], Fiz F. Perez[14], Christopher L. Sabine[15], Toste Tanhua[16], Rik Wanninkhof[17]



C_{ANT}= **MLR** $[C_T + O_2/1.45 - A_T/2]^{2007}$ – **MLR** $[C_T + O_2/1.45 - A_T/2]^{1994}$

Regression eMLR(C*) method in: Gruber *et al.* 2019 Science

Methods

Carbon-based

Back-calculation

Regression

$$C_{ant} = DIC - \Delta C_{bio} - C_{phys}$$

- ✓ Modify a measured DIC concentration for the changes that occurred since being no longer in contact with the ocean surface
- ✓ Estimation of the preformed DIC is critical point.

Methods

Carbon-based

Back-calculation

Regression

- Brewer (1978), Chen and Millero (1979)
- ΔC* (Gruber et al. 1996)
- TrOCA (Touratier & Goyet, 2004).
- φCT° (Vázquez-Rodriguez et al., 2009)

Back-calculation

- Brewer (1978)

VOL. 5, NO. 12 GEOPHYSICAL RESEARCH LETTERS DECEMBER 1978

DIRECT OBSERVATION OF THE OCEANIC CO_2 INCREASE

Peter G. Brewer

Woods Hole Oceanographic Institution
Woods Hole, Massachusetts 02543

- Chen and Millero (1979)

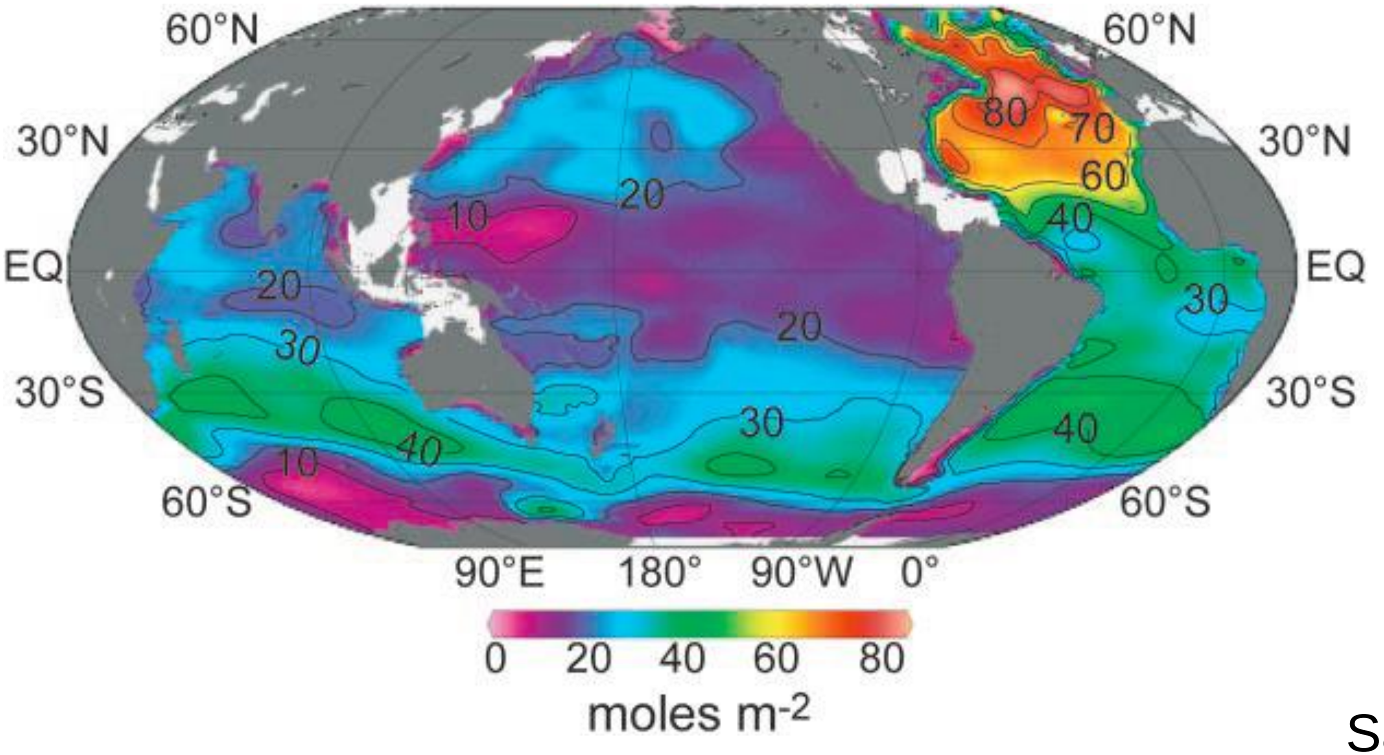
Nature Vol. 277 18 January 1979

Gradual increase of oceanic CO_2

Back-calculation

- ΔC* (Gruber et al. 1996)

