INSTITUTE OF OCEANOLOGY
POLISH ACADEMY OF SCIENCES

Biogeochemical cycles in the Baltic Sea

Karol Kuliński

Climate of the Baltic Sea Region
International Baltic Earth Summer School
20-27 August 2018

Baltic Earth
Earth System Science for the Baltic Sea Region

The National Centre for Research and Development

BONUS
SCIENCE FOR A BETTER FUTURE OF THE BALTIC SEA REGION

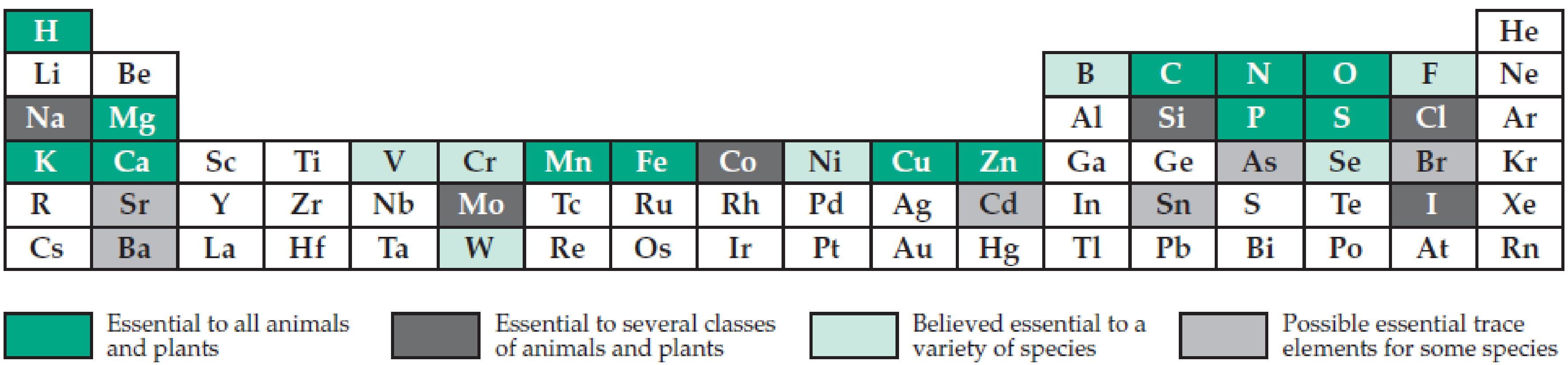
NATIONAL SCIENCE CENTRE POLAND

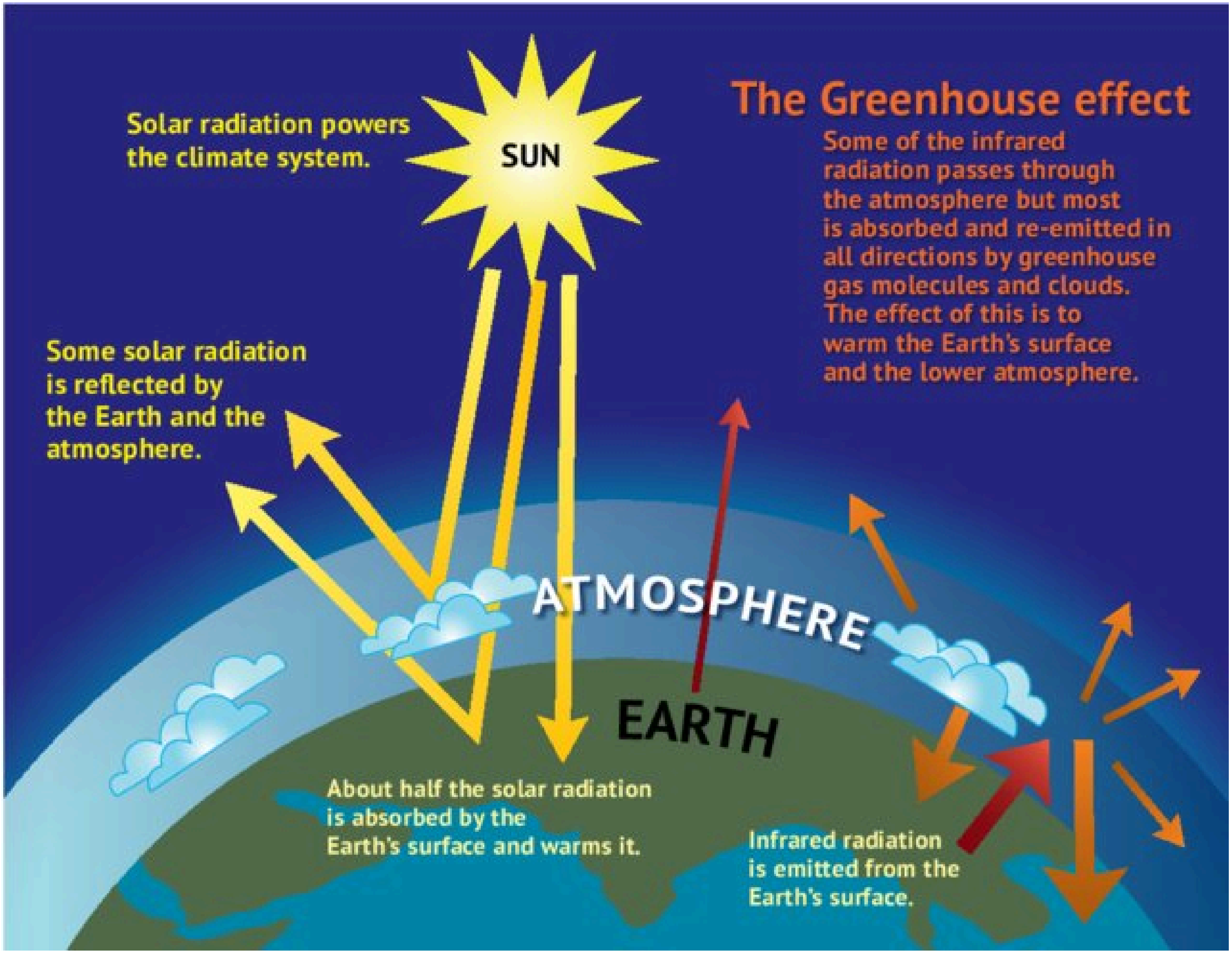
Outline:

I. Carbon – the chemical element conditioning climate
II. Role of marine environment in the carbon cycle
III. Marine CO_2 system and ocean acidification
IV. Peculiarities of the Baltic Sea

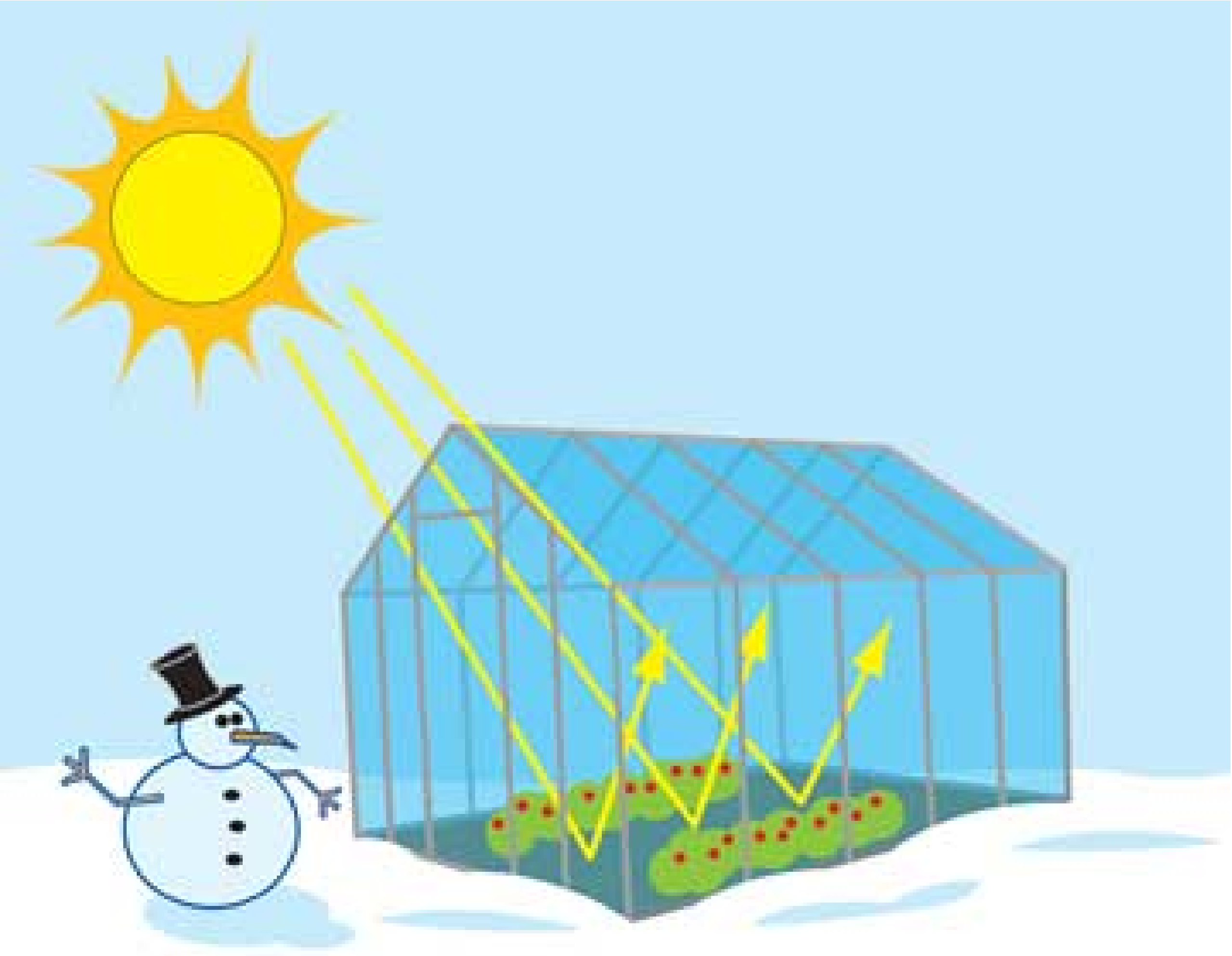
Outline:

I. Carbon – the chemical element conditioning climate
II. Role of marine environment in the carbon cycle
III. Marine CO_2 system and ocean acidification
IV. Peculiarities of the Baltic Sea

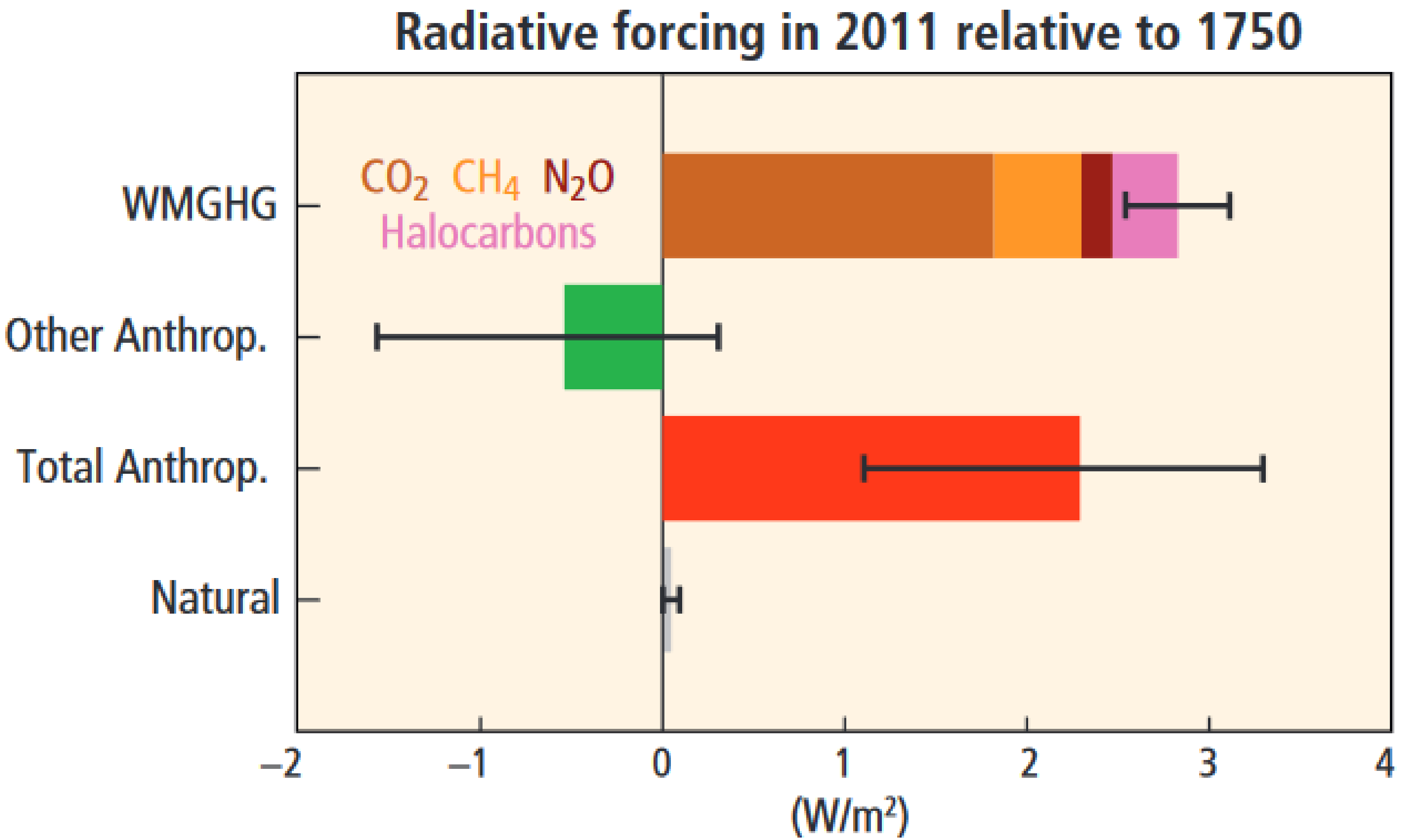




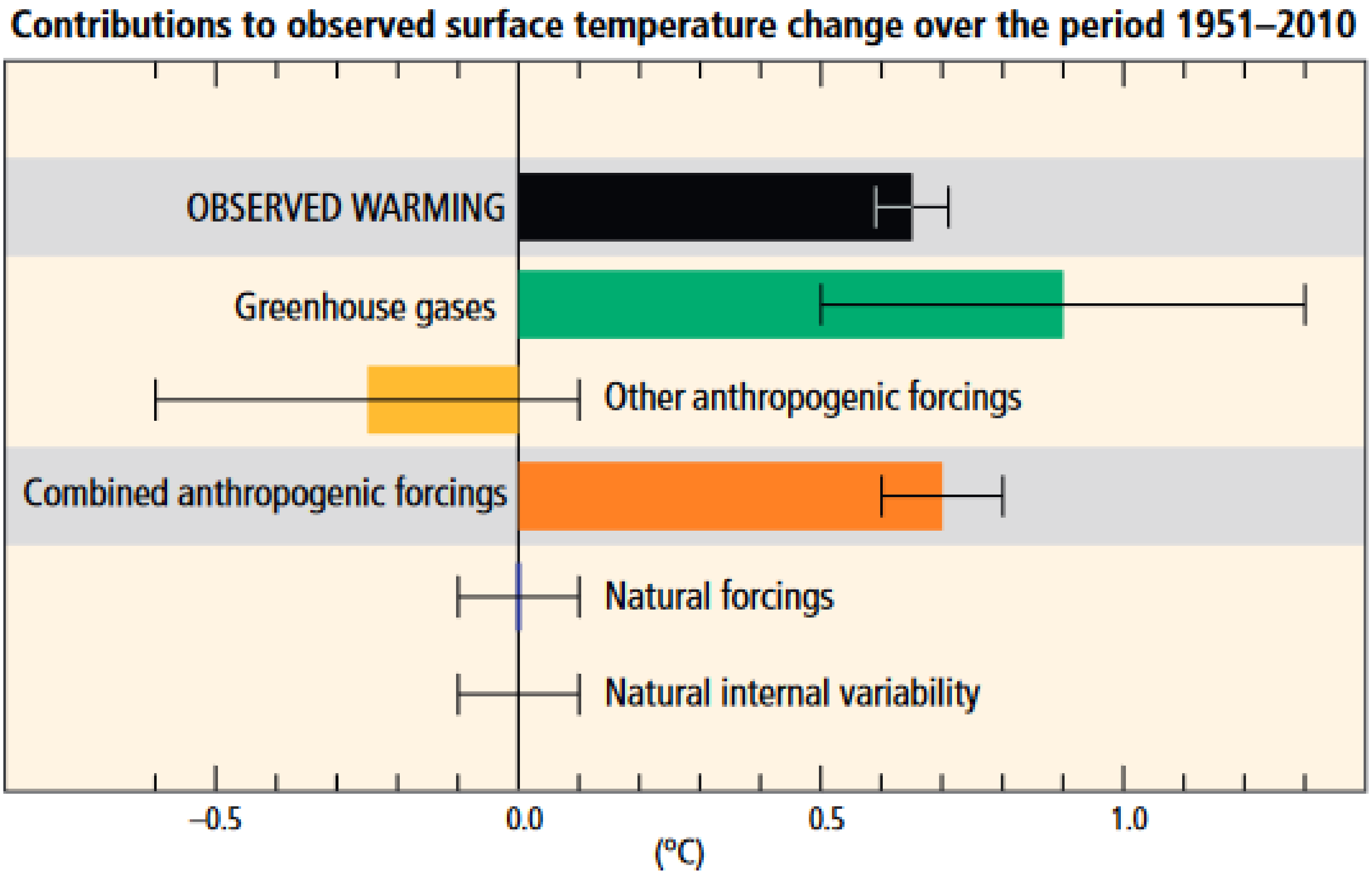
Source: WHO Library Cataloguing-in-Publication Data, 2015



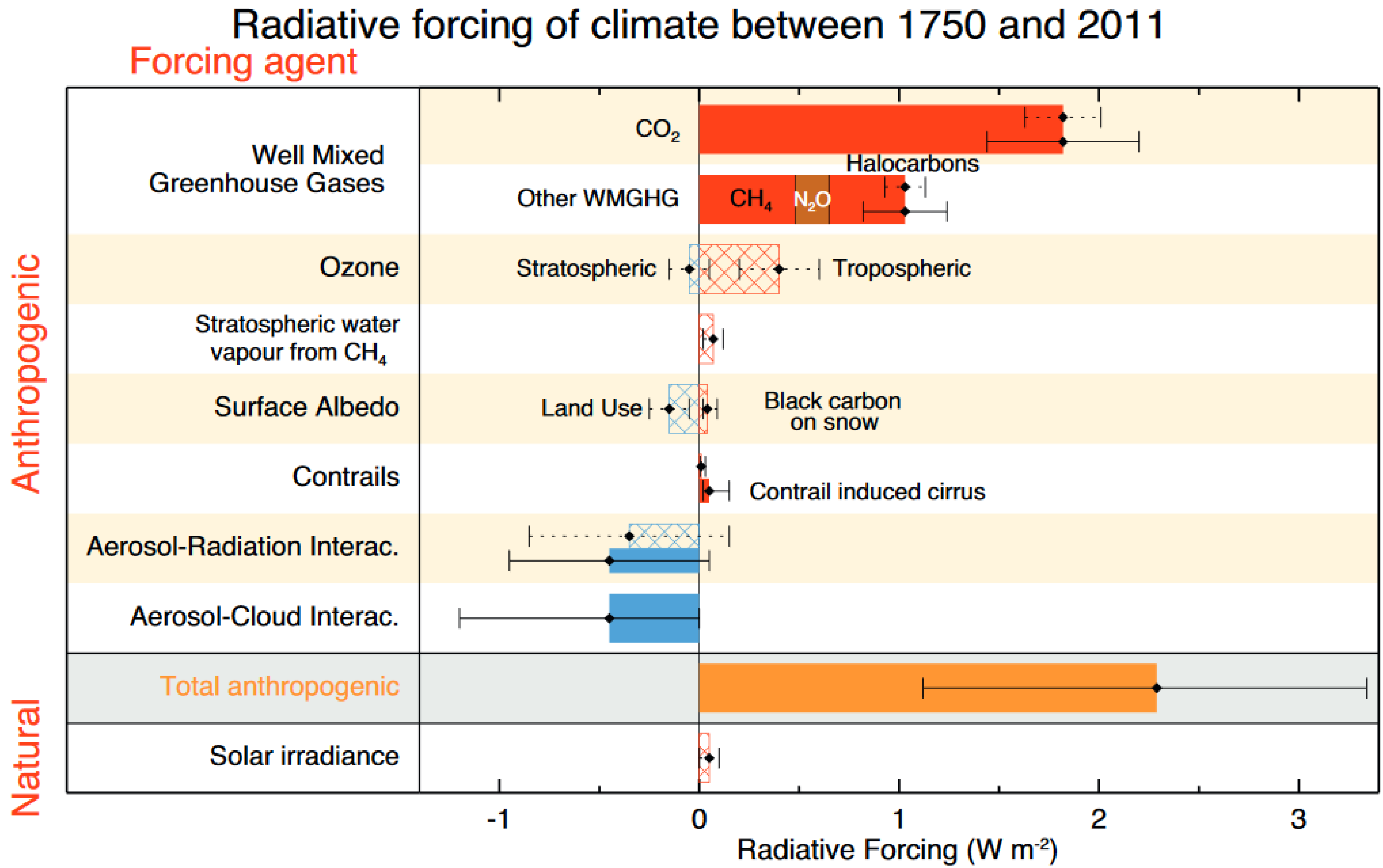
Source: NASA, Climate Kids



Source: IPCC, 2014



Source: IPCC, 2014

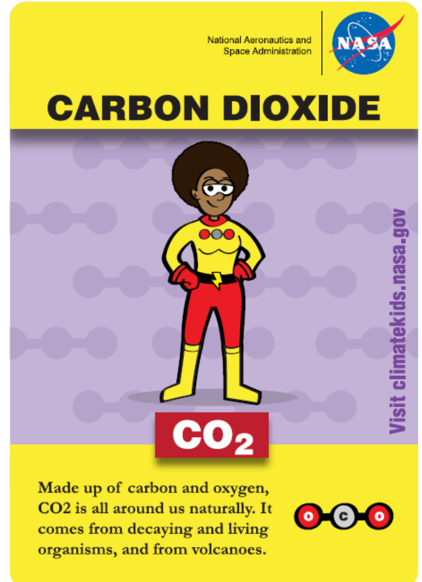


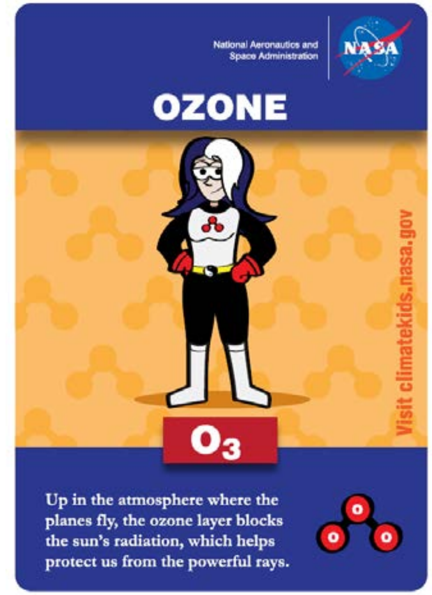
Source: IPCC, 2014

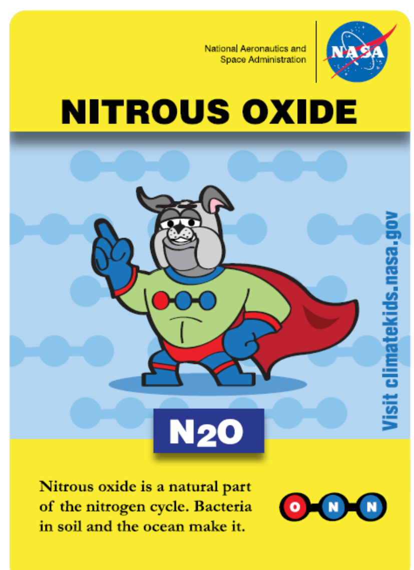
Greenhouse effect and greenhouse gases – good or bad?

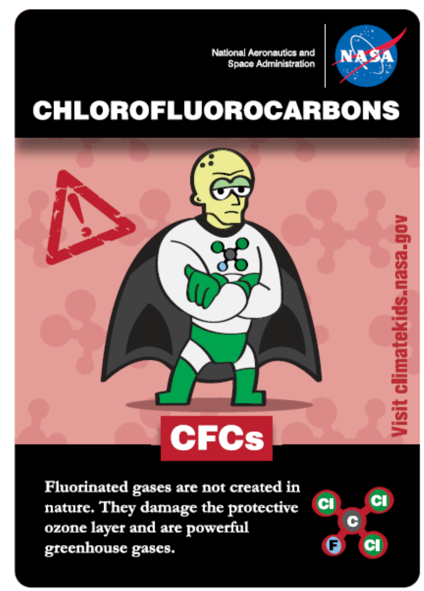
Without greenhouse effect, the Earth would be **extremely cold**.