$$C^* = DIC - r_{C:O_2}O_2 - \frac{1}{2}(Alk + r_{N:O_2}O_2)$$



Sabine et al., 2004

➢ TrOCA (Touratier & Goyet, 2004)

Back-calculation

Tracer combining **O**xygen, inorganic **C**arbon and total **A**lkalinity

The concentration of $C_{\mathrm{ant}}^{\mathrm{TrOCA}}$ is then estimated using eq. 11:

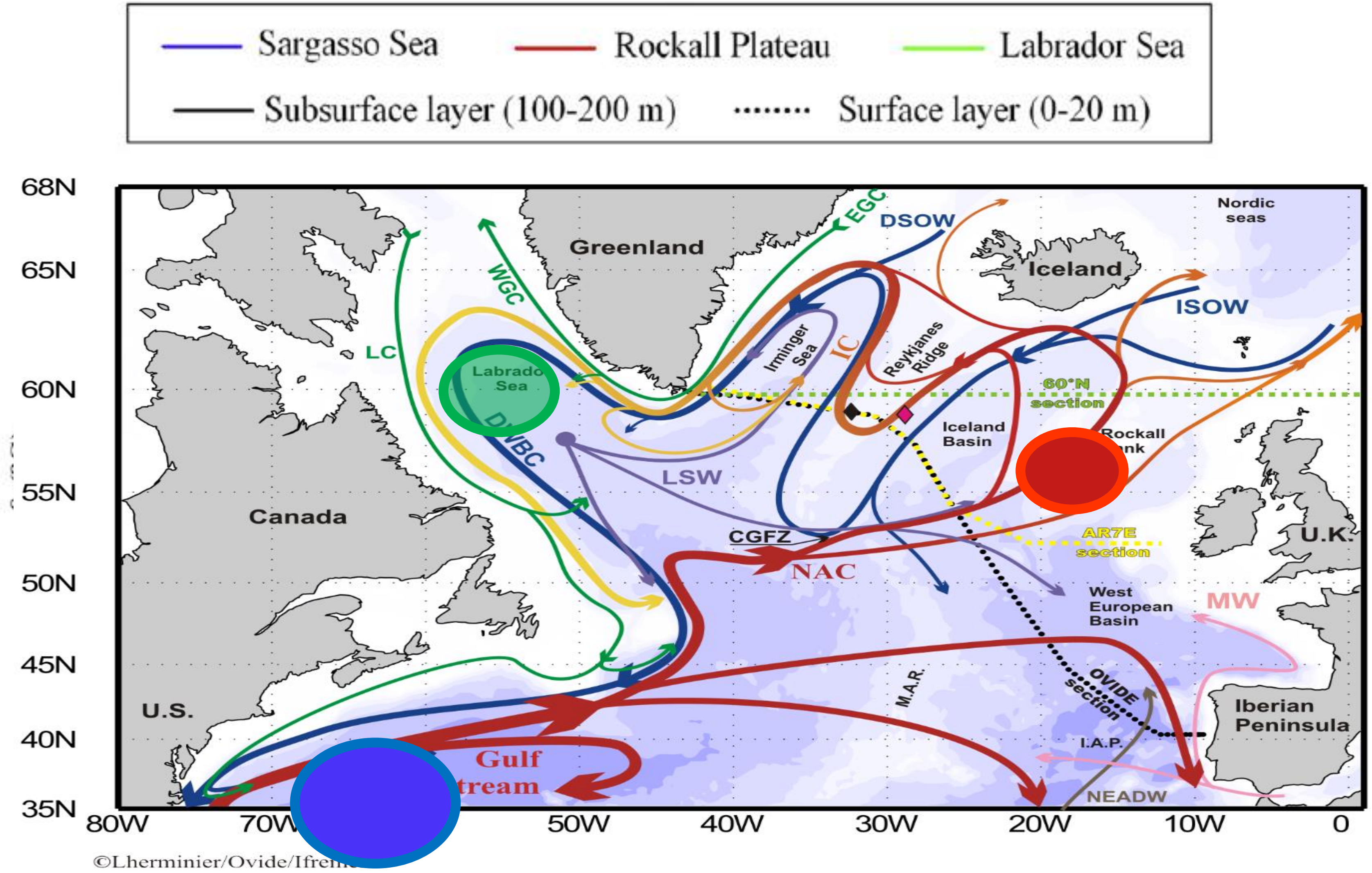
$$C_{\mathrm{ant}}^{\mathrm{TrOCA}} = \frac{O_2 + 1.279\left[C_T - \frac{1}{2}A_T\right] - e^{\left(7.511 - (1.087\times10^{-2})\theta - \frac{7.81\times10^5}{A_T^2}\right)}}{1.279}. \tag{11}$$