Source: slideshare.net

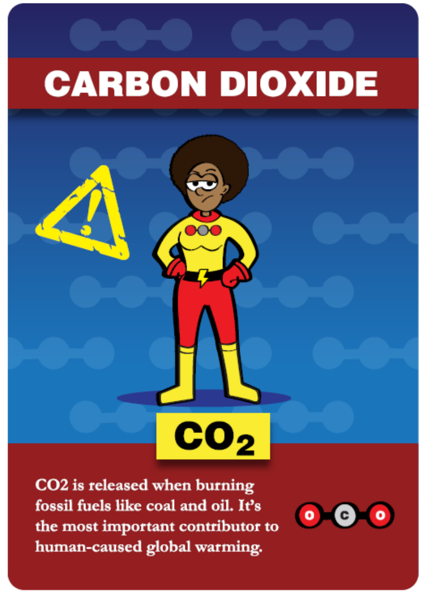


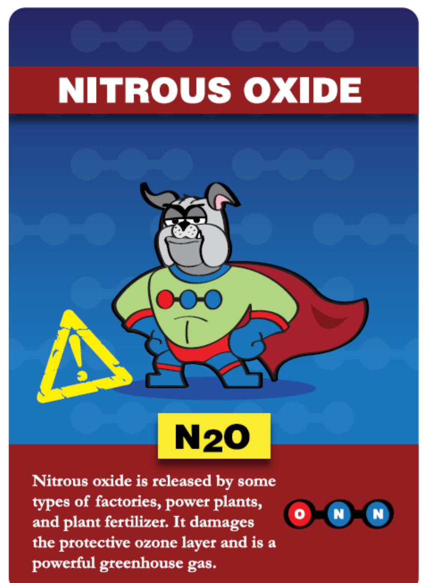






Source: NASA, Climate Kids

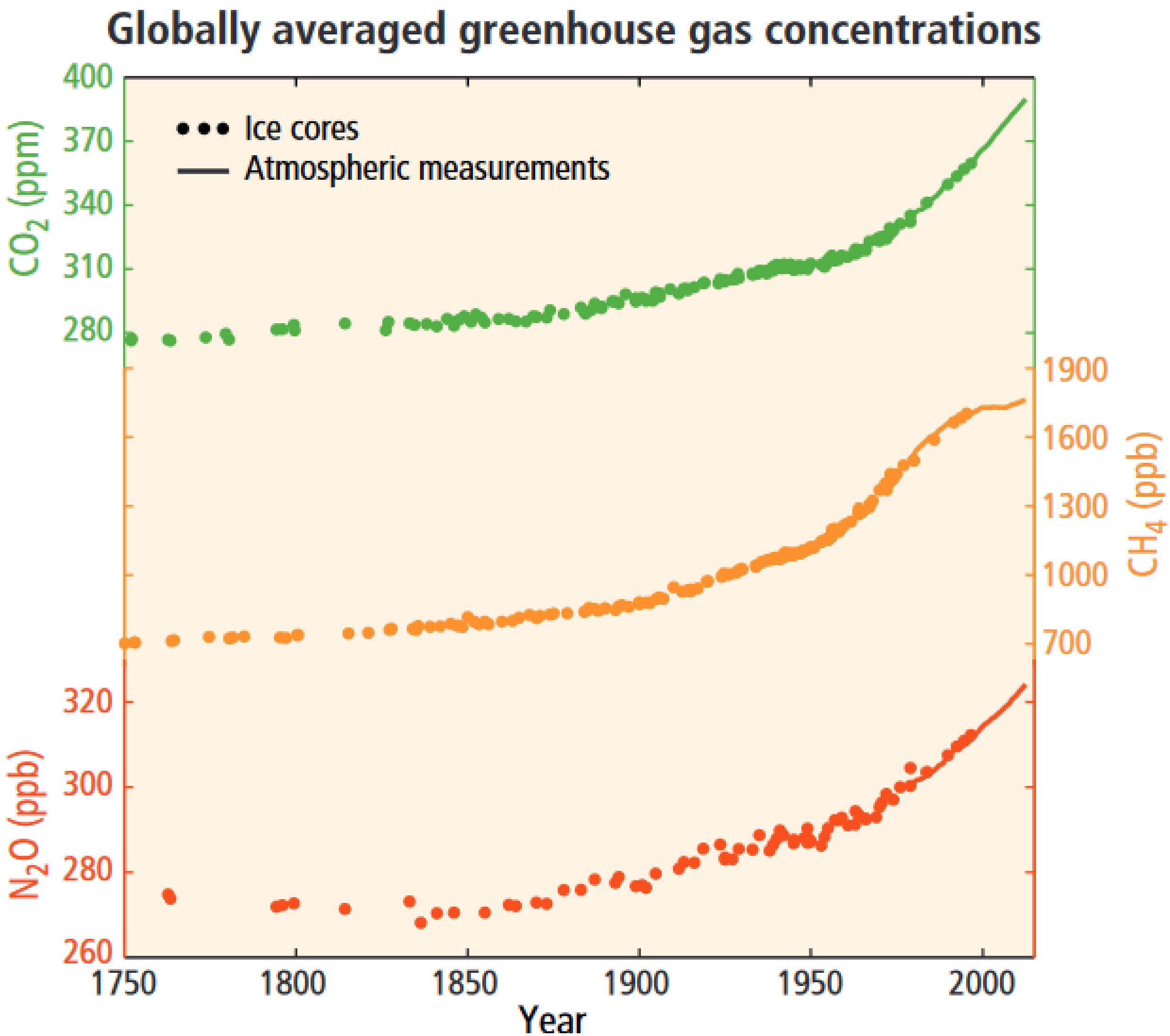




Source: NASA, Climate Kids

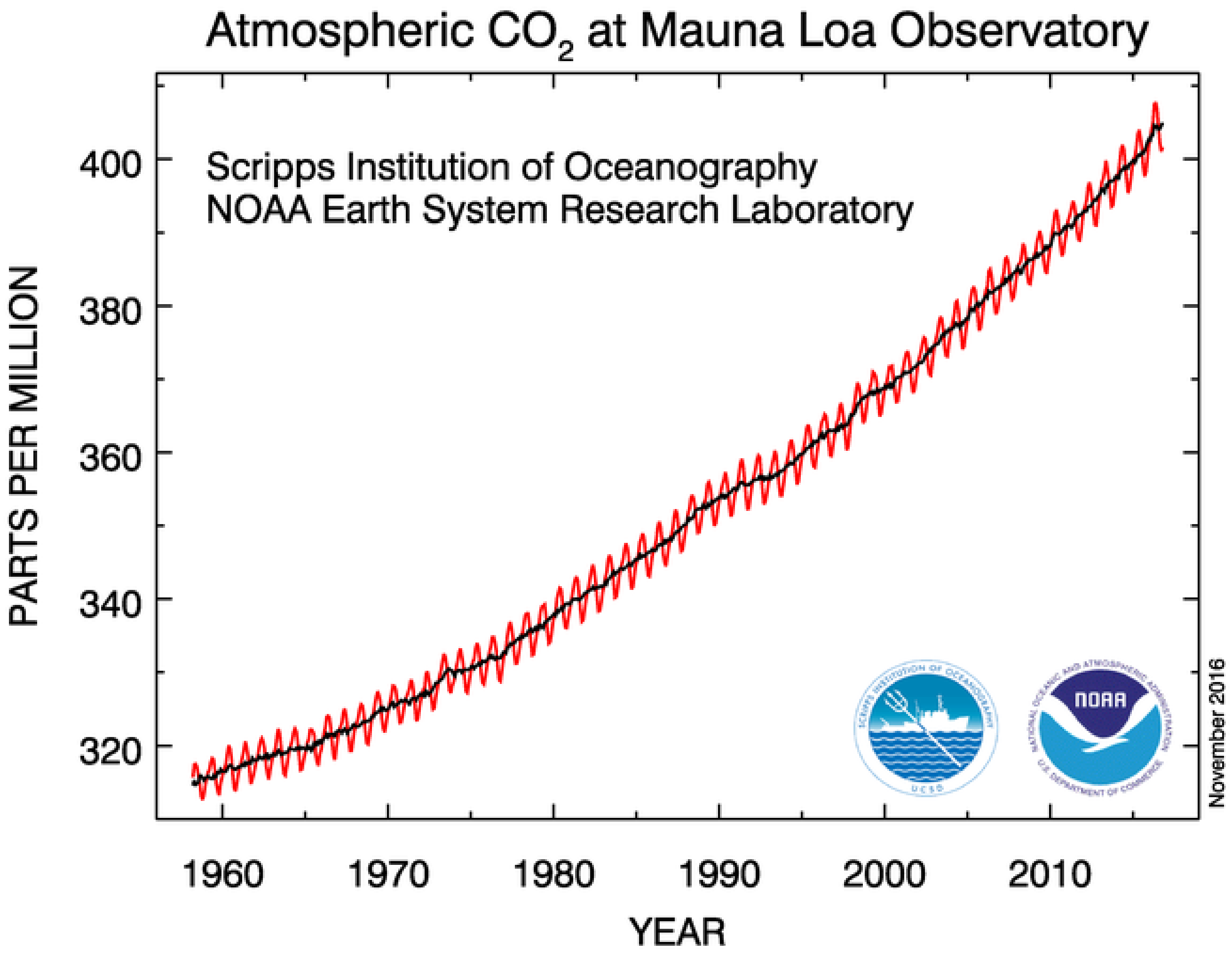
https://climatekids.nasa.gov/time-machine/

Source: NASA, Climate Kids



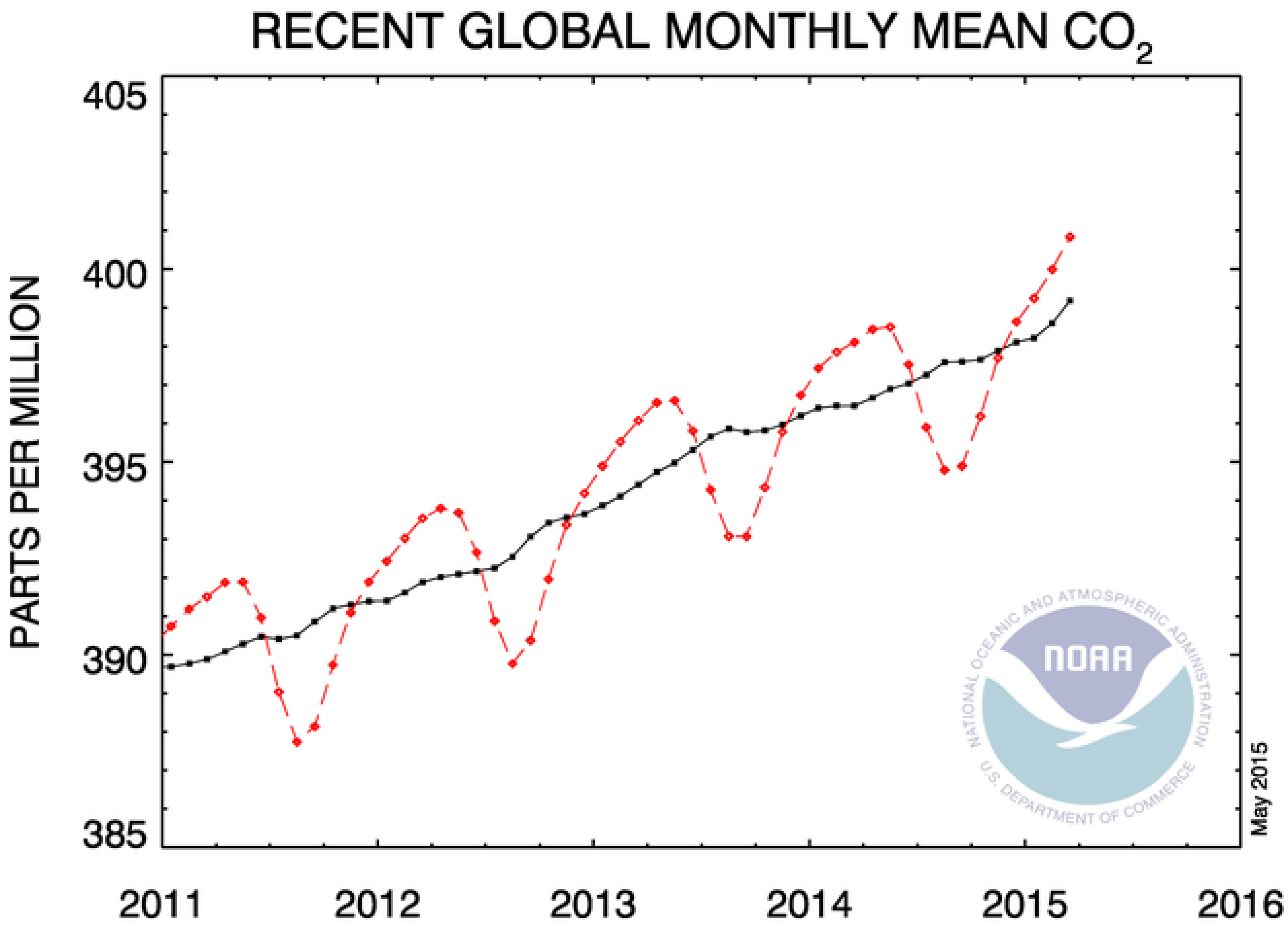
dots – data from ice cores
lines – direct measurements

Source: IPCC, 2014



Atmospheric CO_2 at Mauna Loa Observatory
Scripps Institution of Oceanography
NOAA Earth System Research Laboratory
PARTS PER MILLION
400
380
360
340
320
1960
1970
1980
1990
2000
2010
YEAR
November 2016

Source: NOAA



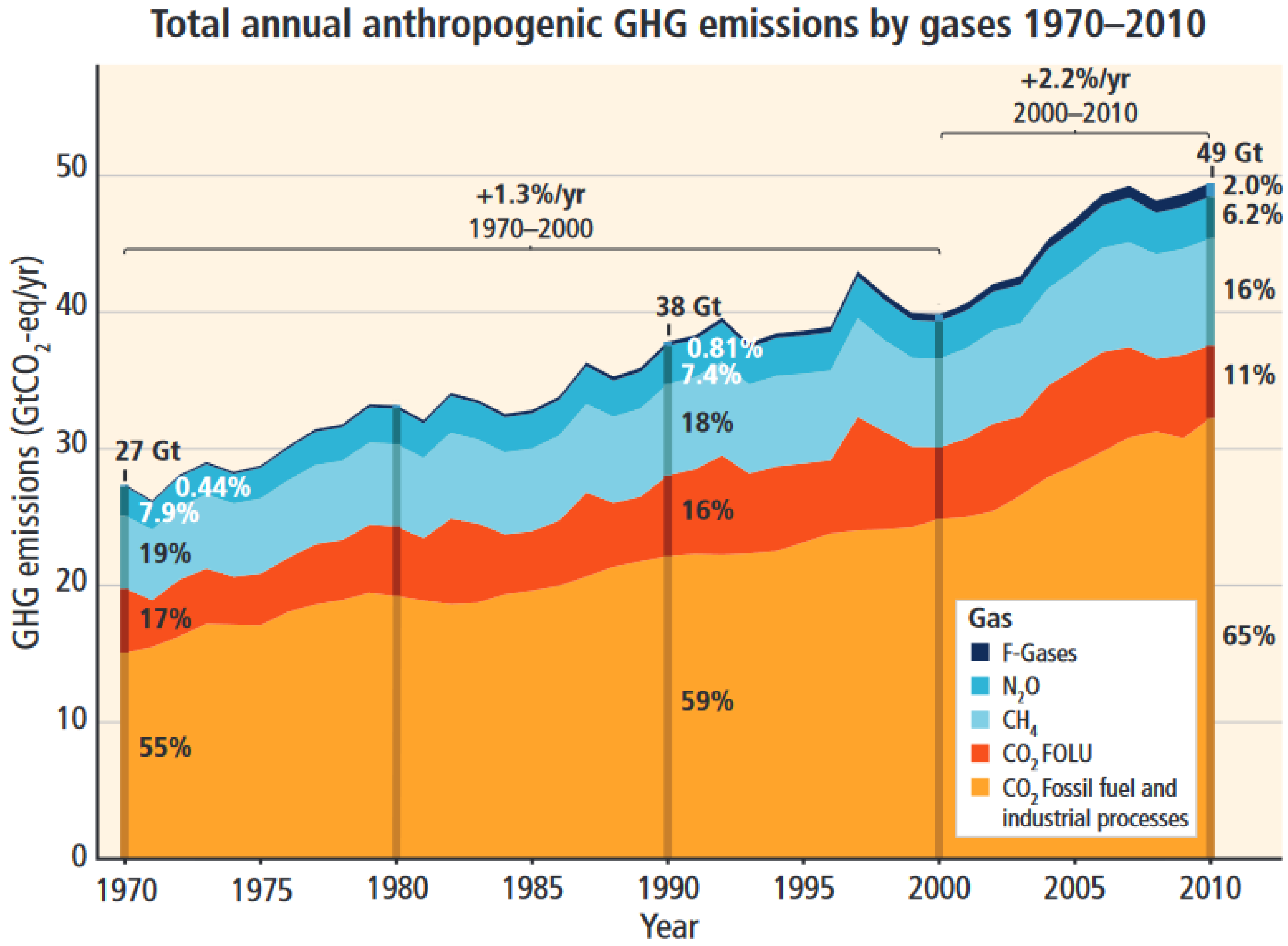
Detailed analysis show that the slope increases

Source: NOAA

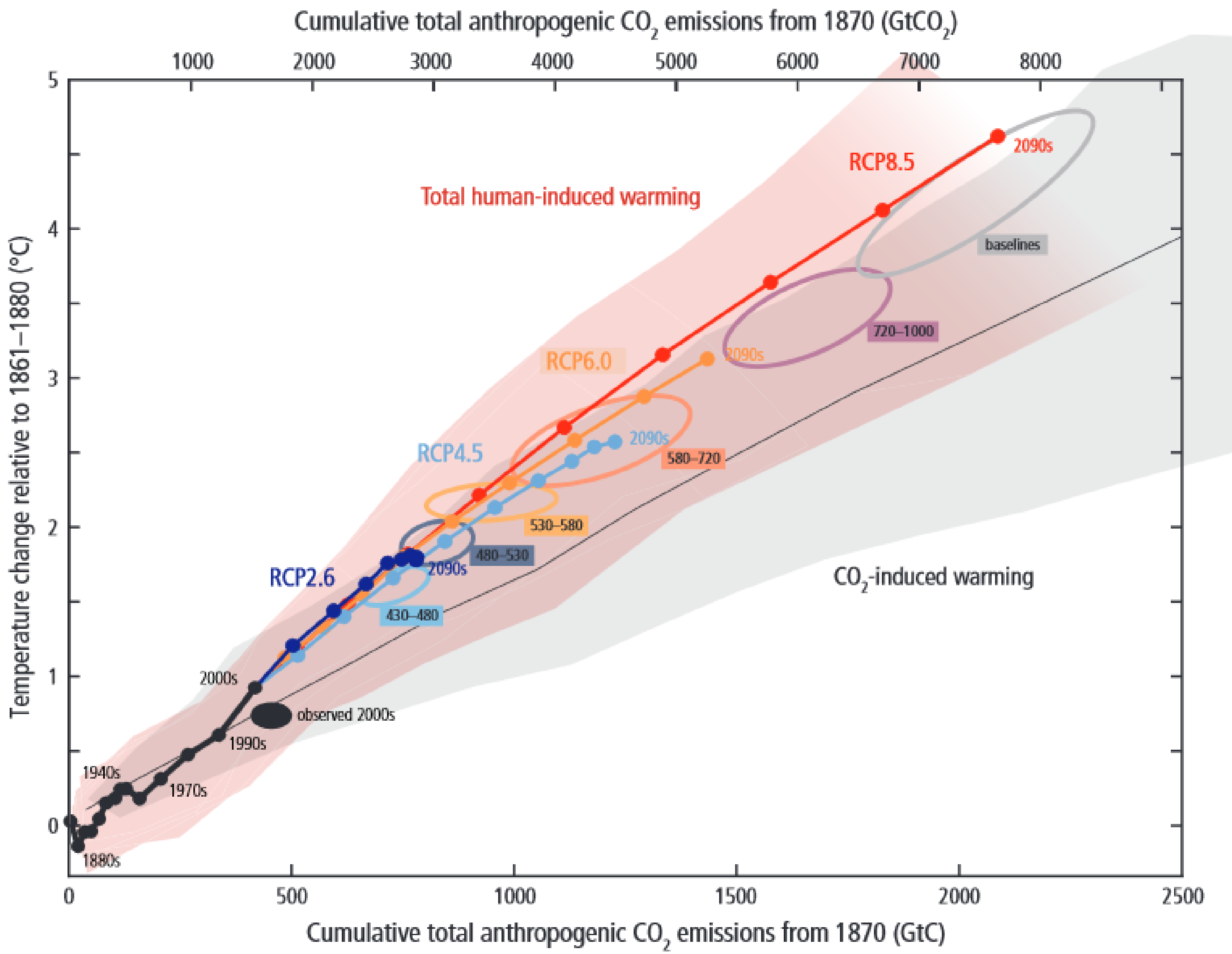
https://www.youtube.com/watch?v=x1SgmFa0r04

https://www.youtube.com/watch?v=SHzRBMBVu-4

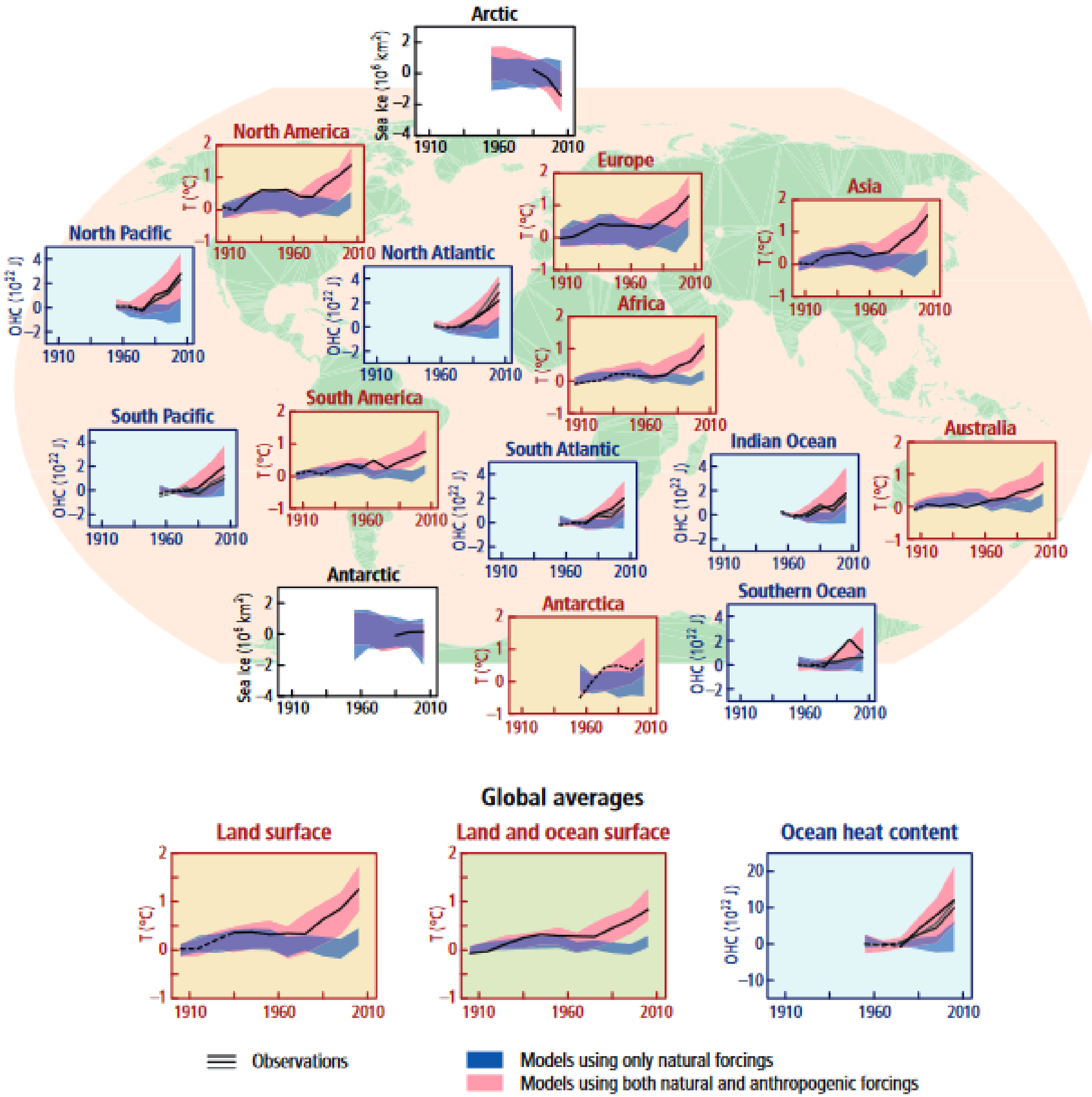
Source: NASA



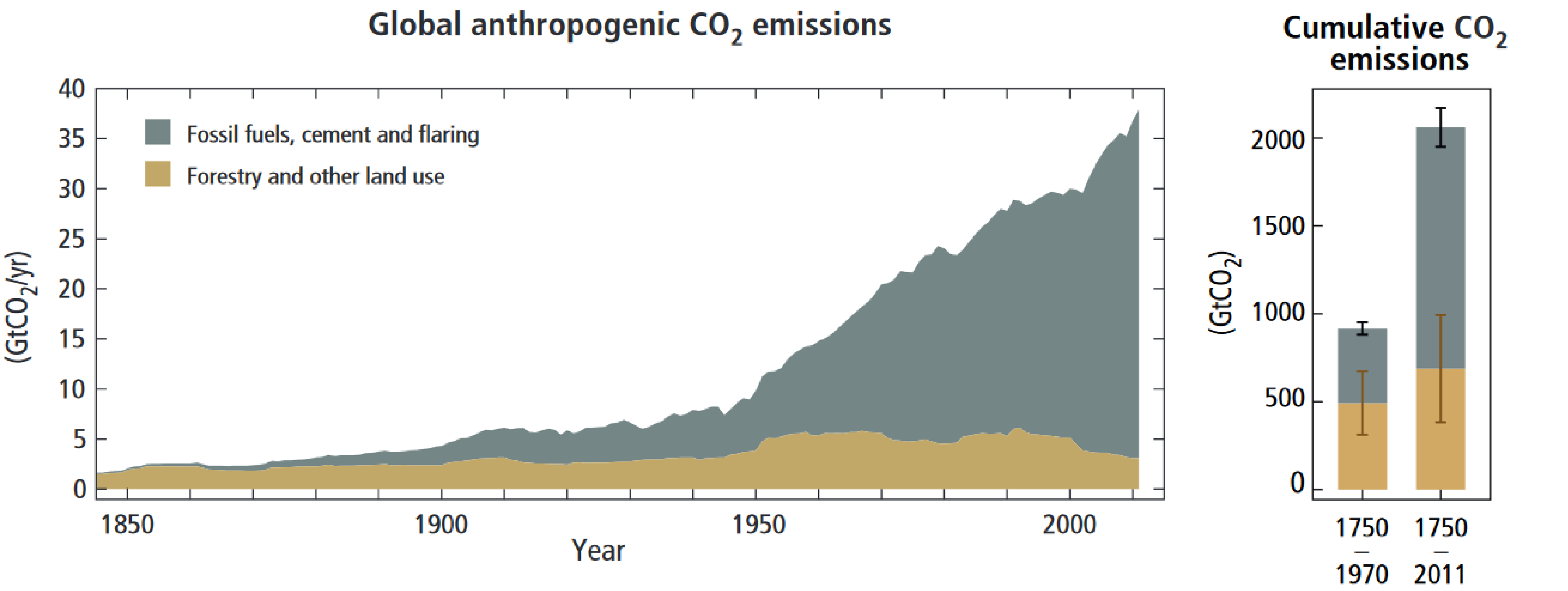
Source: IPCC, 2014



Source: IPCC, 2014



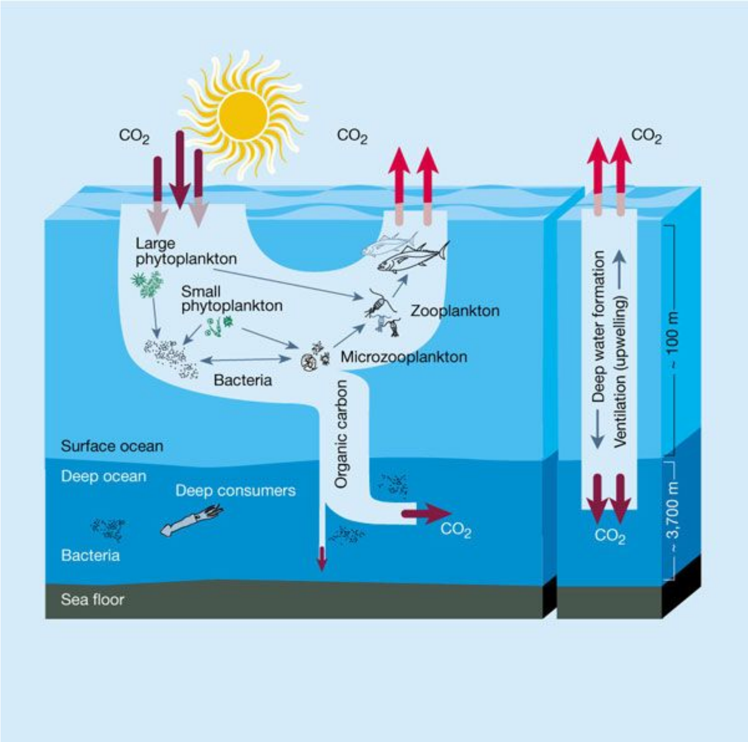
Source: IPCC, 2014



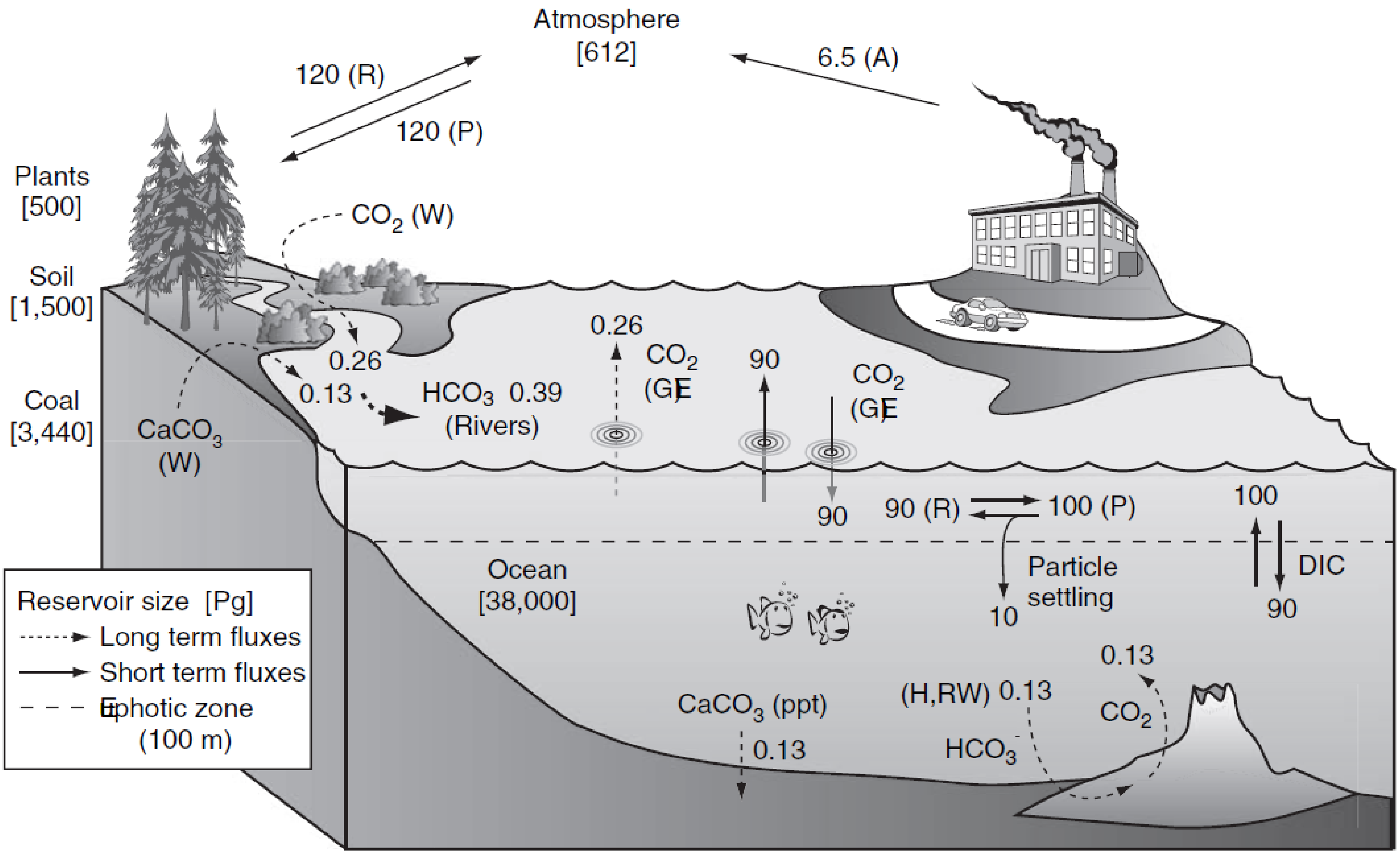
Source: IPCC, 2014

Outline:

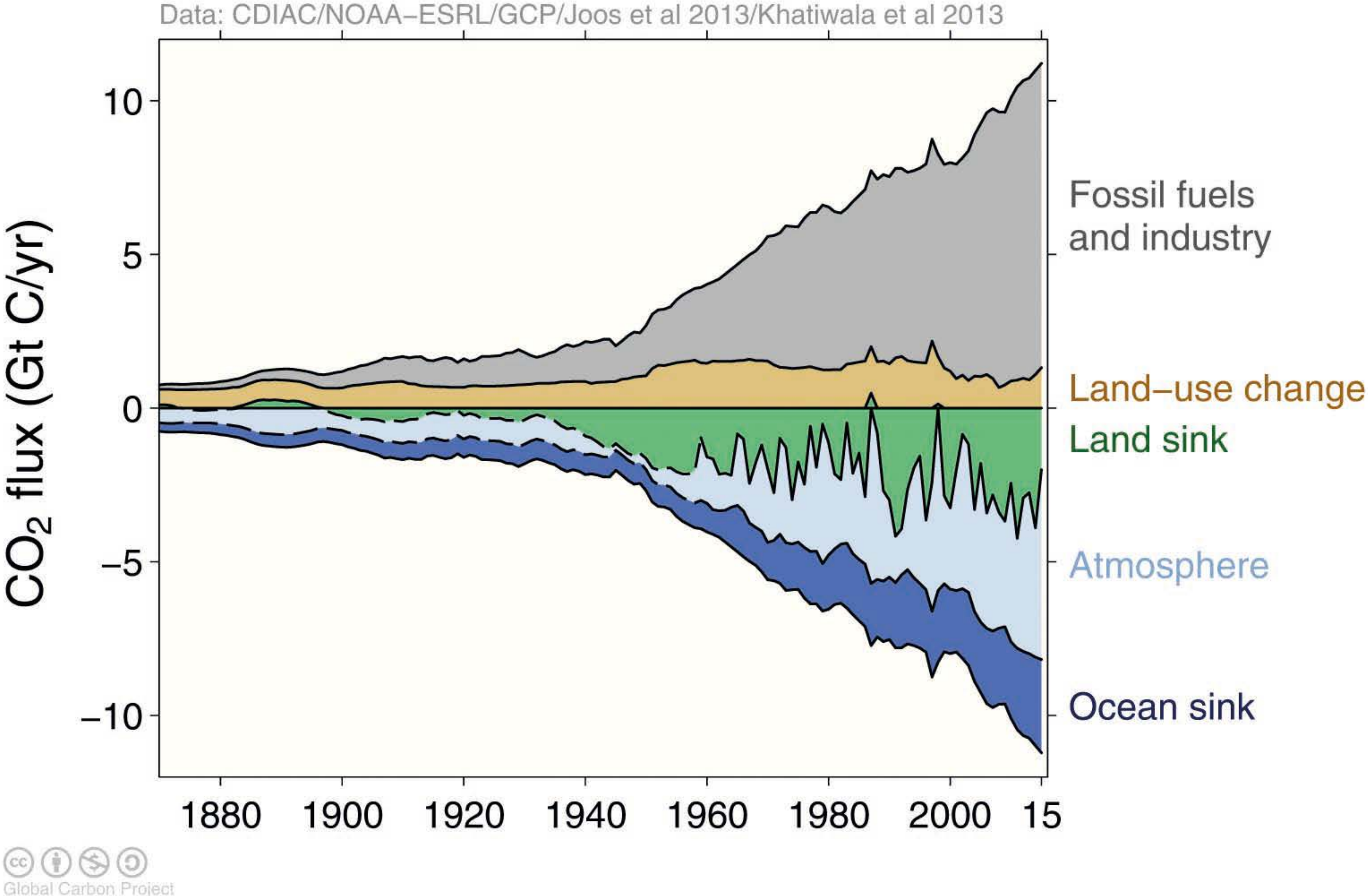
I. Carbon – the chemical element conditioning climate
II. Role of marine environment in the carbon cycle
III. Marine CO_2 system and ocean acidification
IV. Peculiarities of the Baltic Sea



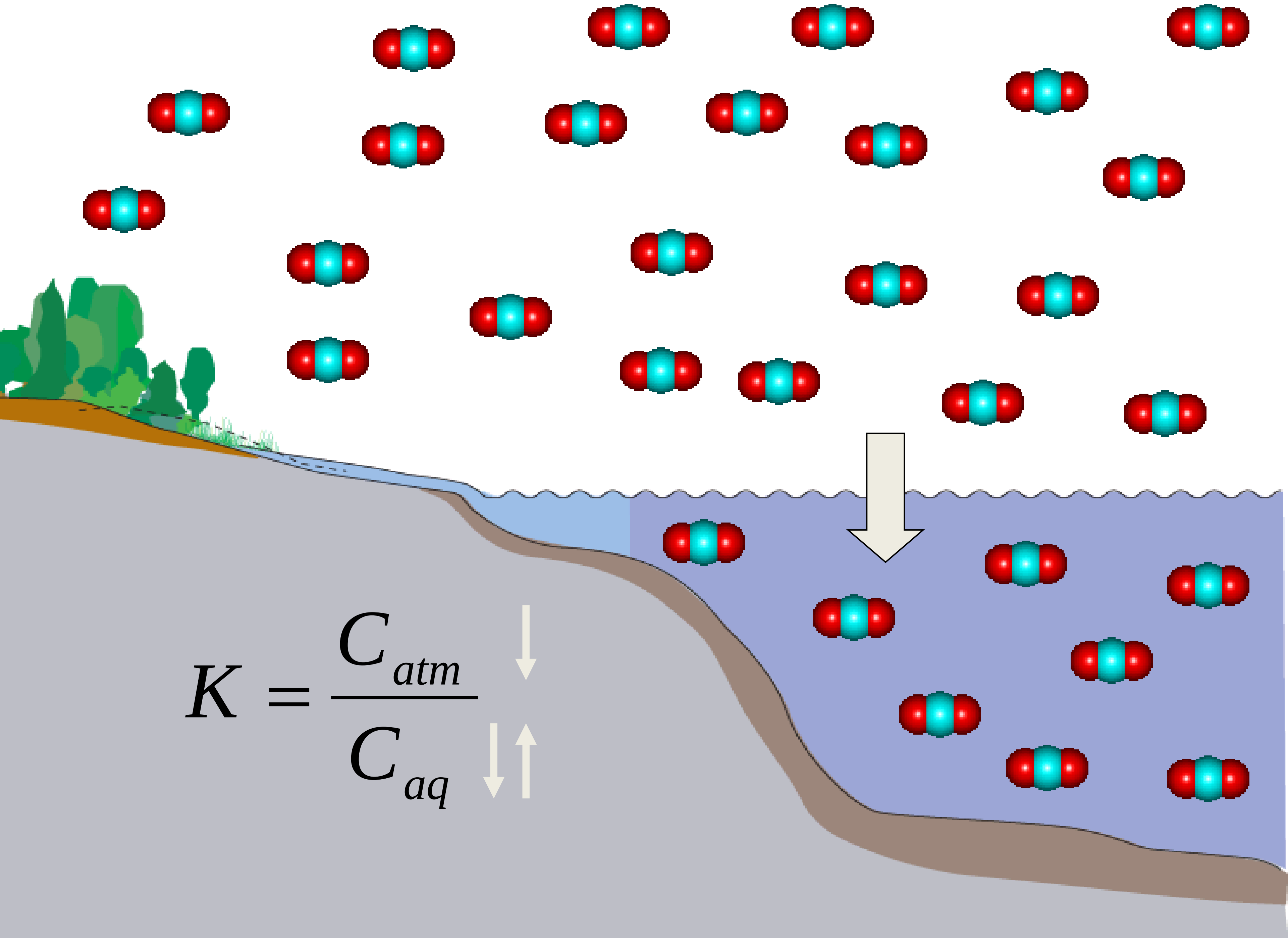
Source: Chisholm, 2000



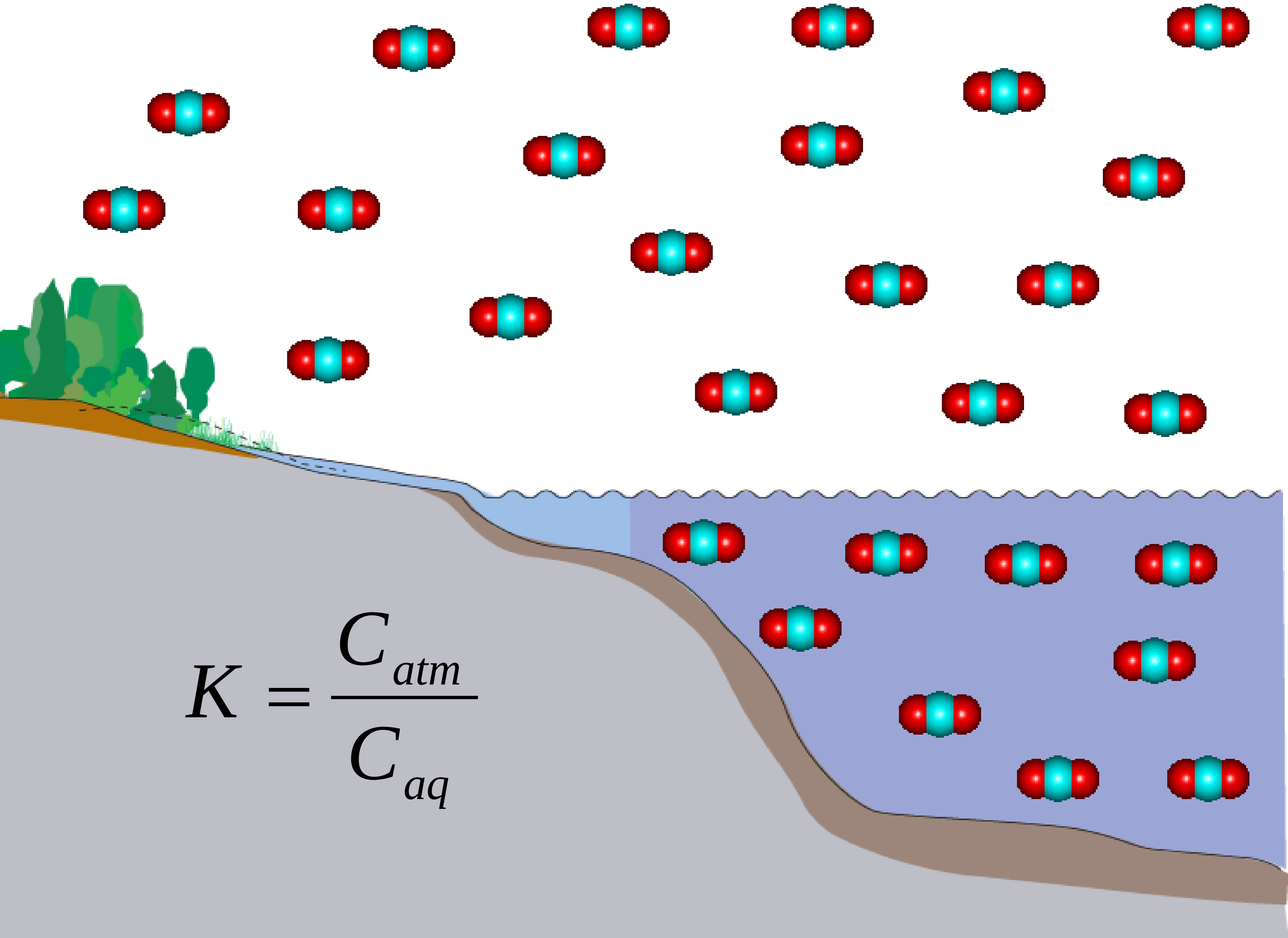
Source: Emerson & Hedges, 2008

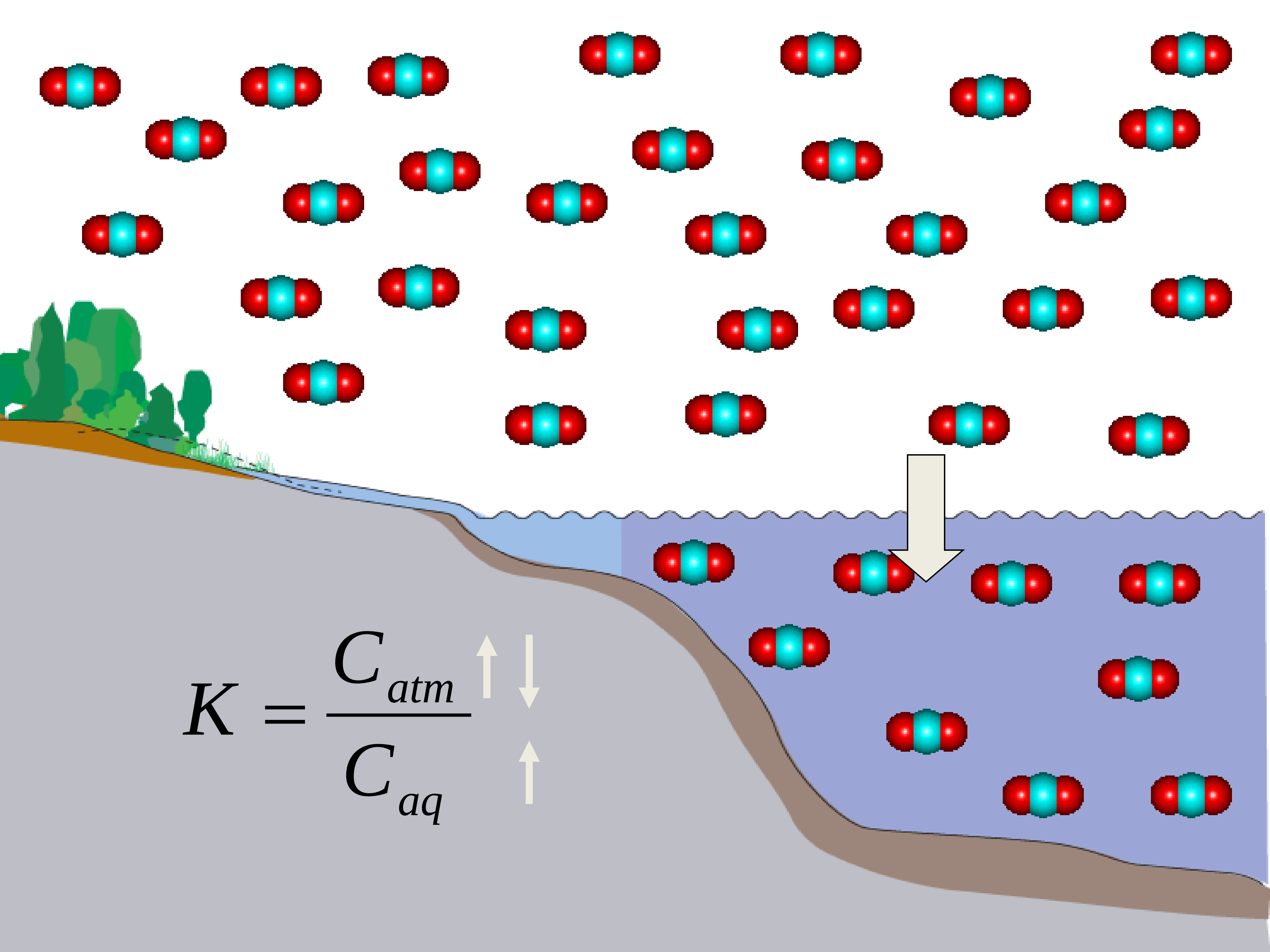


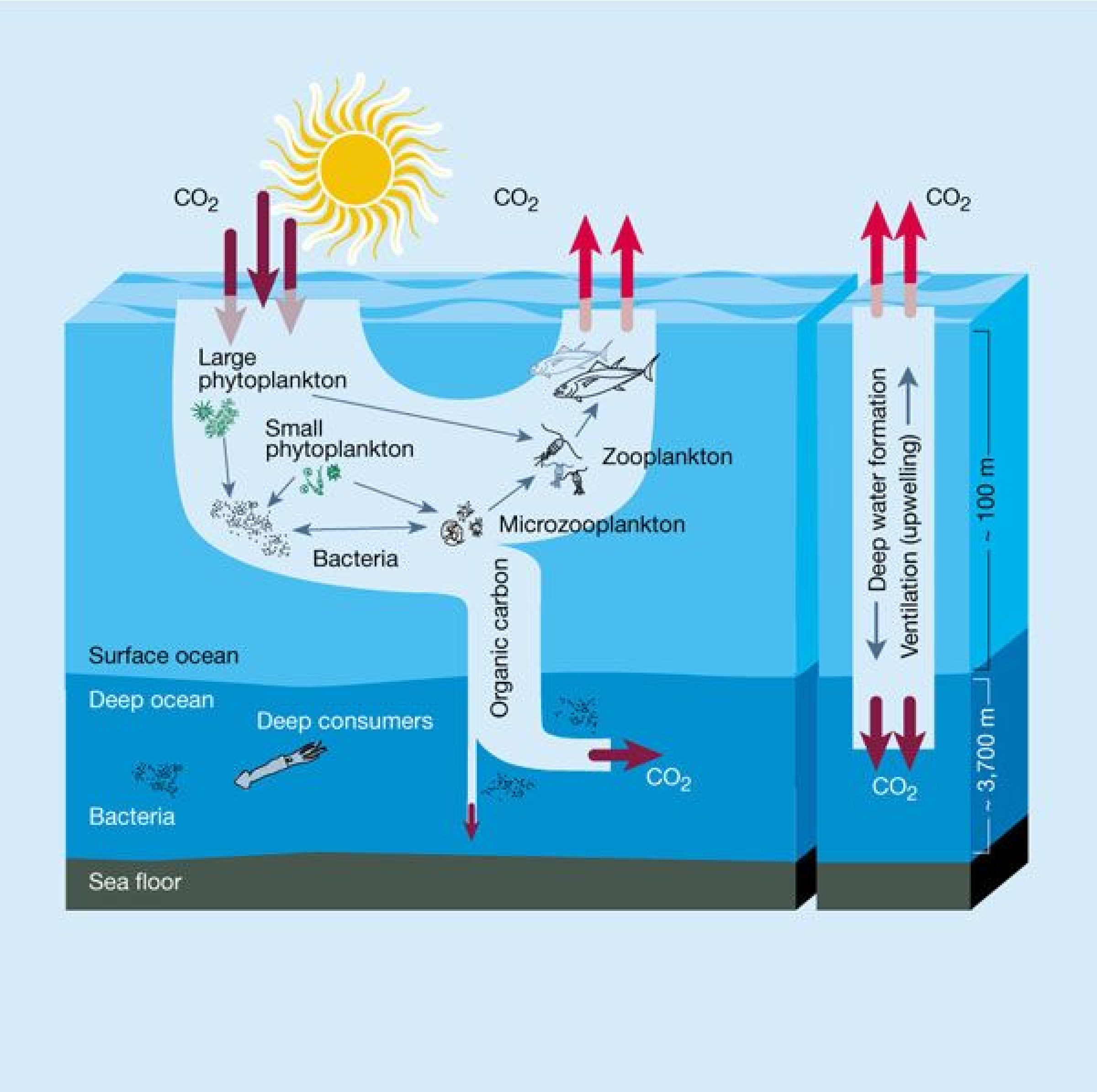
Source: WMO, 2017



$$K = \frac{C_{atm}}{C_{aq}}$$


$$K = \frac{C_{atm}}{C_{aq}}$$


$$K = \frac{C_{atm}}{C_{aq}}$$



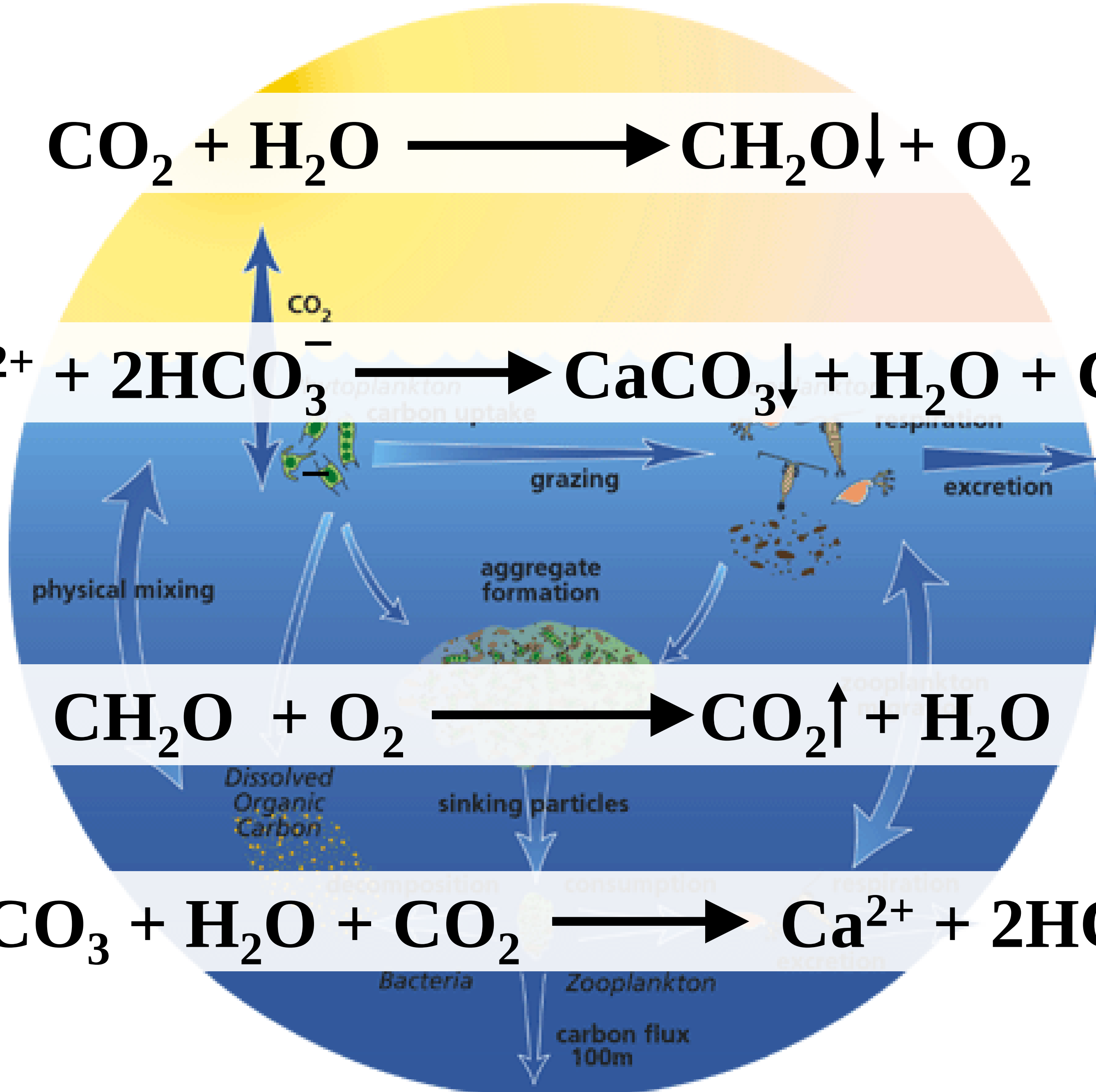
Source: Chisholm, 2000

$$CO_2 + H_2O \longrightarrow CH_2O\downarrow + O_2$$

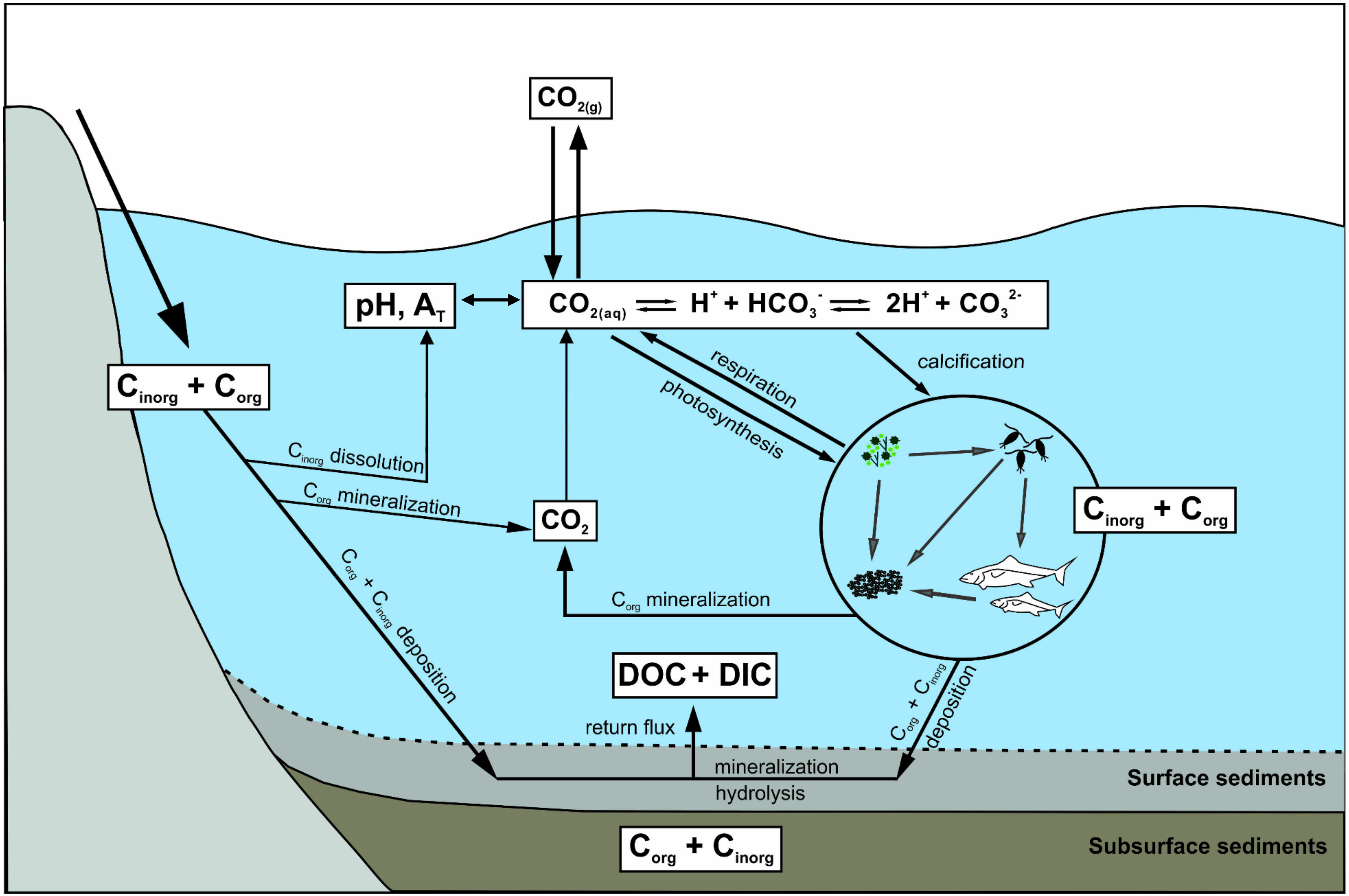
$$Ca^{2+} + 2HCO_3^- \longrightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$$