➢ φCT° (Vázquez-Rodriguez et al., 2009)

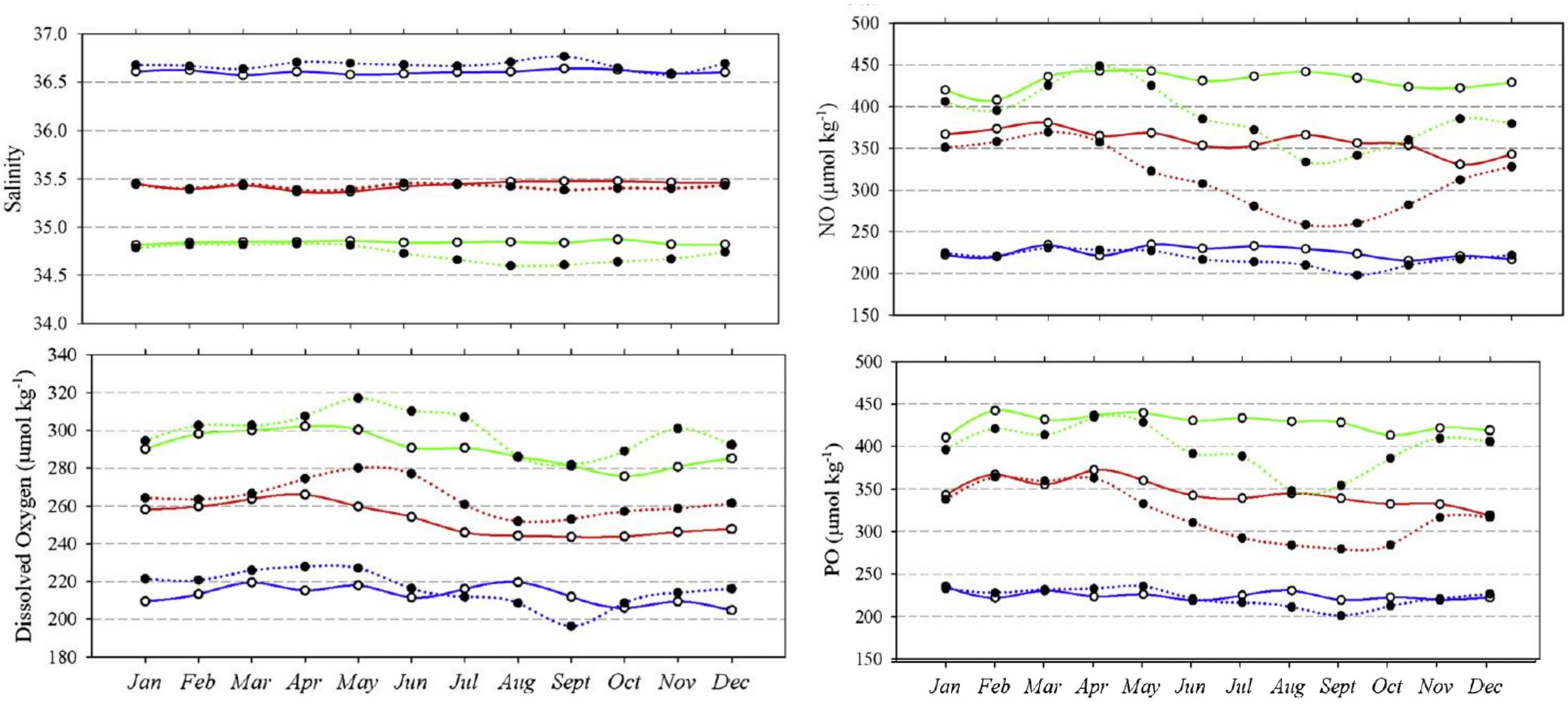
Back-calculation

- ✓ C_{ant} is the difference between the water mass DIC at their formation time and the DIC that it would have in preindustrial times.
- ✓ Takes into account changes in carbon concentration due **organic matter remineralization and $CaCO_3$ dissolution**.
- ✓ Only need **hydrographical** data: carbon, oxygen and inorganic nutrients.
- ✓ Overall uncertainty: **±5.2 μmol·kg^{-1}**
- ✓ Reference layer: **subsurface** layer.

Subsurface layer



Subsurface layer



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Strengths φC_T^o

- Proper characterization of preformed conditions.
- No needs for CFC's data.
- No assumptions about C_{ant} saturation in the water mass formation time.
- Includes corrections for warming and acidification.
- Does not need a "zero" C_{ant} reference
- Is based on biogeochemical and oceanographic knowledge.

Marcos Fontela, 2020

Weaknesses φC_T^o

- Not global, only for the Atlantic Ocean.
- Depends in part on a simplified OMP.
- ΔC_{dis} computation is based on multiple linear regressions (MLR) that are potentially improved.
- Assume constant and homogeneus stoichiometric ratios.

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More info in:

Vázquez-Rodríguez, M., F. Touratier, C. Lo Monaco, D. W. Waugh, X. a. Padin, R. G. J. Bellerby, C. Goyet, N. Metzl, a. F. Ríos, and F. F. Pérez (2008), Anthropogenic carbon distributions in the Atlantic Ocean: data-based estimates from the Arctic to the Antarctic, *Biogeosciences Discuss.*, *5*(2), 1421–1443, doi:10.5194/bgd-5-1421-2008.