$$CH_2O + O_2 \longrightarrow CO_2\uparrow + H_2O$$

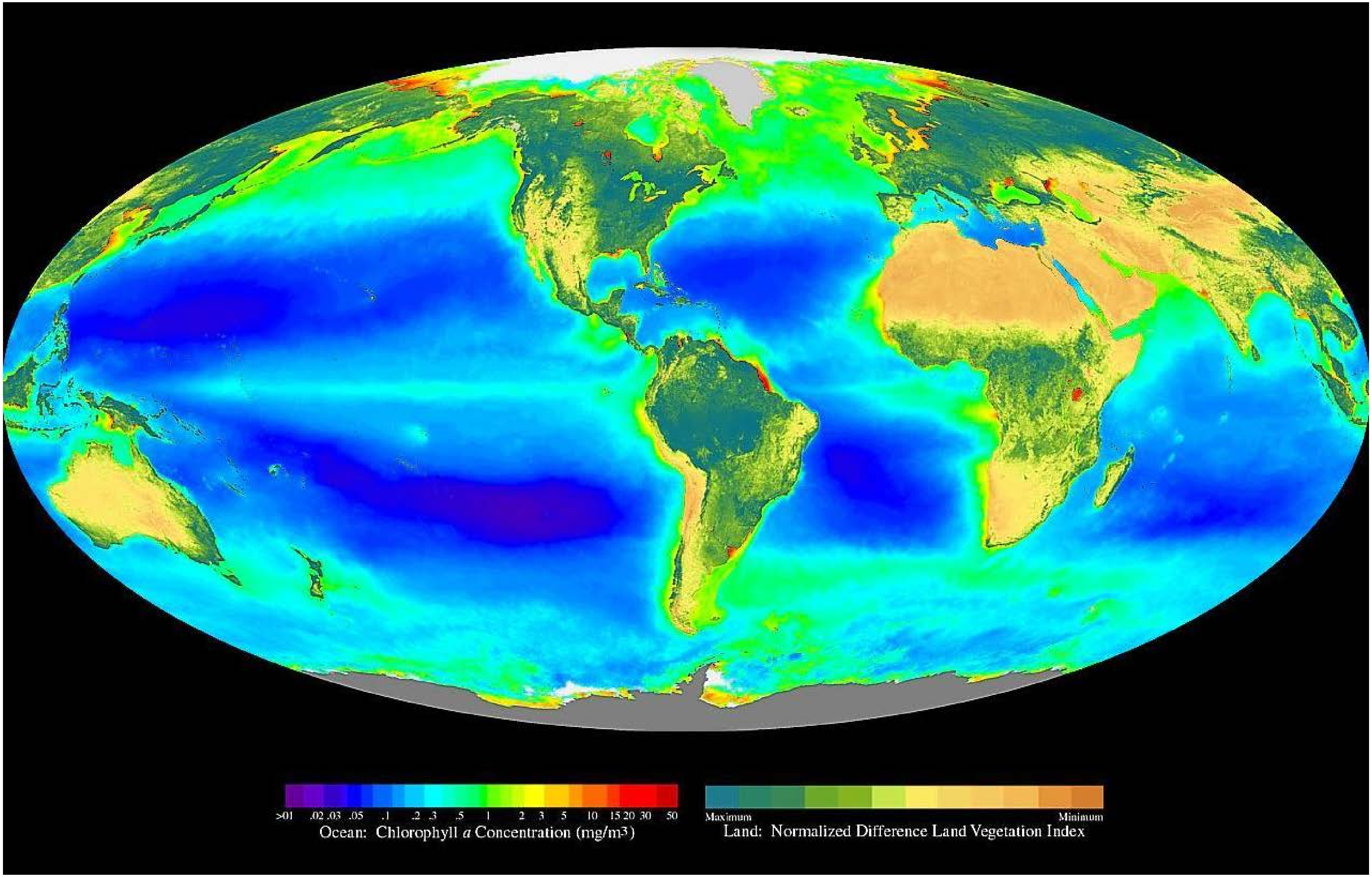
$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca^{2+} + 2HCO_3^-$$



Source: www.learner.org

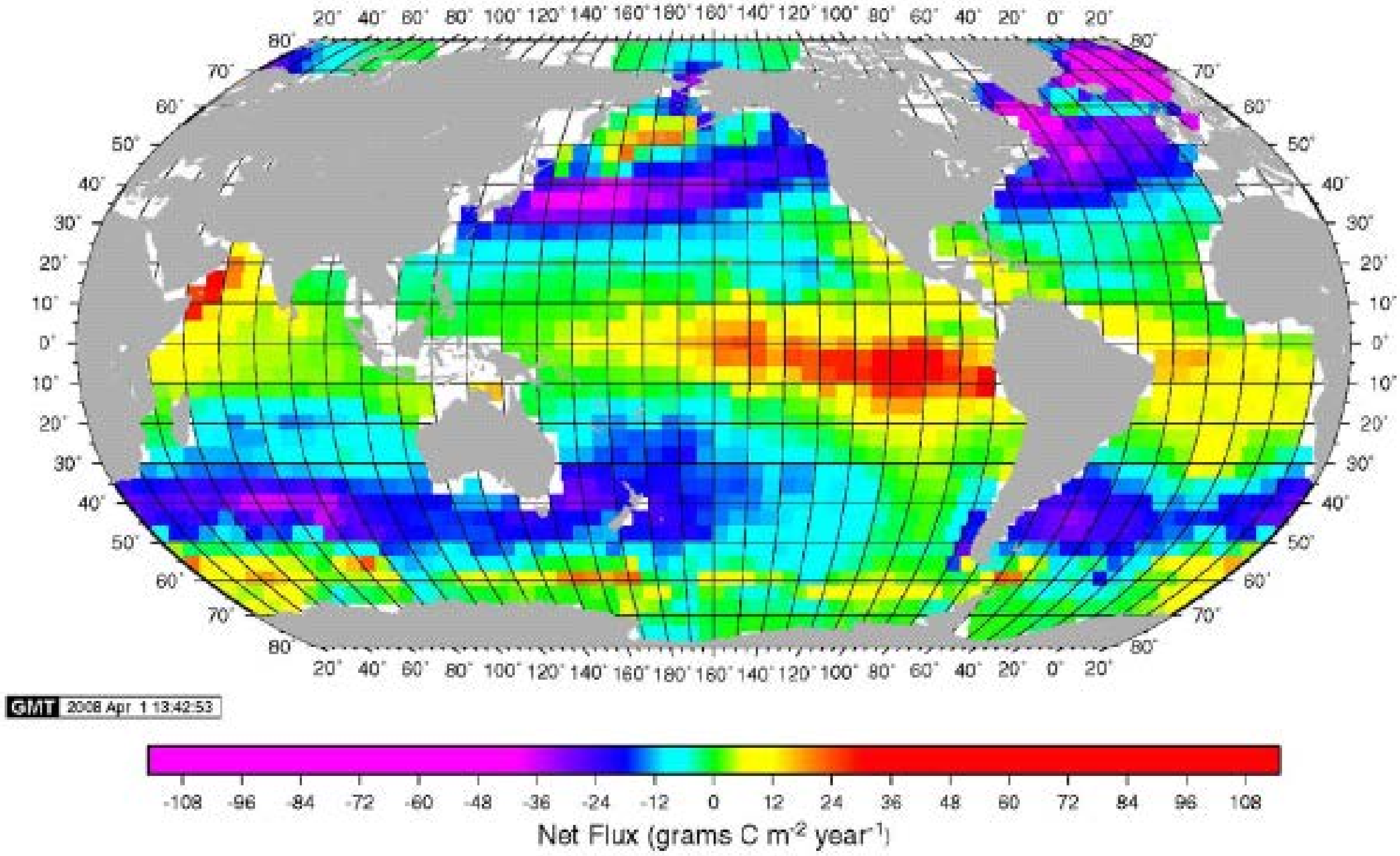


Source: K. Koziorowska

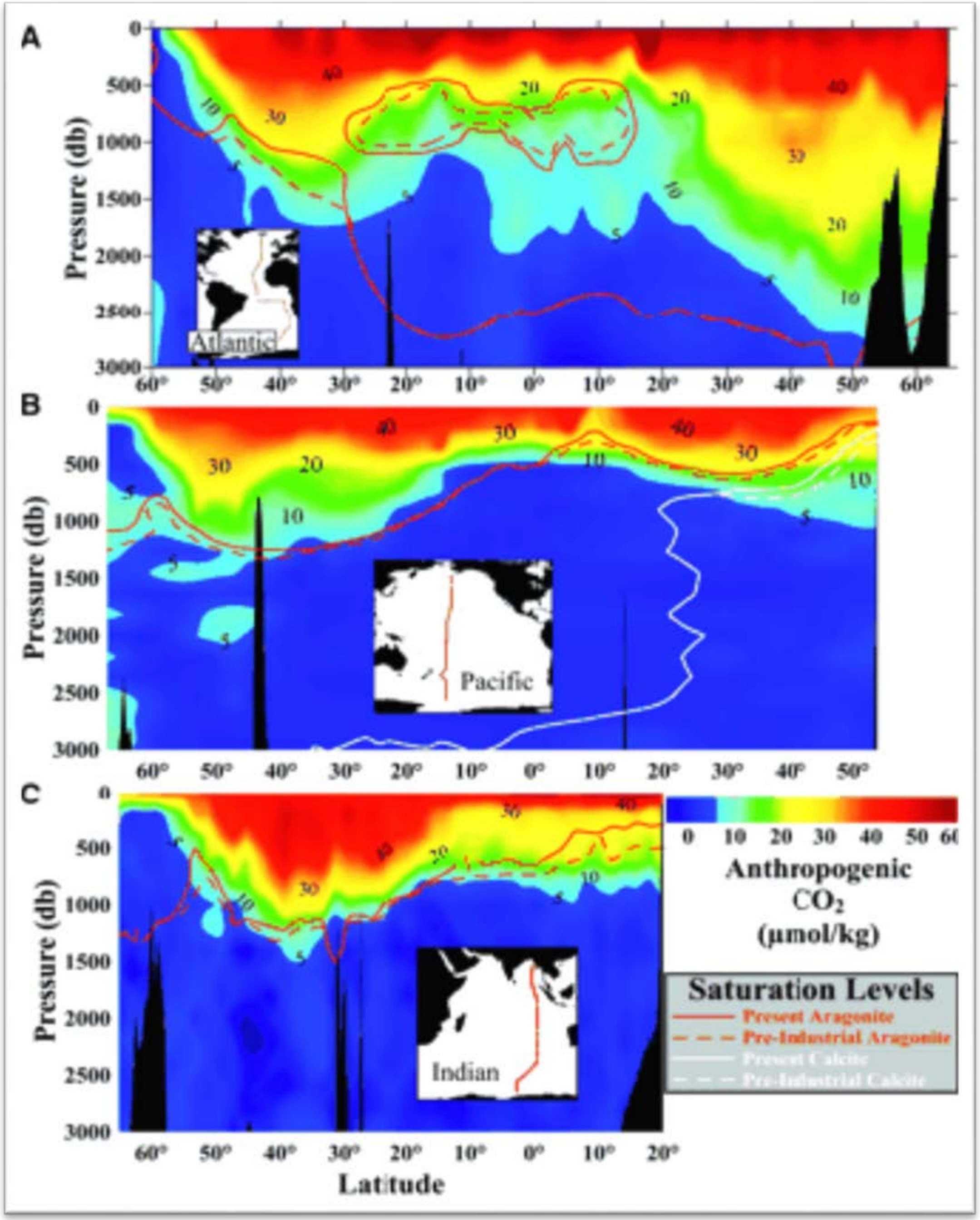

>01 .02 .03 .05 .1 .2 .3 .5 1 2 3 5 10 15 20 30 50
Ocean: Chlorophyll a Concentration (mg/m3)
Maximum
Minimum
Land: Normalized Difference Land Vegetation Index

Source: NASA

Oceans absorb globally 1,6±0,9 Pg C yr^{-1}

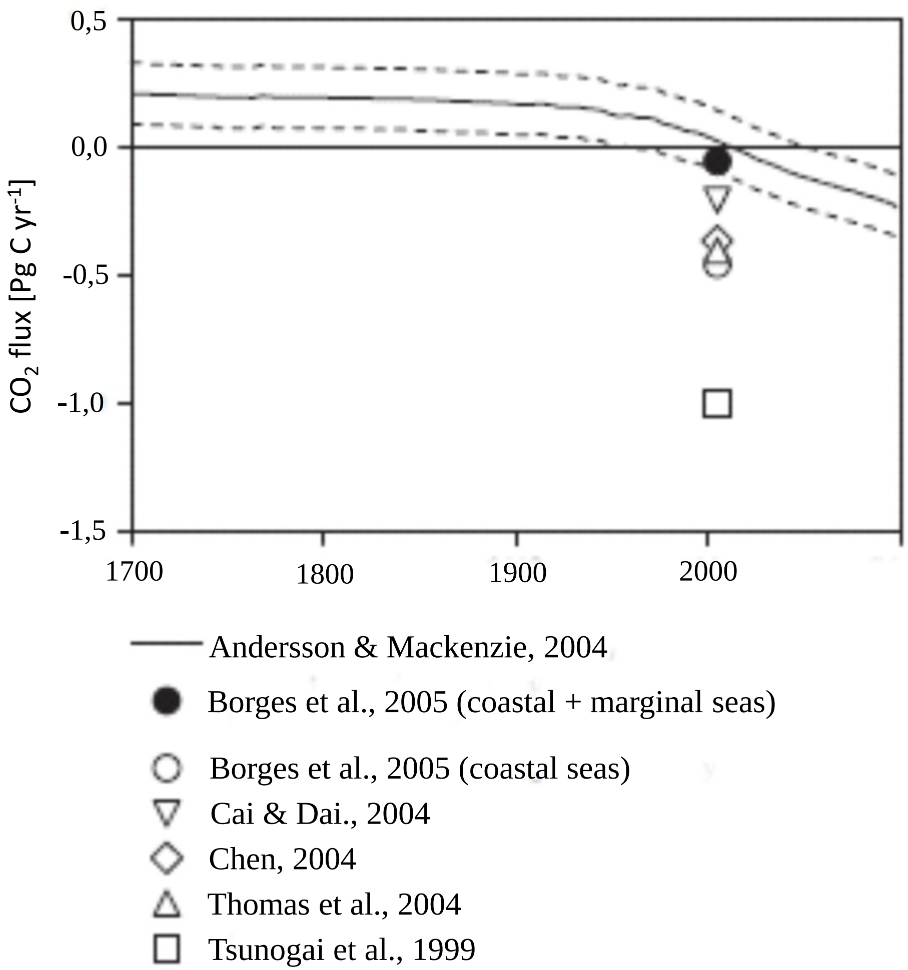


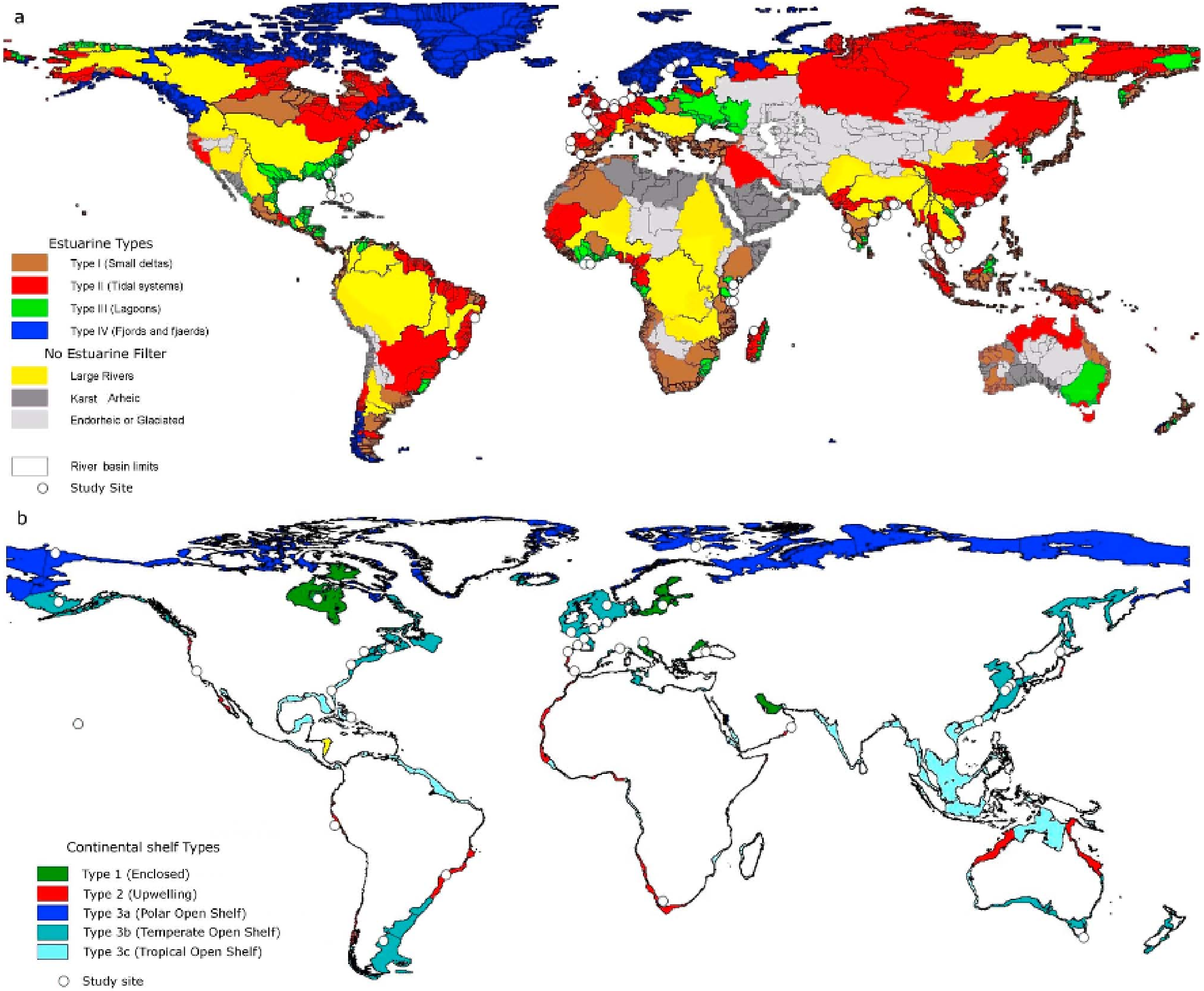
Source: Takahashi et al., 2009



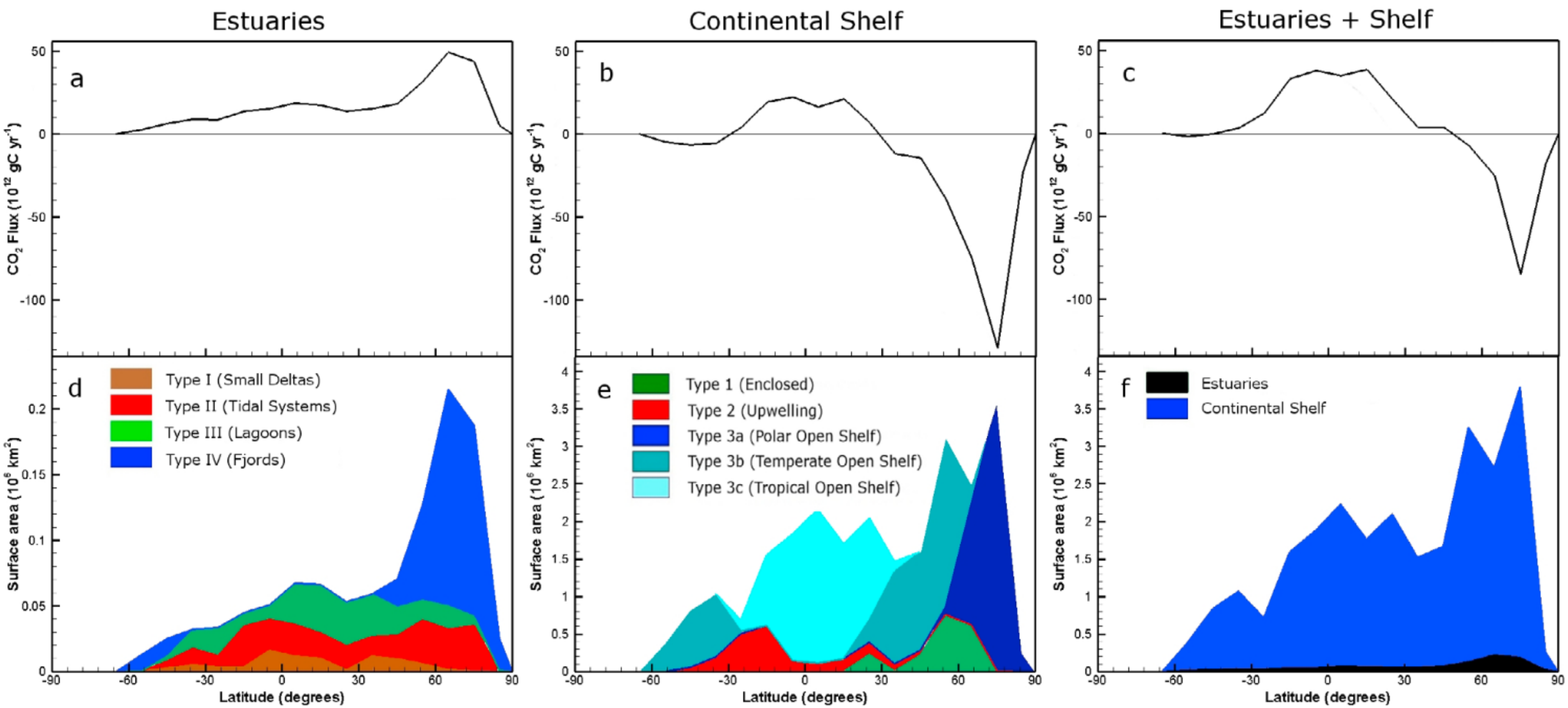
Source: Feely et al., 2004

Role of the shelf seas





Source: Laruelle et al., 2010



Source: Laruelle et al., 2010

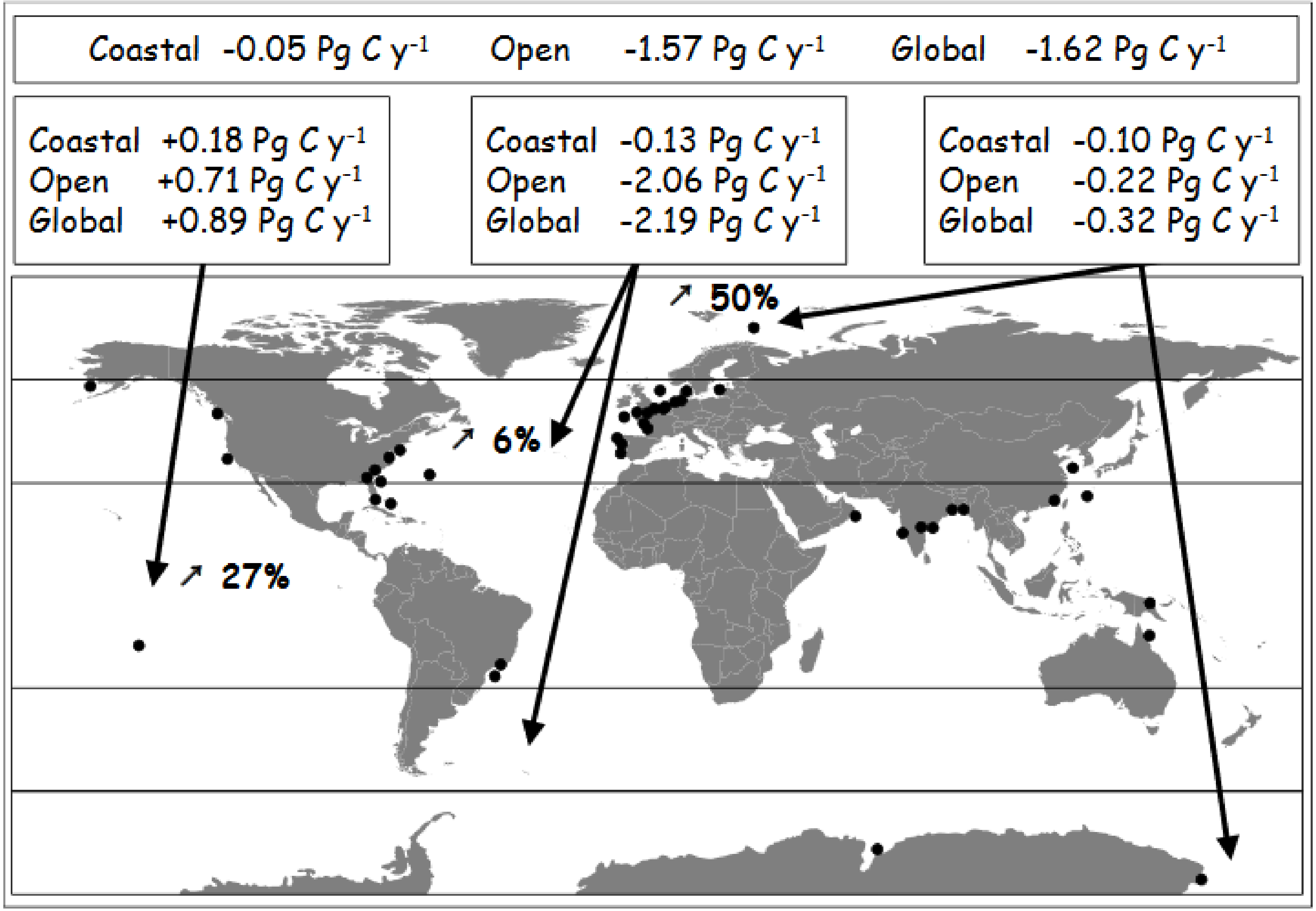
Table 1. Air-Water CO_2 Fluxes per Surface Area and Scaled Globally for Four Estuarine Types[a]

	Surface Area (10^6 km^2)	Air-Water CO_2 Flux (molC m^{-2} yr^{-1})	Air-Water CO_2 Flux (PgC yr^{-1})
Small deltas and estuaries (Type I)	0.084	25.7 ± 15.8	0.026 ± 0.016
Tidal systems and embayments (Type II)	0.276	28.5 ± 24.9	0.094 ± 0.082
Lagoons (Type III)	0.252	17.3 ± 16.6	0.052 ± 0.050
Fjords and fjärds (Type IV)	0.456	17.5 ± 14.0[b]	0.096 ± 0.077
Total	1.067	21.0 ± 17.6	0.268 ± 0.225

Table 2. Air-Water CO_2 Fluxes per Surface Area and Scaled Globally for Different Types of Continental Shelves Along Three Climatic Zones[a]

	Surface Area (10^6 km^2)	Air-Water CO_2 Flux (molC m^{-2} yr^{-1})	Air-Water CO_2 Flux (PgC yr^{-1})
Polar (>60°)			
Enclosed	0.189	−0.8 ± 1.1	−0.002 ± 0.003
Open Shelf	5.477	−3.3 ± 1.7	−0.216 ± 0.111
Upwelling Pacific	0.086	3.2 ± 2.4	0.003 ± 0.002
Sub-total	5.752	−3.1 ± 1.7	−0.214 ± 0.116
Temperate (30°–60°)			
Enclosed	1.410	−0.8 ± 1.1	−0.014 ± 0.019
Open Shelf	7.170	−1.0 ± 1.0	−0.086 ± 0.087
Upwelling Pacific	0.293	3.2 ± 2.4	0.011 ± 0.008
Upwelling Atlantic	0.086	−1.6 ± 1.0	−0.002 ± 0.001
Upwelling Indian	0.123	0.9 ± 1.2[b]	0.001 ± 0.002
Sub-total	9.082	−0.8 ± 1.1	−0.090 ± 0.117
Tropical (0–30°)			
Enclosed	0.231	−0.8 ± 1.1	−0.002 ± 0.003
Open Shelf	7.909	0.9 ± 1.0	0.083 ± 0.097
Upwelling Pacific	0.515	3.2 ± 2.4	0.020 ± 0.015
Upwelling Atlantic	0.715	−1.6 ± 1.0	−0.014 ± 0.009
Upwelling Indian	0.520	0.9 ± 1.2[b]	0.006 ± 0.008
Sub-total	9.890	0.8 ± 1.1	0.093 ± 0.131
Total	24.724	−0.7 ± 1.2	−0.211 ± 0.364

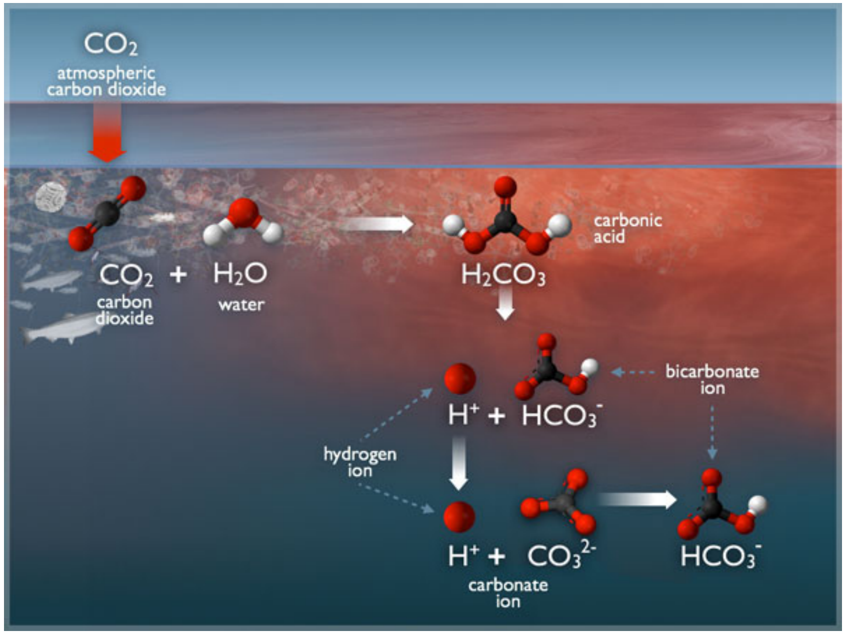
Source: Laruelle et al., 2010



Source: Borges & Delille

Outline:

I. Carbon – the chemical element conditioning climate
II. Role of marine environment in the carbon cycle
III. Marine CO_2 system and ocean acidification
IV. Peculiarities of the Baltic Sea



Source: www.whoi.edu

Seawater acid-base system

Measurable parameters:

- C_T – total CO_2 concentration (DIC)

  $C_T = [CO_2]^* + [HCO_3^-] + [CO_3^{2-}]$

- A_T – total alkalinity

  $A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + \ldots - [H^+] - \ldots$

- pCO_2 – CO_2 partial pressure

- pH –spectrophotometric measurement with m-cresol purple, total scale

  $pH_T = -\log ([H^+]_F + [HSO_4^-]) = -\log [H^+]_T$

It is possible to calculate 2 parameters when the following is known:

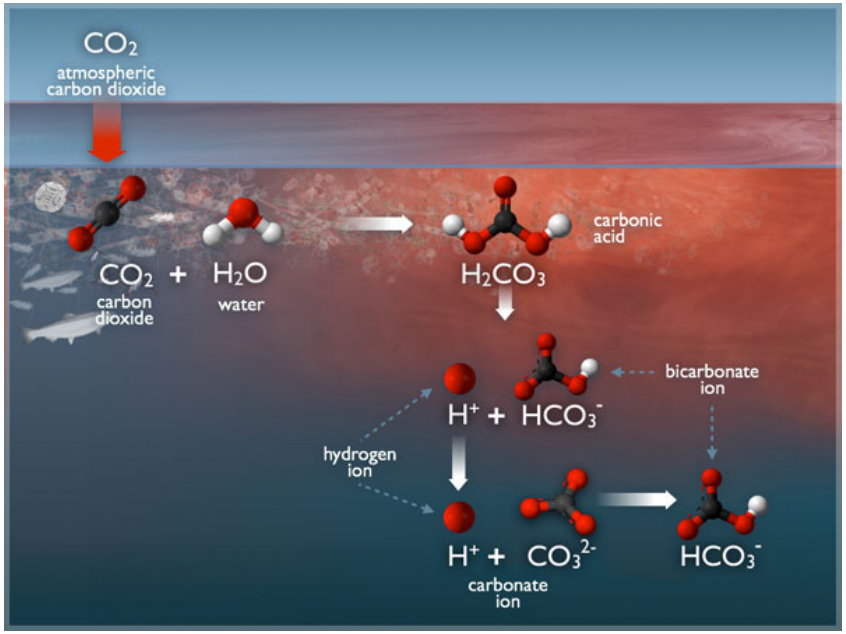
- other 2 parameters
- temperature & salinity
- equilibrium constants for each of the acid dissociation reactions
- total concentrations for each non-CO_2 substances

The pair used in the calculations:

- C_T & A_T – recommended, used in biogeochemical modelling

CO_2 system

$$CO_2 + H_2O \overset{k_0}{\longleftrightarrow} H_2CO_3 \overset{k_1}{\longleftrightarrow} HCO_3^- + H^+ \overset{k_2}{\longleftrightarrow} CO_3^{2-} + 2H^+$$



Source: www.whoi.edu

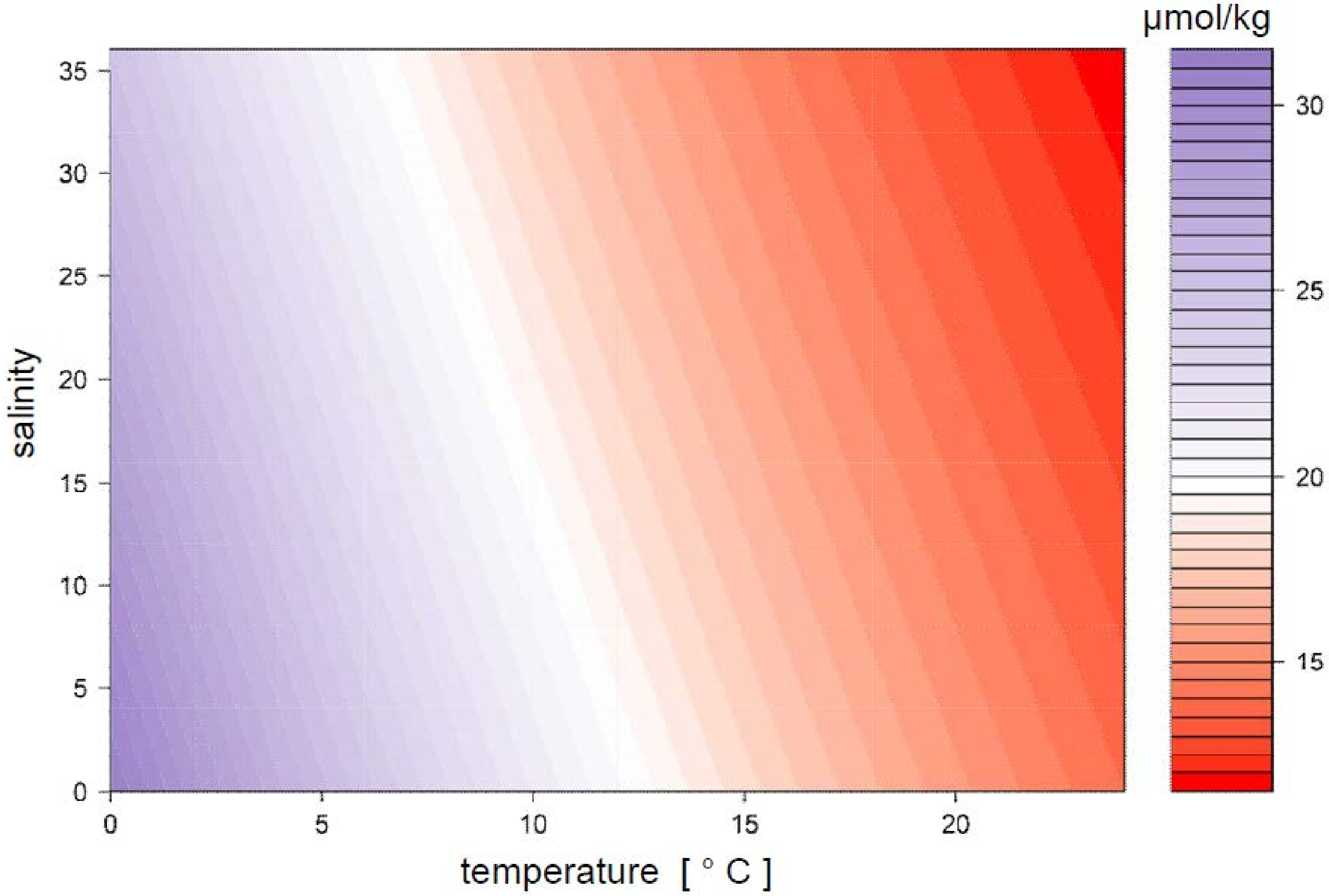
$$k_0 = \frac{[H_2CO_3]}{pCO_2}$$

$$k_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

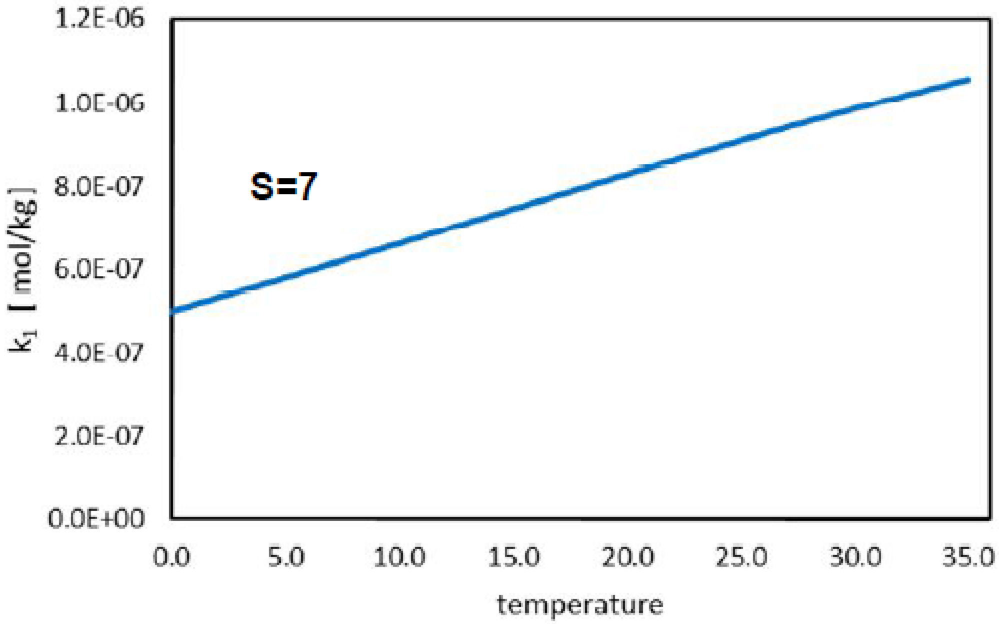
$$k_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

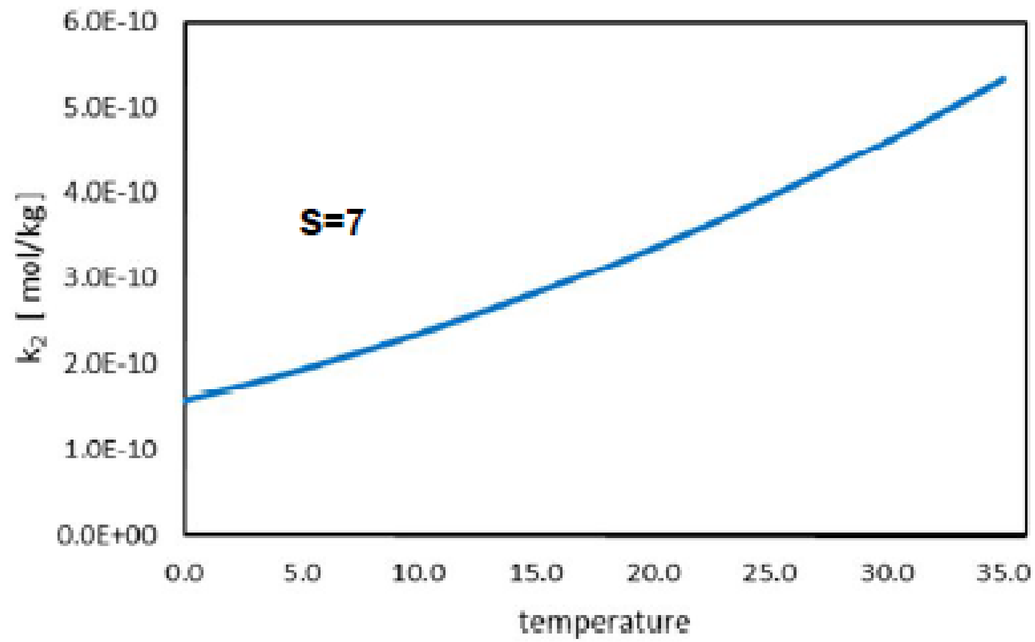
$$CO_2^* = CO_2 + H_2CO_3$$

Concentration of CO_2^* as a function of S and T



Source: B. Schneider





Source: B. Schneider

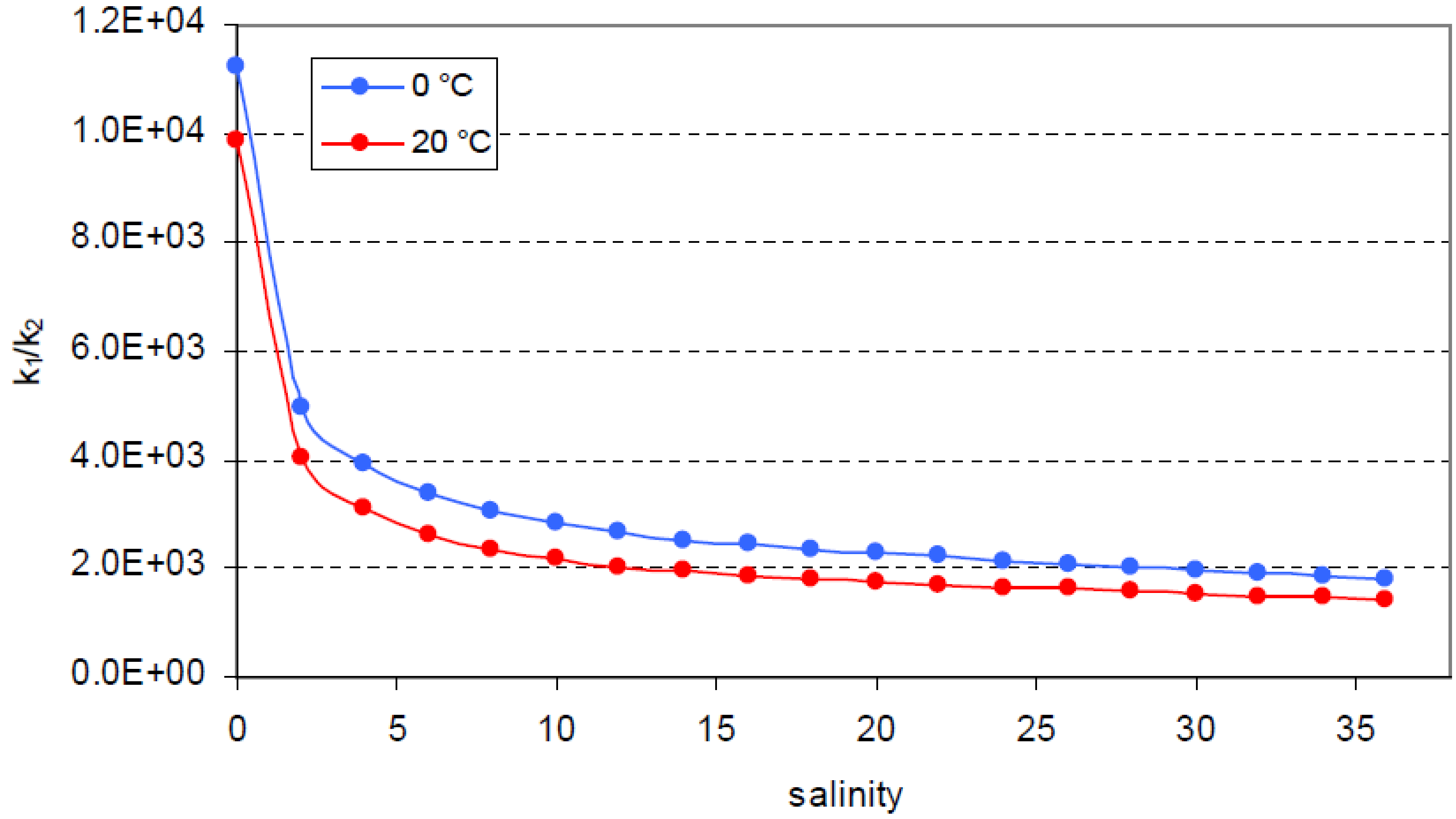
Buffer reaction

$$CO_2^* + CO_3^{2-} + H_2O \longleftrightarrow 2\,HCO_3^-$$

$$k_1 = \frac{[H^+][HCO_3^-]}{[CO_2^*]}$$

$$k_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

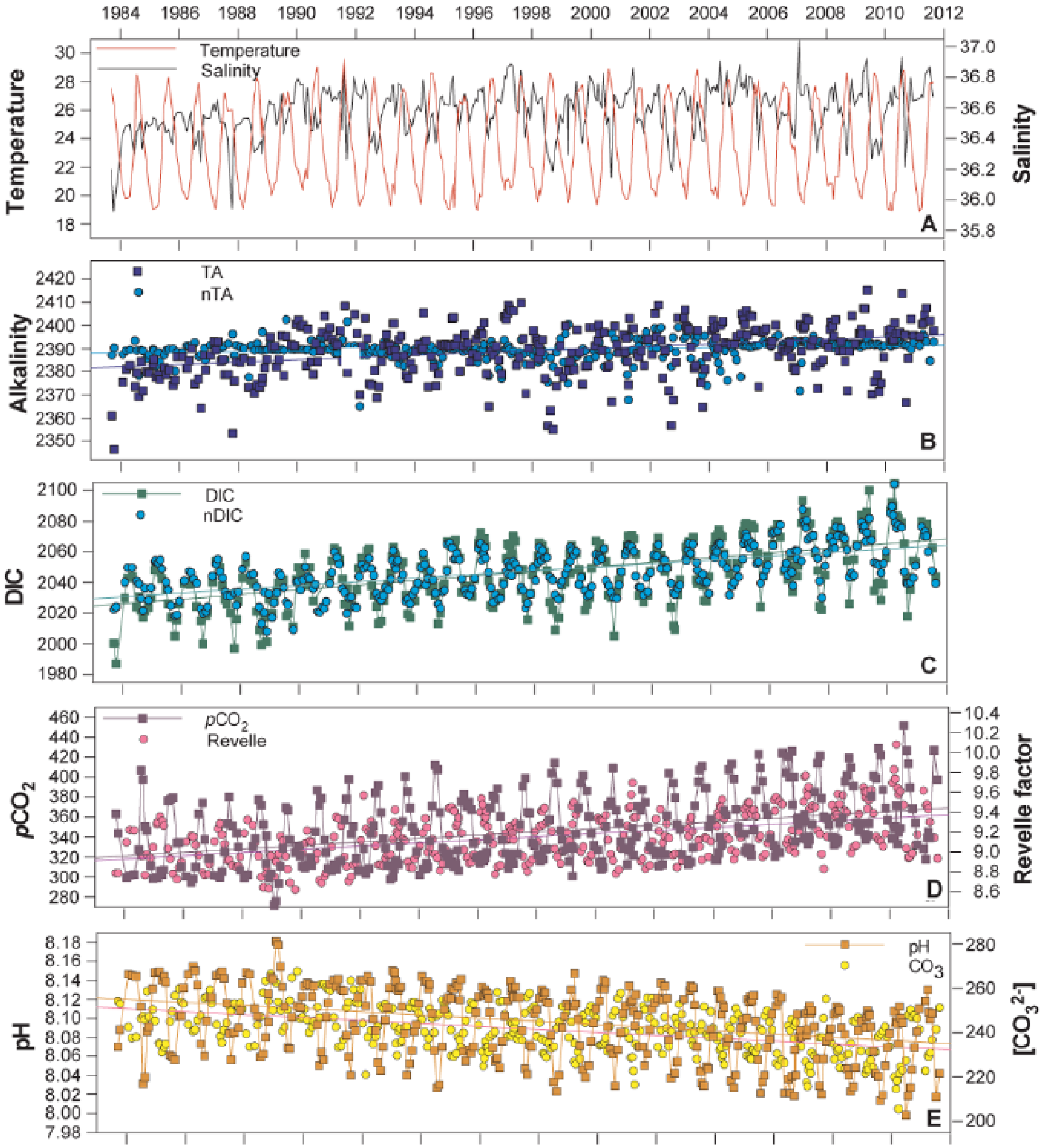
$$\frac{k_1}{k_2} = \frac{[HCO_3^-]^2}{[CO_2^*]\,[CO_3^{2-}]}$$