Pérez, F. F., M. Vázquez-Rodríguez, H. Mercier, A. Velo, P. Lherminier, and A. F. Ríos (2010), Trends of anthropogenic CO2 storage in North Atlantic water masses, *Biogeosciences*, *7*(5), 1789–1807, doi:10.5194/bg-7-1789-2010.

Pérez, F. F., H. Mercier, M. Vázquez-Rodríguez, P. Lherminier, A. Velo, P. C. Pardo, G. Rosón, and A. F. Ríos (2013), Atlantic Ocean CO2 uptake reduced by weakening of the meridional overturning circulation, *Nat. Geosci.*, *6*(2), 146–152, doi:10.1038/ngeo1680.

Vázquez-Rodríguez, M., X. a. Padin, a. F. Ríos, R. G. J. Bellerby, and F. F. Pérez (2009), An upgraded carbon-based method to estimate the anthropogenic fraction of dissolved CO_2 in the Atlantic Ocean, *Biogeosciences Discuss.*, *6*(2), 4527–4571, doi:10.5194/bgd-6-4527-2009.

Fajar, N. M., P. C. Pardo, L. Carracedo, M. Vázquez-Rodríguez, A. F. Ríos, and F. F. Pérez (2012), Trends of anthropogenic CO^2 along 20°W in the Iberian Basin | Tendencias del CO^2 antropogénico a lo largo de 20°W en la Cuenca Ibérica, *Ciencias Mar.*, *38*(1 B), 287–306.

Khatiwala, S. *et al.* Global ocean storage of anthropogenic carbon. *Biogeosciences* **10**, 2169–2191 (2013).

Gruber, N. *et al.* The oceanic sink for anthropogenic CO 2 from 1994 to 2007. *Science (80-.).* **363**, 1193–1199 (2019).

Orr, J. C. *et al.* Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature* **437**, 681–686 (2005).

Clement, D. & Gruber, N. The eMLR(C*) Method to Determine Decadal Changes in the Global Ocean Storage of Anthropogenic CO 2. *Global Biogeochem. Cycles* (2018). doi:10.1002/2017GB005819

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mmfontela@ualg.pt
@MarcosFontela
www.marcosfontela.com