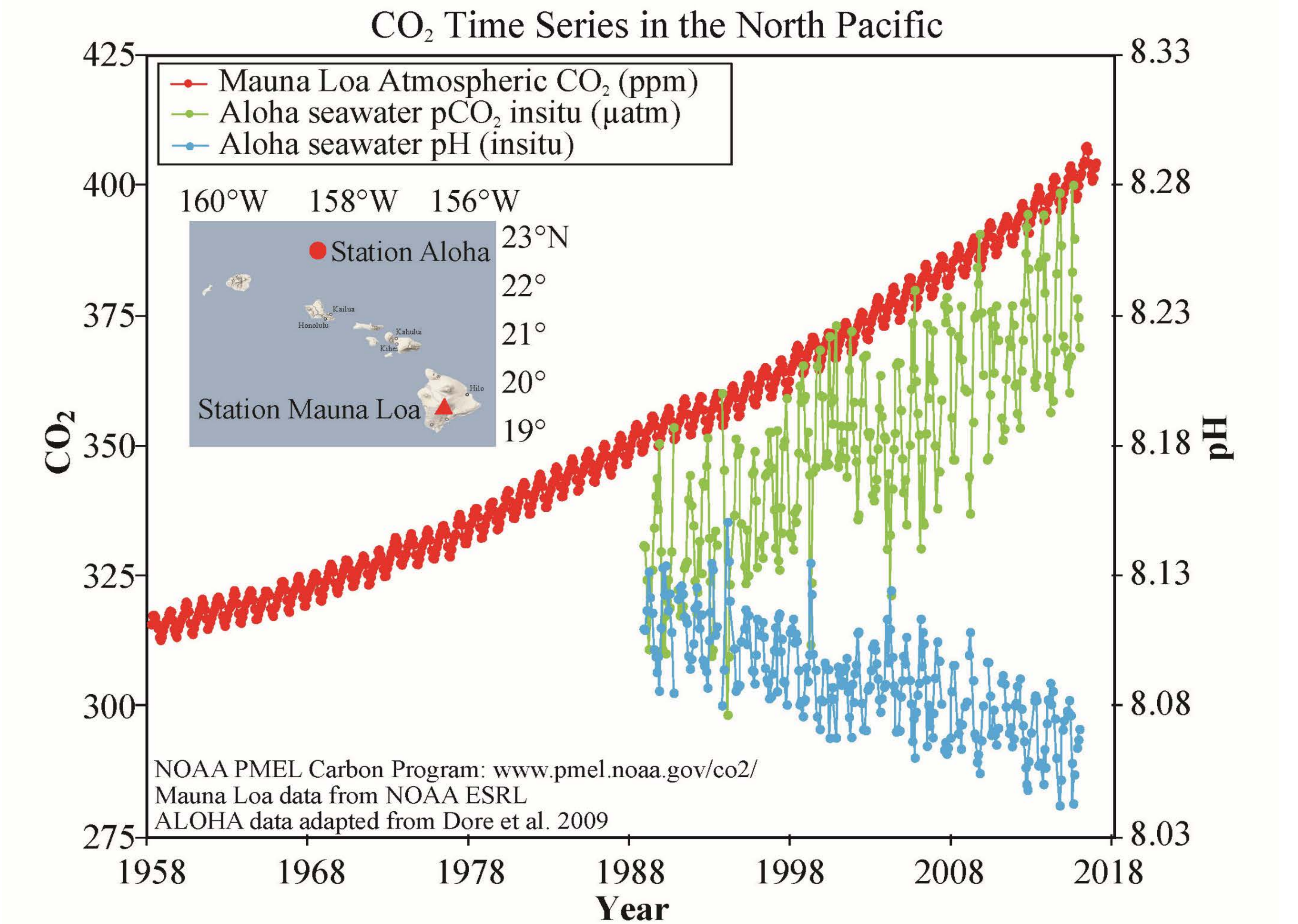
$$\frac{k_1}{k_2} = \frac{[HCO_3^-]^2}{[CO_2^*][CO_3^{2-}]}$$

Source: B. Schneider

BATS - Bermuda Atlantic Time-series Study

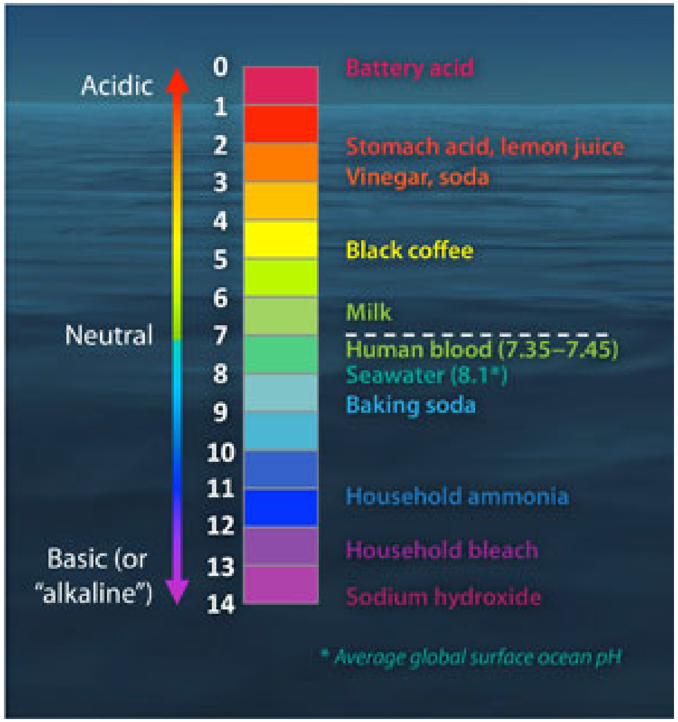


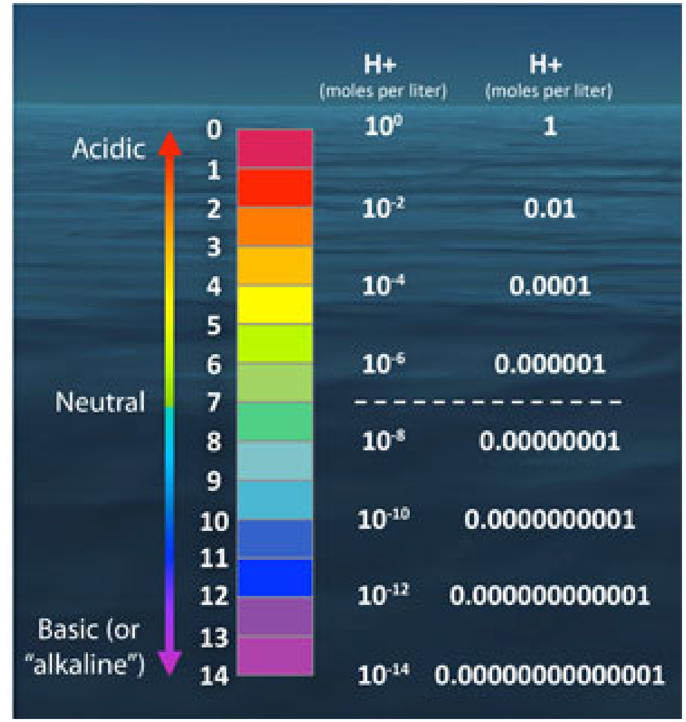
Source: Bates et al., 2012



CO2 Time Series in the North Pacific
Mauna Loa Atmospheric CO2 (ppm)
Aloha seawater pCO2 insitu (µatm)
Aloha seawater pH (insitu)
160°W
158°W
156°W
23°N
22°
21°
20°
19°
Station Aloha
Station Mauna Loa
Kailua
Honolulu
Kahului
Kihei
Hilo
CO2
pH
425
400
375
350
325
300
275
8.33
8.28
8.23
8.18
8.13
8.08
8.03
1958
1968
1978
1988
1998
2008
2018
Year
NOAA PMEL Carbon Program: www.pmel.noaa.gov/co2/
Mauna Loa data from NOAA ESRL
ALOHA data adapted from Dore et al. 2009

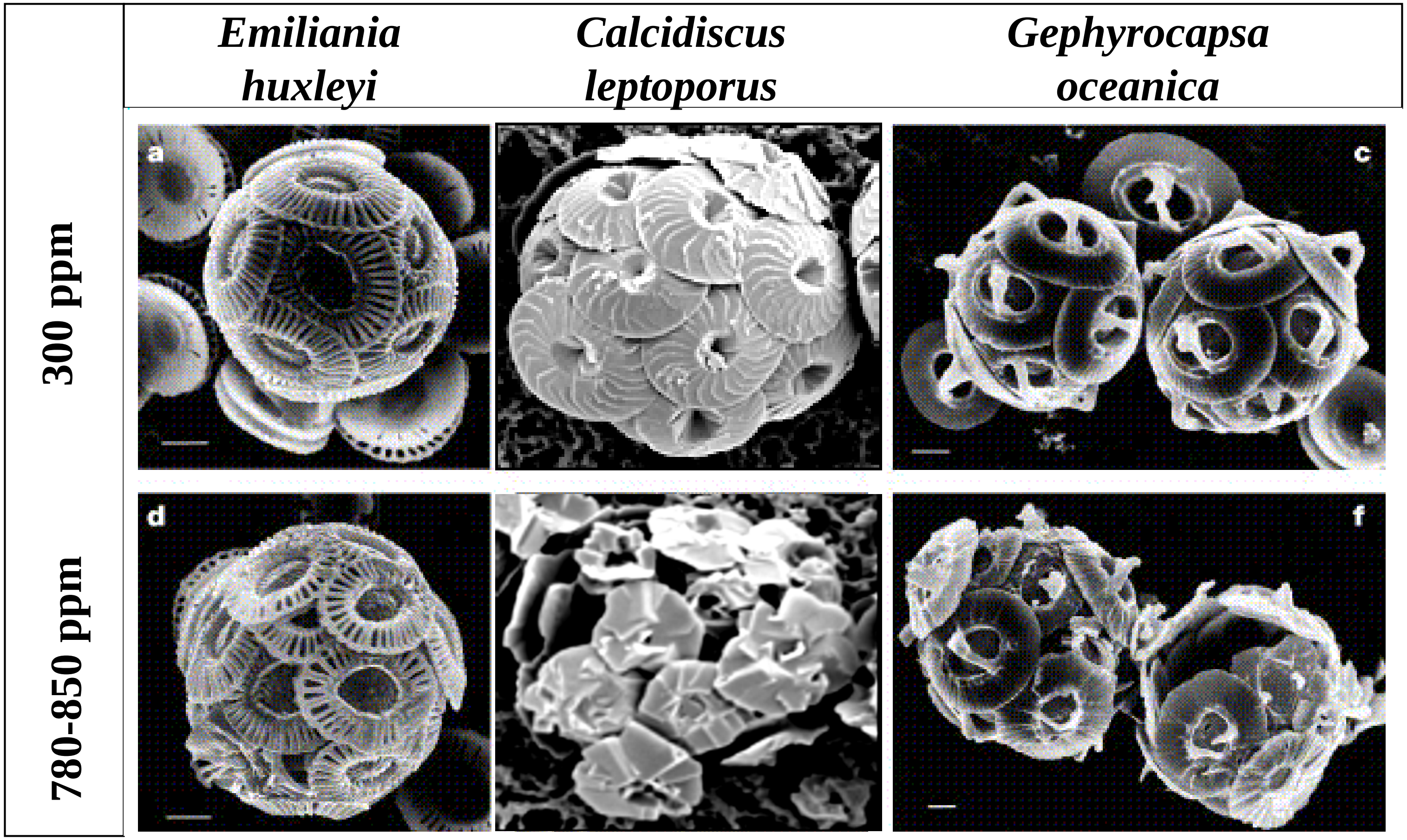
Source: NOAA


Acidic
Neutral
Basic (or "alkaline")
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Battery acid
Stomach acid, lemon juice
Vinegar, soda
Black coffee
Milk
Human blood (7.35–7.45)
Seawater (8.1*)
Baking soda
Household ammonia
Household bleach
Sodium hydroxide
* Average global surface ocean pH

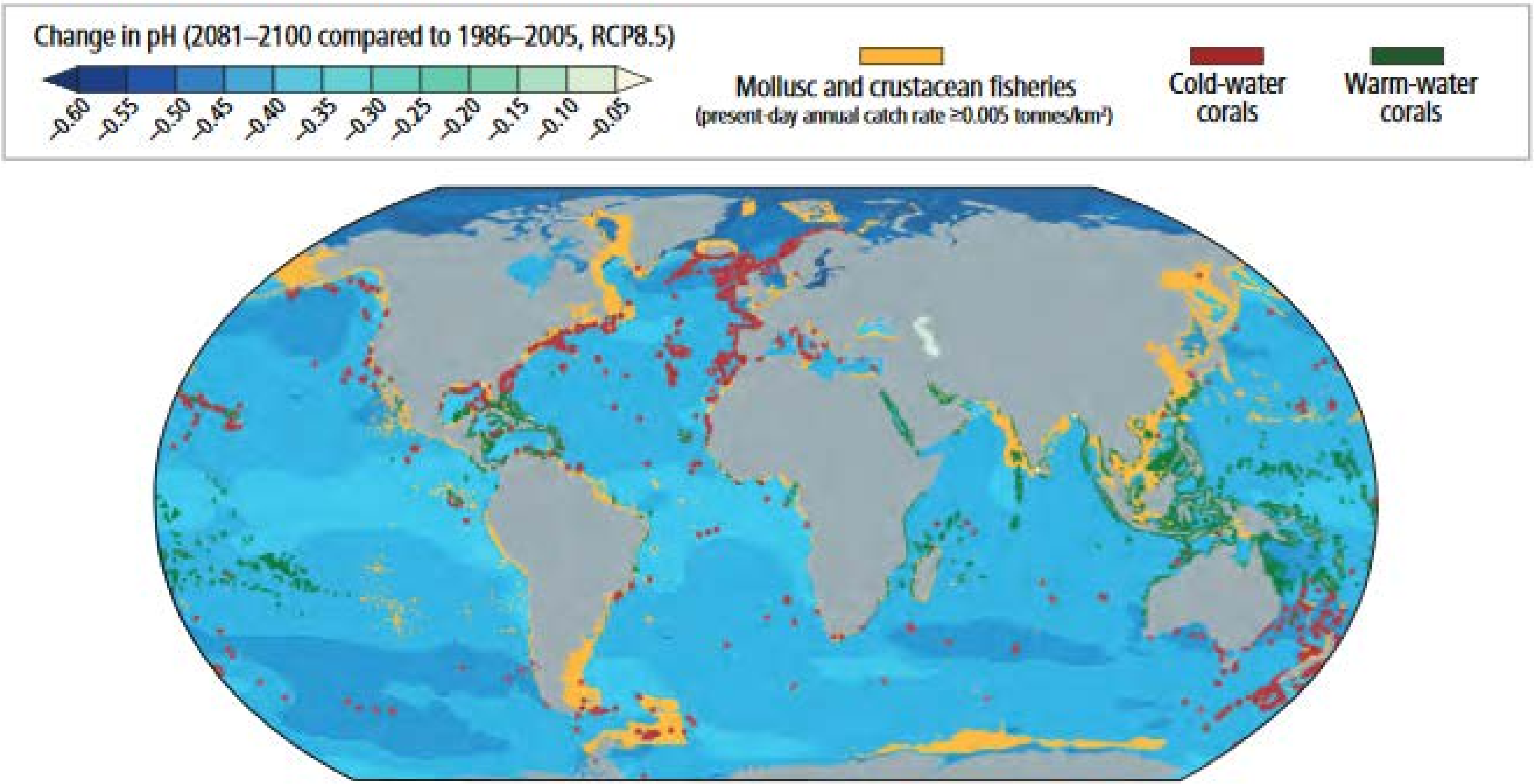

H+ (moles per liter)
H+ (moles per liter)
Acidic
Neutral
Basic (or "alkaline")
0 10^{0} 1
1
2 10^{-2} 0.01
3
4 10^{-4} 0.0001
5
6 10^{-6} 0.000001
7
8 10^{-8} 0.00000001
9
10 10^{-10} 0.0000000001
11
12 10^{-12} 0.000000000001
13
14 10^{-14} 0.00000000000001


pH
H+ (moles per liter)
change in acidity
7.2 6.3×10^{-8} +900%
7.3 5.0×10^{-8} +694%
7.4 4.0×10^{-8} +531%
7.5 3.2×10^{-8} +401%
7.6 2.5×10^{-8} +298%
7.7 2.0×10^{-8} +216%
7.8 1.6×10^{-8} +151%
7.9 1.3×10^{-8} +100%
8.0 1.0×10^{-8} +58%
8.1 7.9×10^{-9} +26%
8.2 6.3×10^{-9}

Source: NOAA

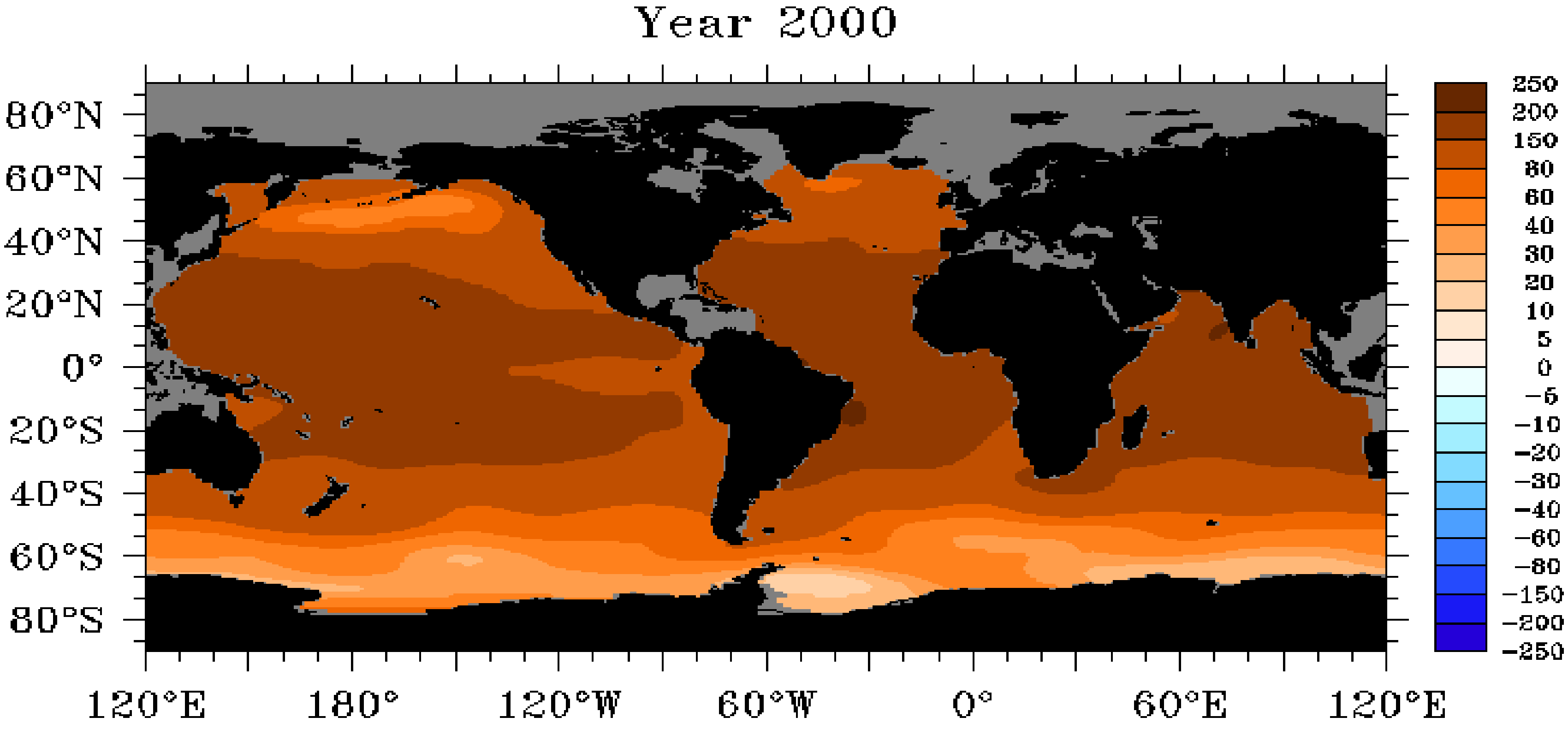


Source: Riebesell et al., 2000



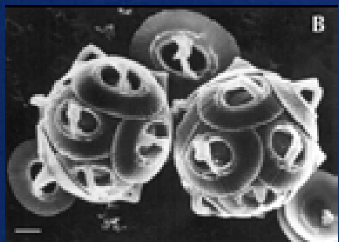
Source: IPCC, 2014

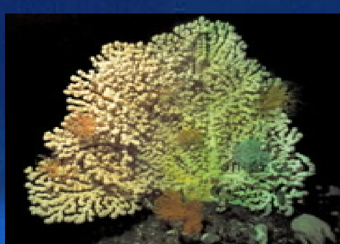
Global aragonite saturation 2099



Source: Orr et al., 2005

Calciferous organisms





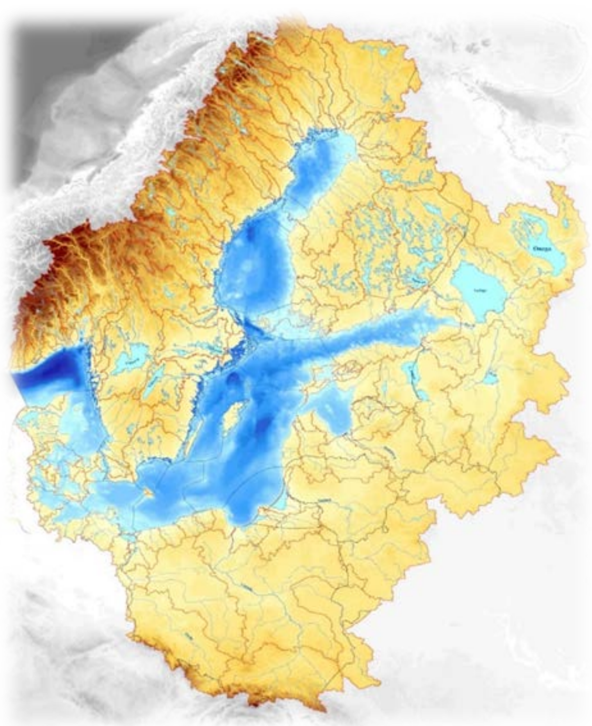
	$CaCO_3$	production period
coccolithophores	calcite	days
foraminifera	calcite	weeks
pteropods	aragonite	months
corals	aragonite	months/years

doubling of CO_2 in the atmosphere → decrease in calcification by 20-40 %

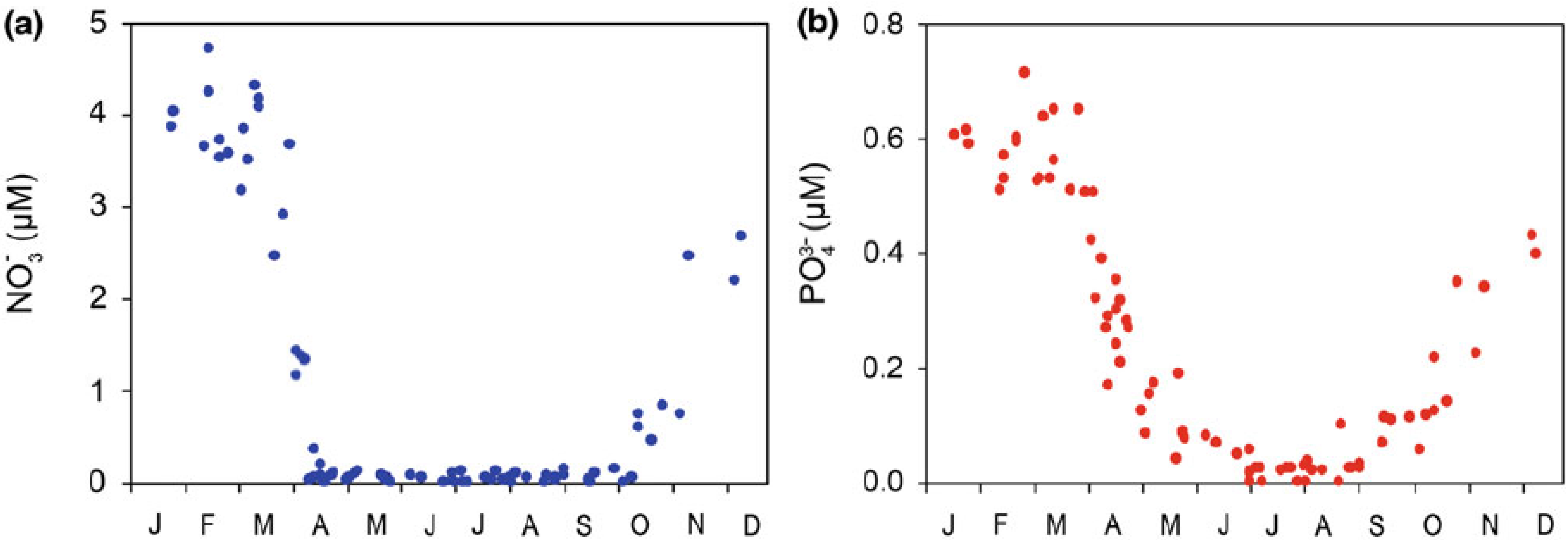
Source: NOAA

Outline:

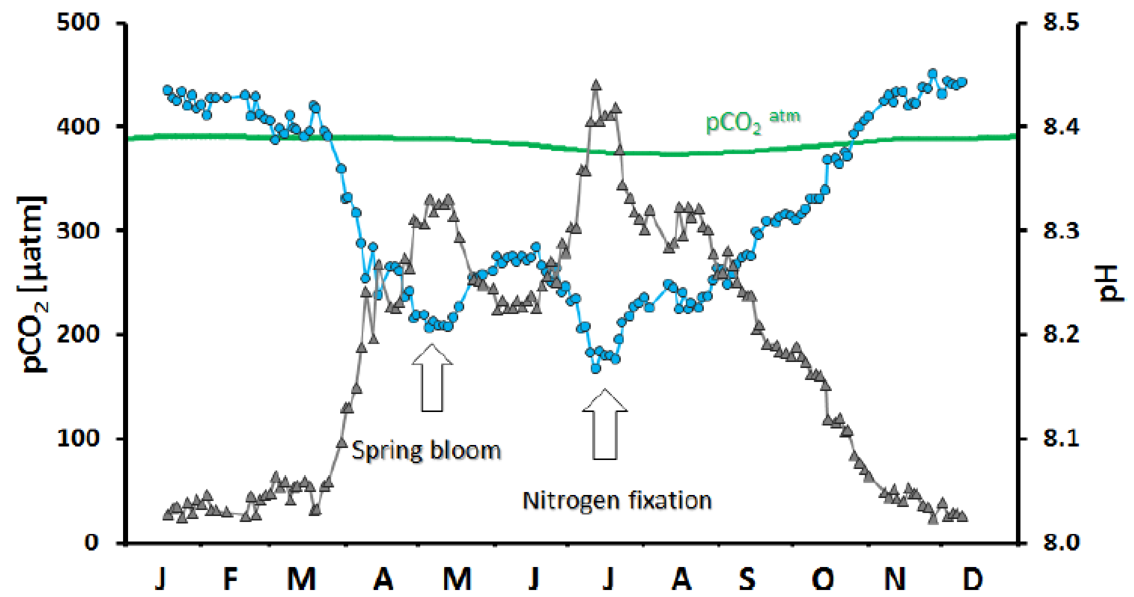
I. Carbon – the chemical element conditioning climate
II. Role of marine environment in the carbon cycle
III. Marine CO_2 system and ocean acidification
IV. Peculiarities of the Baltic Sea



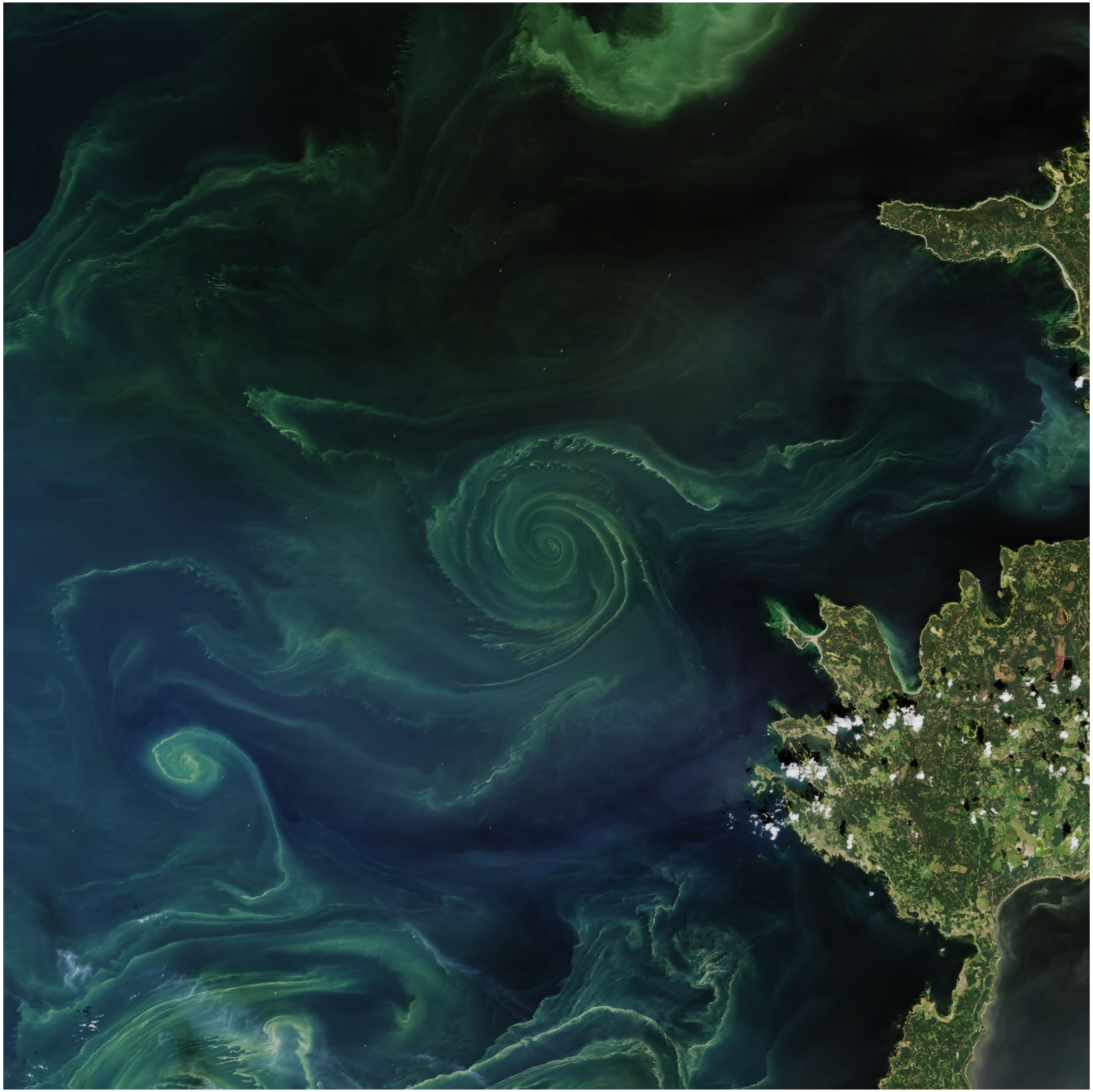
Source: SMHI



Source: Biological Oceanography of the Baltic Sea

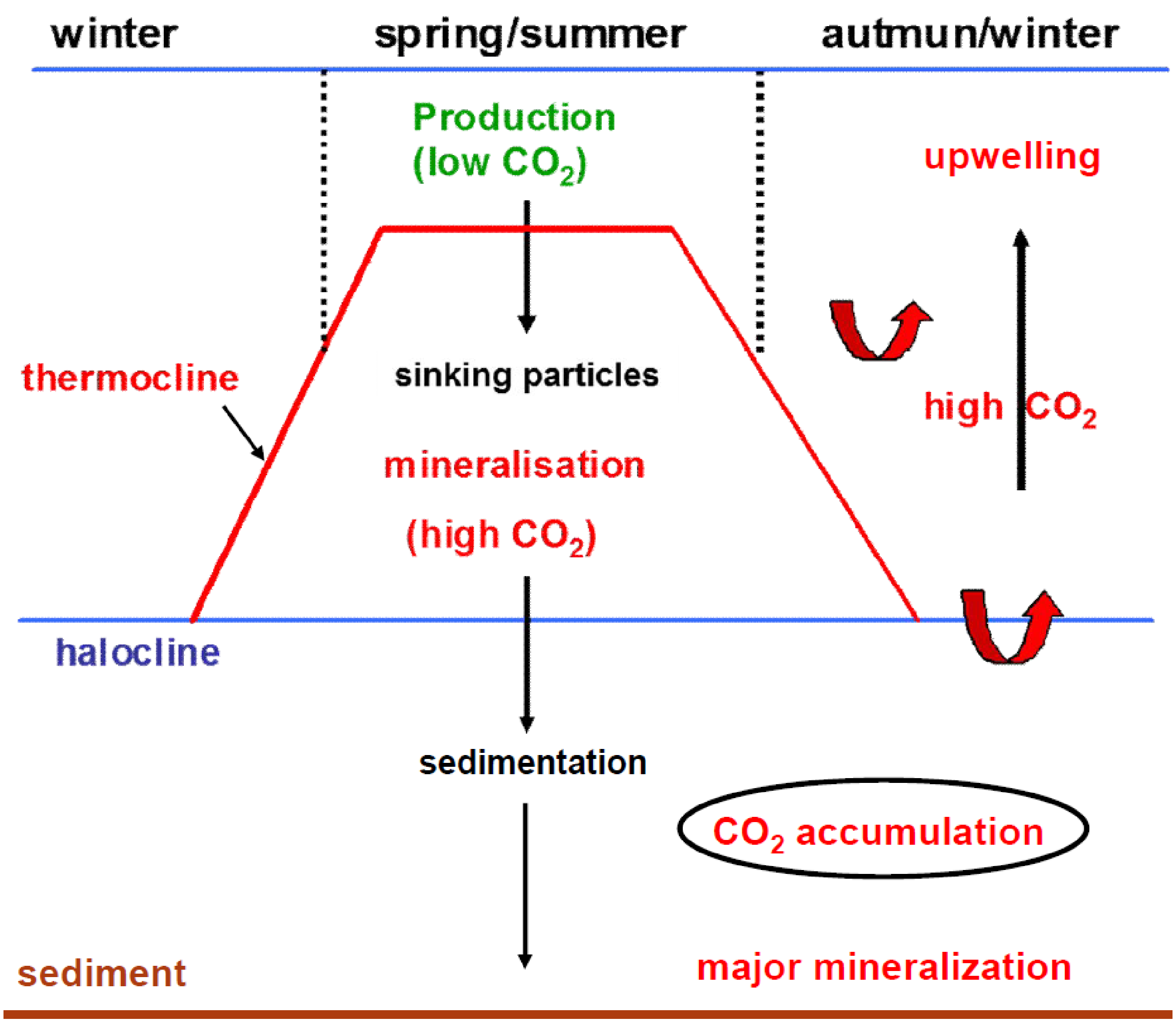


Source: Kuliński et al., 2017 modified after Schneider , 2011

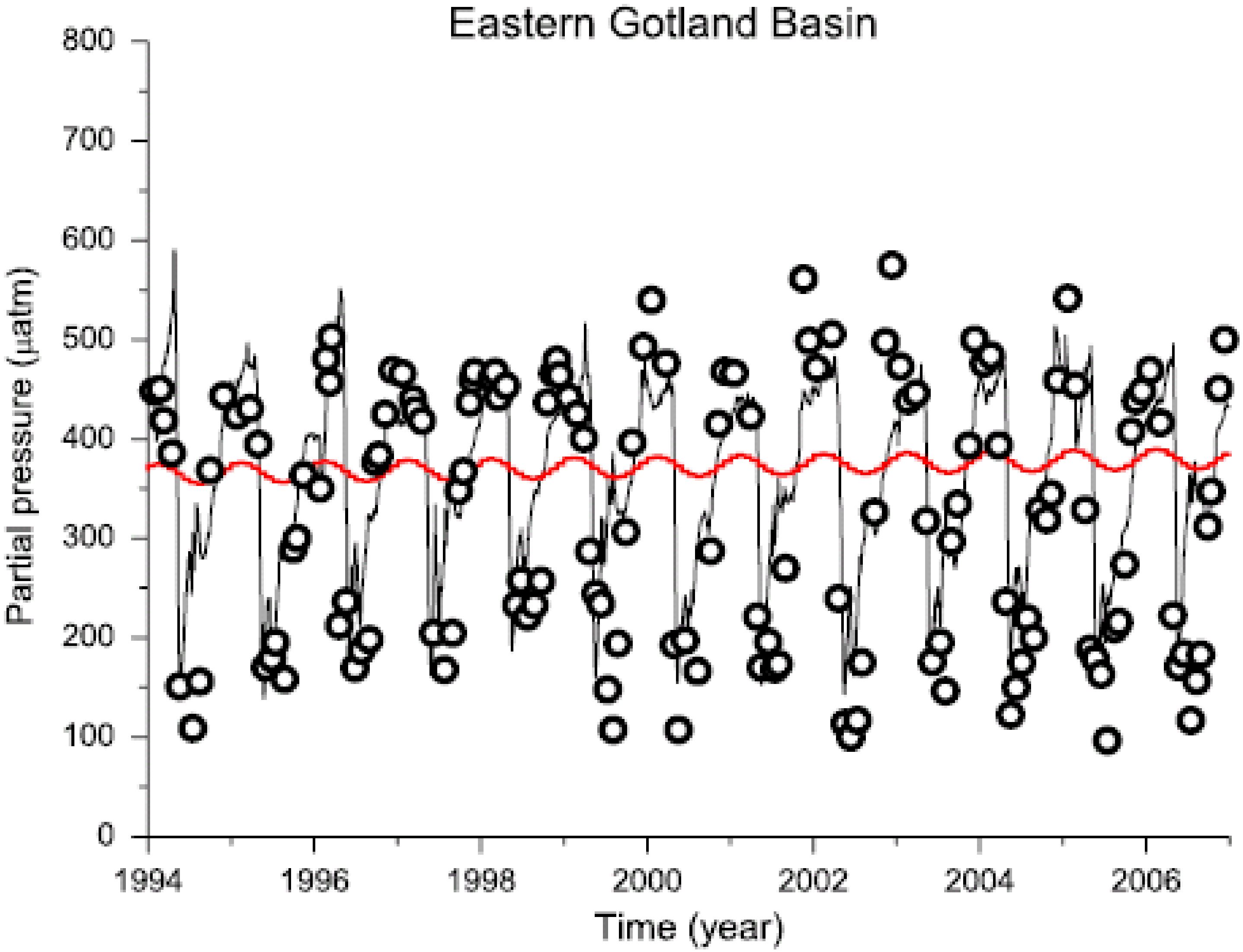


Source: NASA

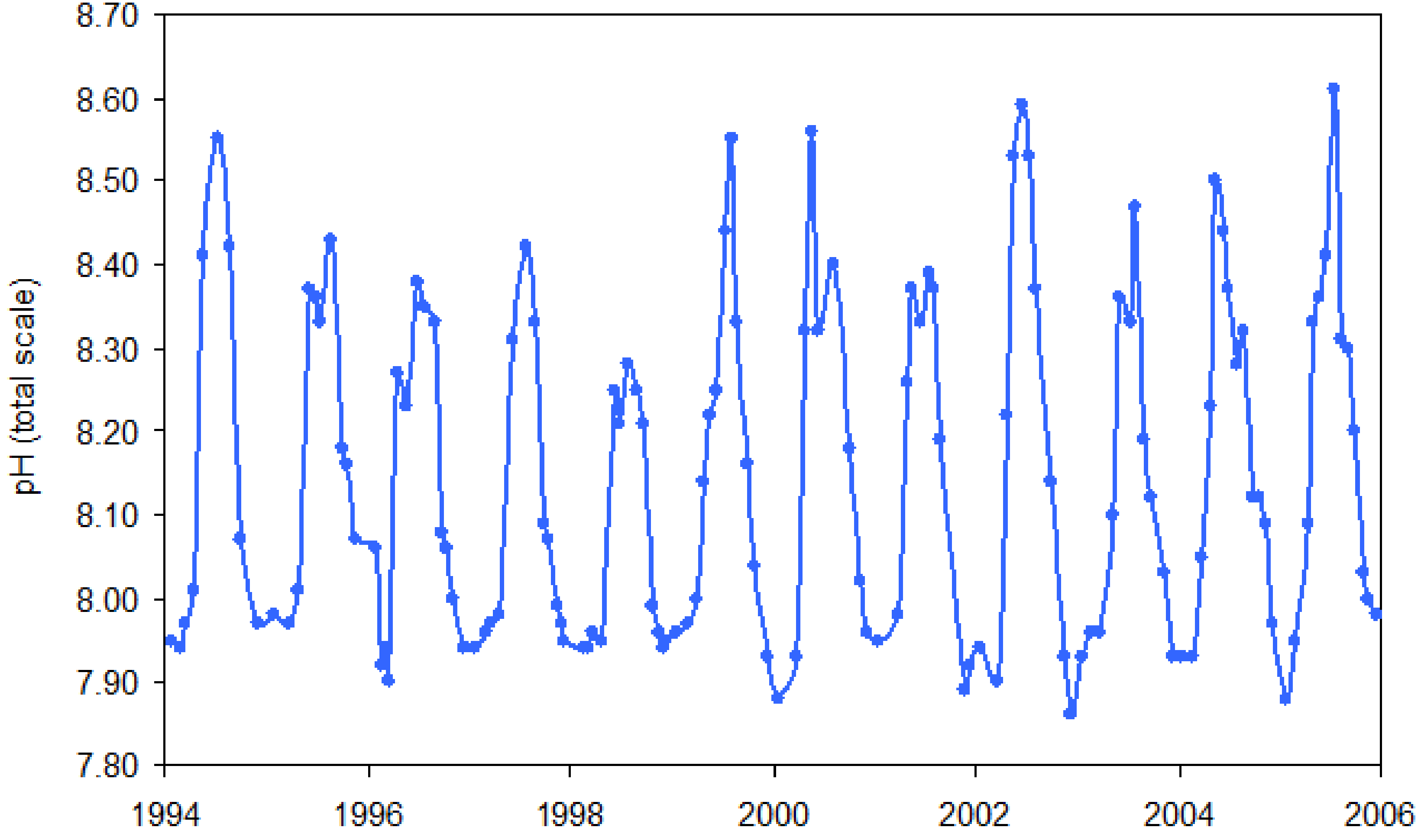
Source: PAP



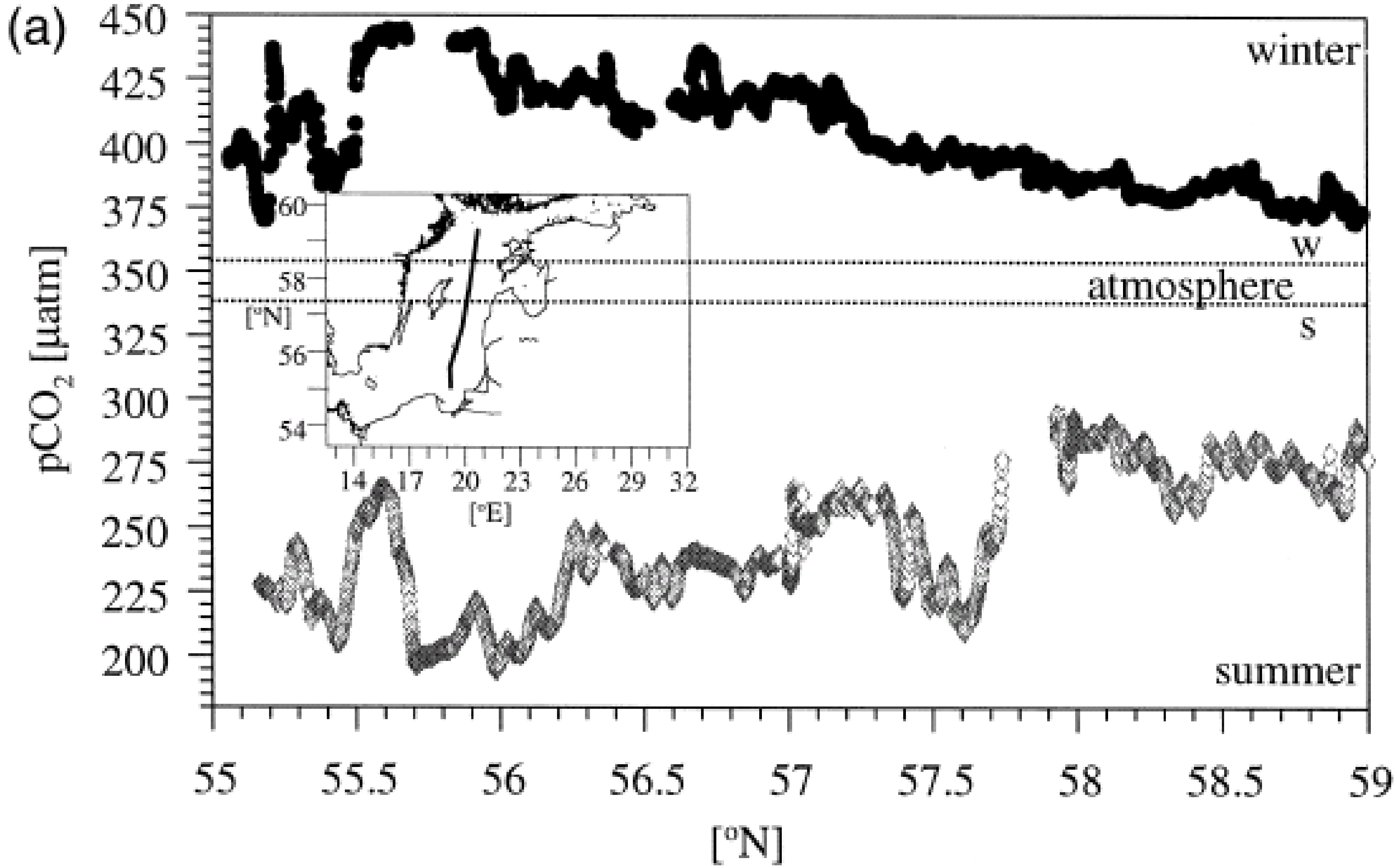
Source: B. Schneider



Source: Omstedt et al., 2009

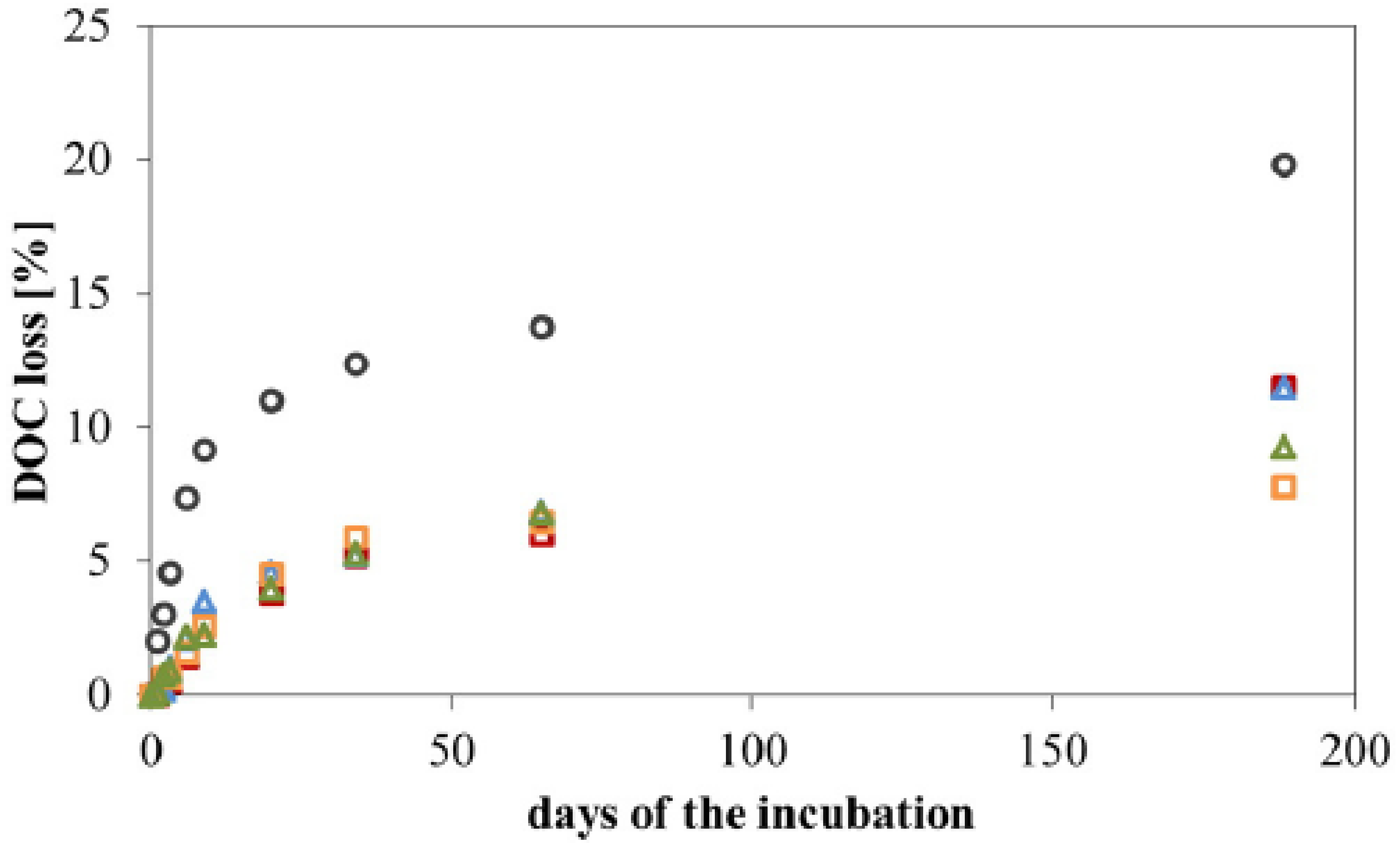

8.70
8.60
8.50
8.40
8.30
8.20
8.10
8.00
7.90
7.80
pH (total scale)
1994
1996
1998
2000
2002
2004
2006

Source: SMHI



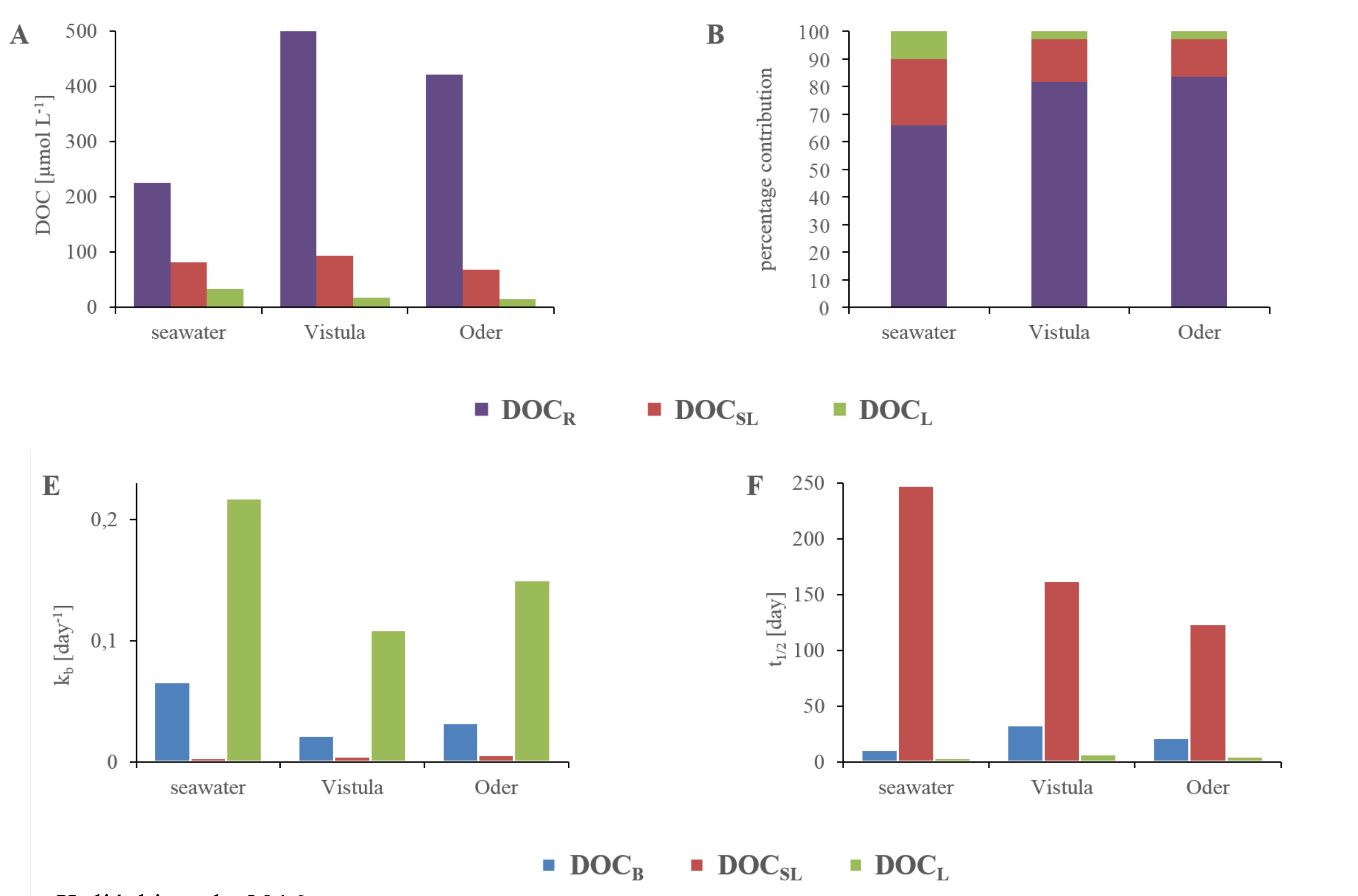
Source: Thomas & Schneider, 2009

$$DOC_{(t)} = DOC_{L(t=0)} \cdot e^{-k_{b(L)} \cdot t} + DOC_{SL(t=0)} \cdot e^{-k_{b(SL)} \cdot t} + DOC_R$$



Source: Kuliński et al., 2016

$$DOC_{(t)} = DOC_{L(t=0)} \cdot e^{-k_{b(L)} \cdot t} + DOC_{SL(t=0)} \cdot e^{-k_{b(SL)} \cdot t} + DOC_R$$



Source: Kuliński et al., 2016

Baltic Sea sink or source???

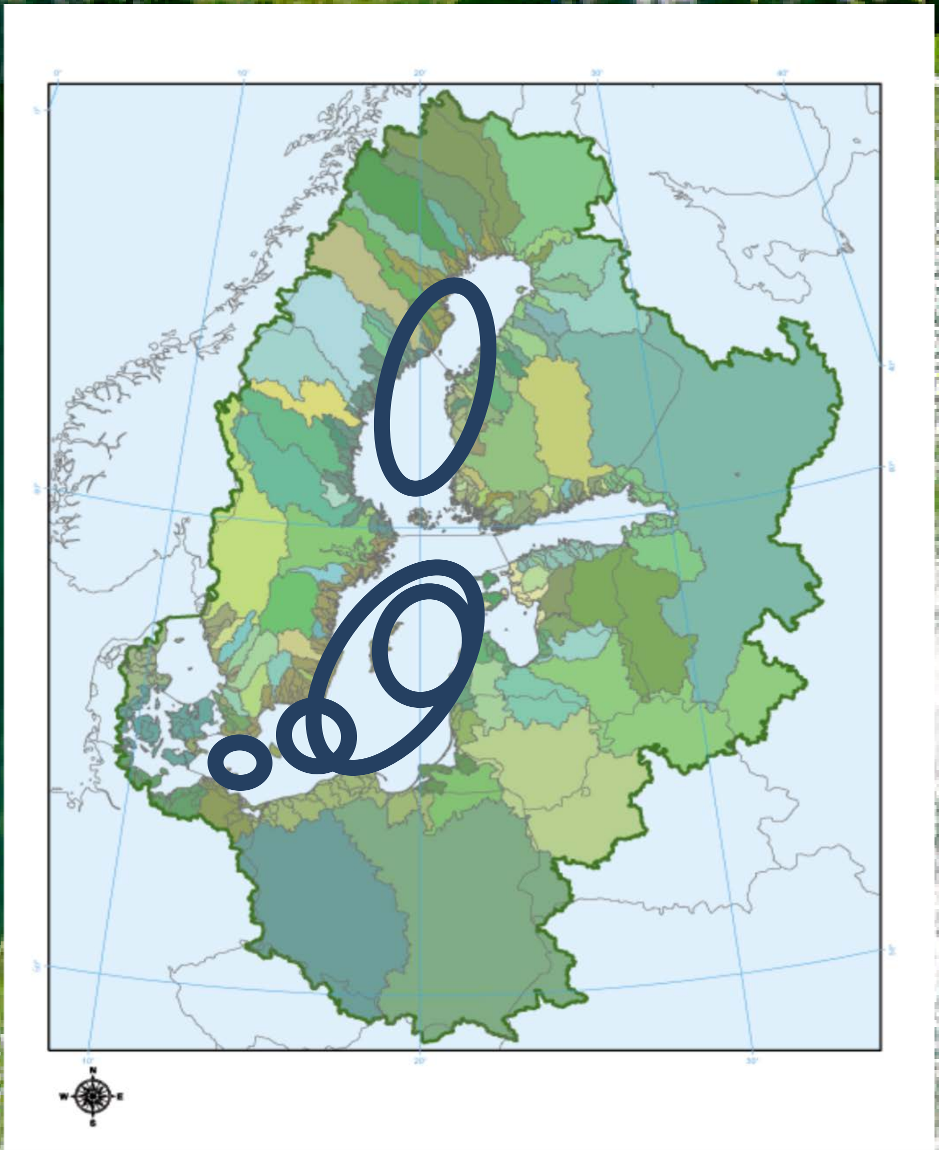
- **10.8 g C m^{-2} yr^{-1}**
(Thomas et al., 2003)

- **36.0 g C m^{-2} yr^{-1}**
(Kuss et al., 2006)

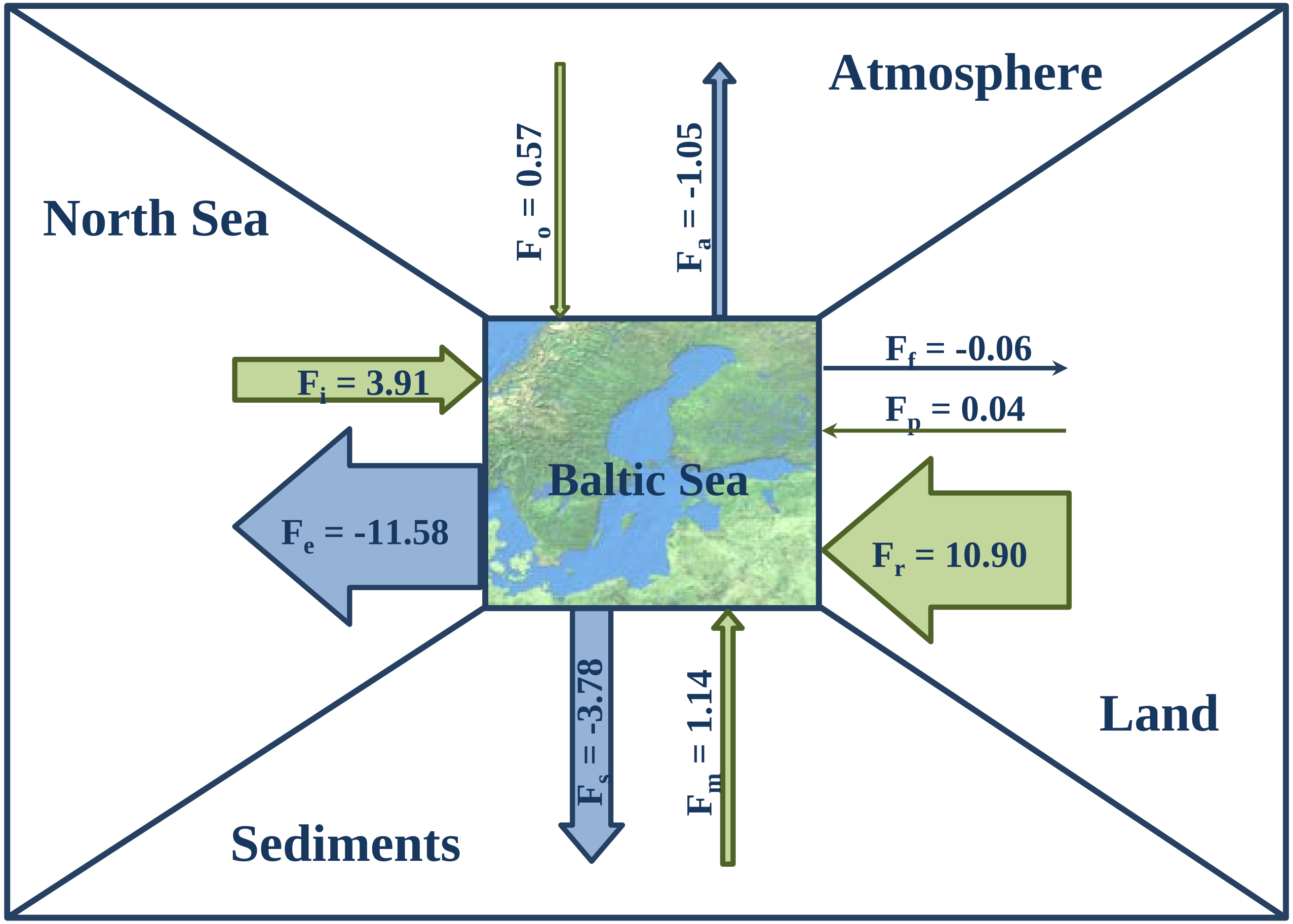
- **-35.4 g C m^{-2} yr^{-1}**
(Algesten et al., 2006)

- **-19.7 g C m^{-2} yr^{-1}**
(Wesslander et al., 2010)

- **-28.1 g C m^{-2} yr^{-1}**
(Wesslander et al., 2010)



HELCOM, 2007



Values are in Tg (10^{12} g) C yr^{-1}

River run-off
IC: 62%
OC: 38%

Import from the North Sea
IC: 95%
OC: 5%

Export to the North Sea
IC: 83%
OC: 17%

Return flux from the sediments
IC: 91%
OC: 9%

Net CO_2 emission to the atmosphere?

-1.05 ± 1.71 Tg C yr^{-1}

-3.0 ± 4.88 g C m^{-2} yr^{-1}

Source: Kuliński & Pempkowiak, 2011

Seawater acid-base system

Measurable parameters:

- C_T – total CO_2 concentration (DIC)

  $C_T = [CO_2]^* + [HCO_3^-] + [CO_3^{2-}]$

- A_T – total alkalinity

  $A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + \ldots - [H^+] - \ldots$

- pCO_2 – CO_2 partial pressure

- pH –spectrophotometric measurement with m-cresol purple, total scale

  $pH_T = -\log ([H^+]_F + [HSO_4^-]) = -\log [H^+]_T$

It is possible to calculate 2 parameters when the following is known:

- other 2 parameters
- temperature & salinity
- <u>equilibrium constants for each of the acid dissociation reactions</u>
- <u>total concentrations for each non-CO_2 substances</u>

The pair used in the calculations:

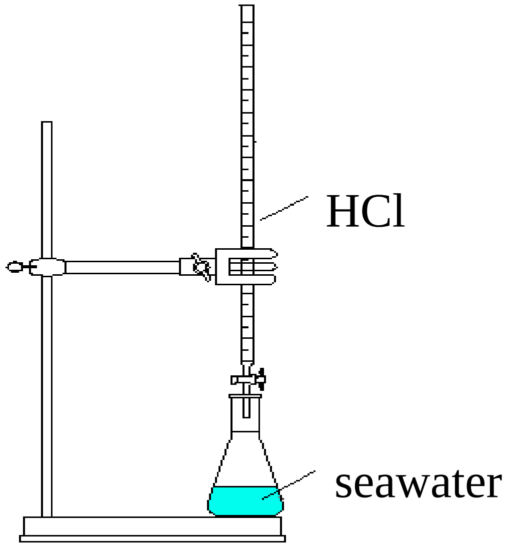
- <u>C_T & A_T – recommended, used in biogeochemical modelling</u>

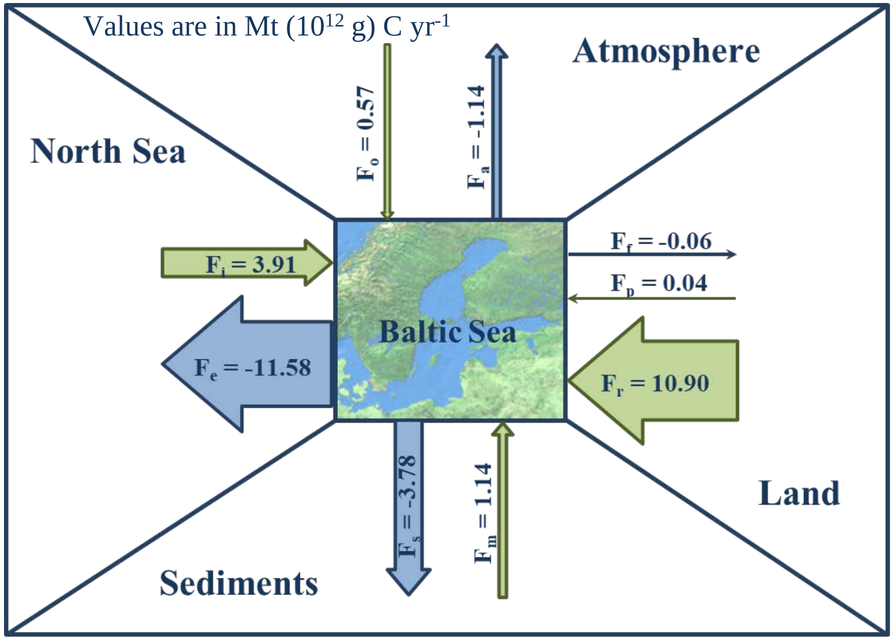
Total alkalinity

The total alkalinity of seawater is defined as the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$ at 25ºC) over proton donors (acids with $K > 10^{-4.5}$) and expressed as a hydrogen ion equivalent in one kilogram of sample (Dickson, 1981):

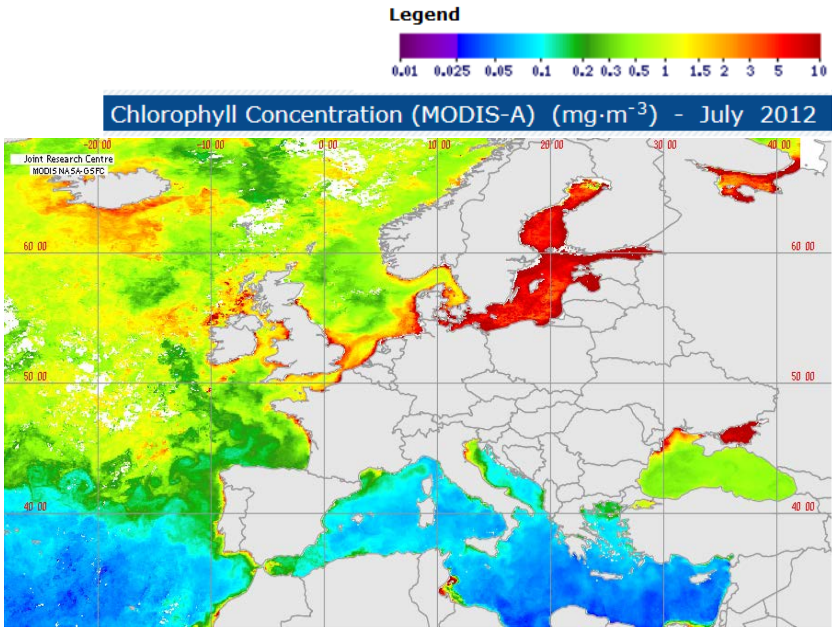
$$\mathbf{A_T} = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] + \ldots + \text{minor bases}$$

$$- [H^+]_{wolny} - [HSO_4^-] - [HF] - [H_3PO_4] - \ldots - \text{minor acids}$$

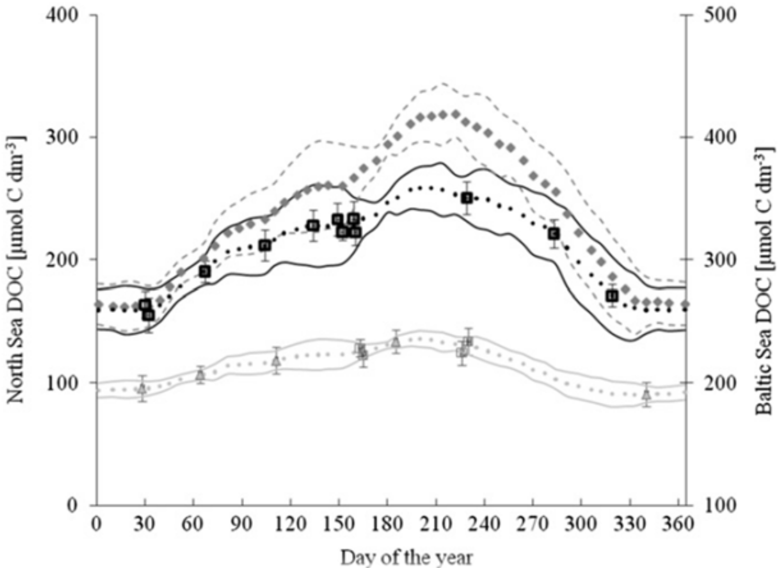




Source: Kuliński & Pempkowiak, 2011



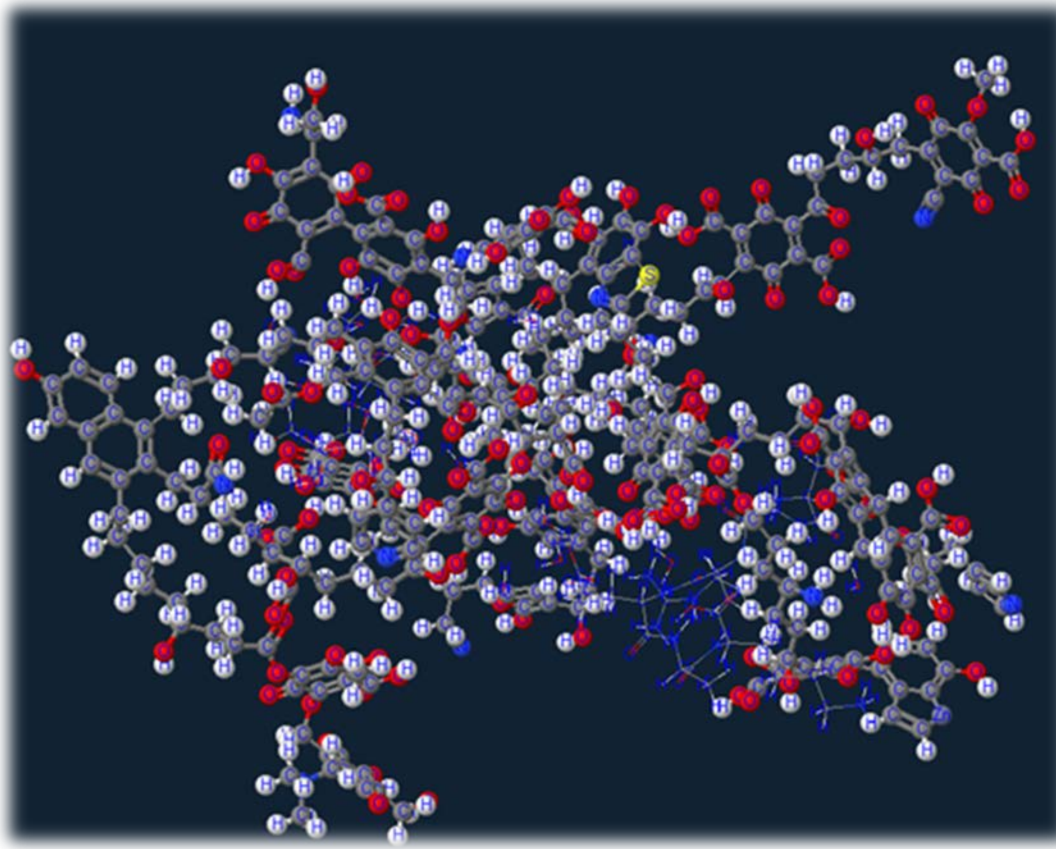
Source: HELCOM



Source: Kuliński et al., 2011

Functional groups in DOM

Group	Structure	Exchange H ?
Alcohol	—C—O—H	Yes
Phenol	(benzene ring)—O—H	Yes
Ether	—C—O—C—	
Aldehyde	—C—C(=O)—H	No
Ketone	—C—C(=O)—C—	
Carboxyl	—C—C(=O)—O—H	Yes
Ester	—C—C(=O)—O—C—	
Amine	—C—N<	Yes
Amide	—C—C(=O)—N<	Yes



hypothetical structure of humic-like substances

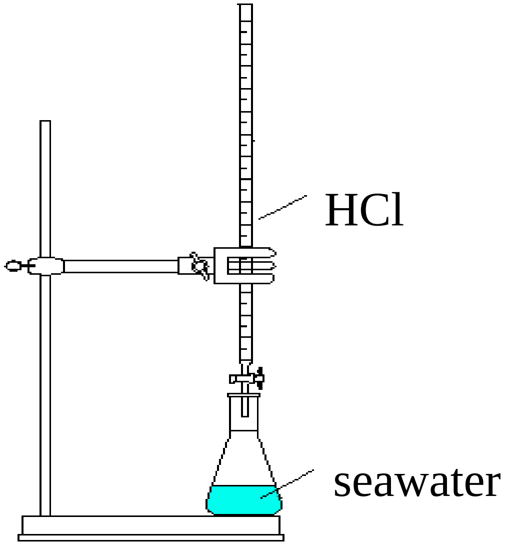
Total alkalinity

The total alkalinity of seawater is defined as the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$ at 25ºC) over proton donors (acids with $K > 10^{-4.5}$) and expressed as a hydrogen ion equivalent in one kilogram of sample (Dickson, 1981):

$$\mathbf{A_T} = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}]$$
$$+ 2[PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] + \ldots + \text{Organics}$$

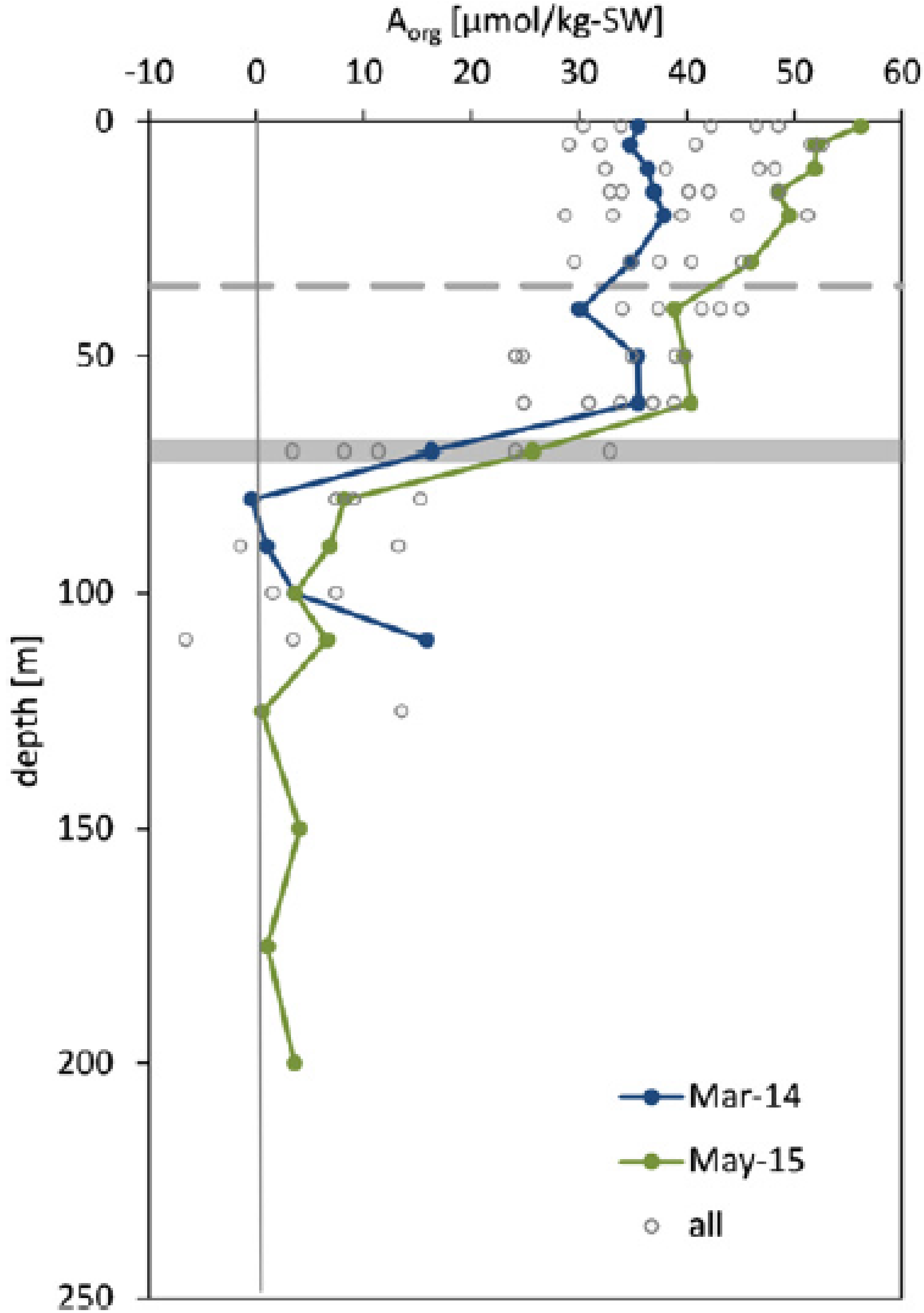
$$- [H^+]_{wolny} - [HSO_4^-] - [HF] - [H_3PO_4] - \ldots$$

$$A_T = A_{inorganic} + A_{org}$$



$f = 0.12$

$pK_{DOM} = 7.34$



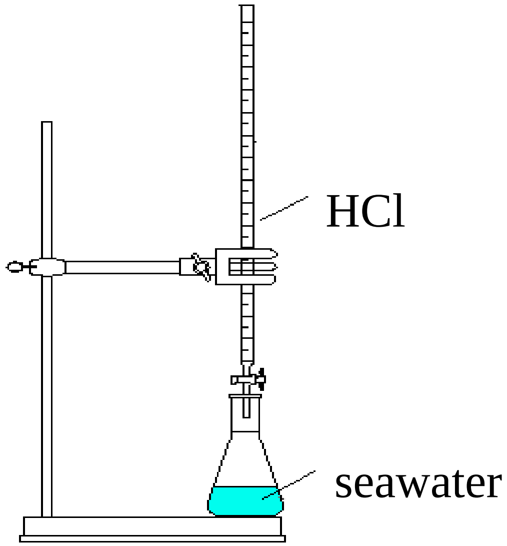
Source: Hammer et al., 2014

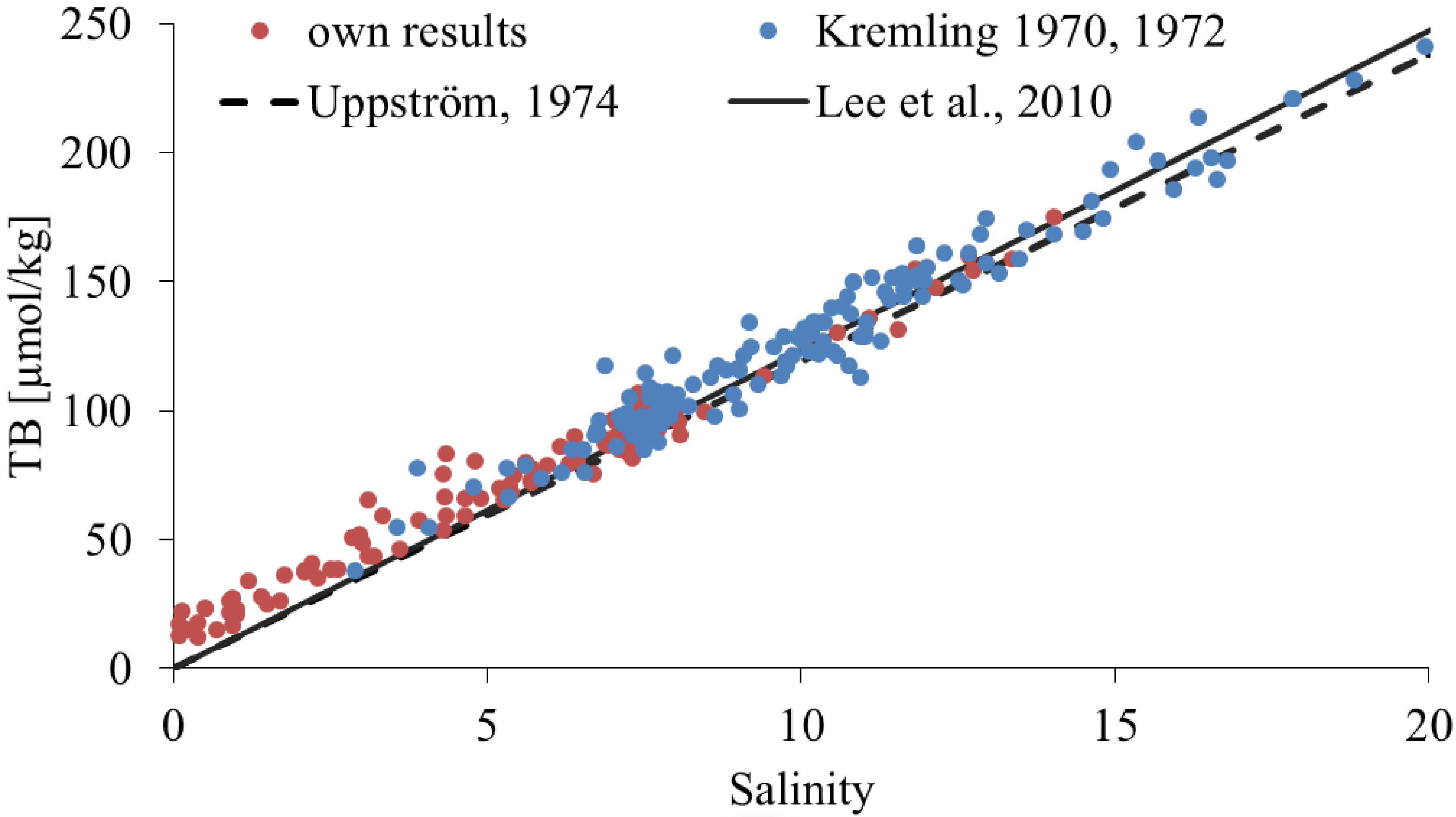
Total alkalinity

The total alkalinity of seawater is defined as the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$ at 25ºC) over proton donors (acids with $K > 10^{-4.5}$) and expressed as a hydrogen ion equivalent in one kilogram of sample (Dickson, 1981):

$$\mathbf{A_T} = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] + \ldots + \text{minor bases}$$

$$- [H^+]_{wolny} - [HSO_4^-] - [HF] - [H_3PO_4] - \ldots - \text{minor acids}$$

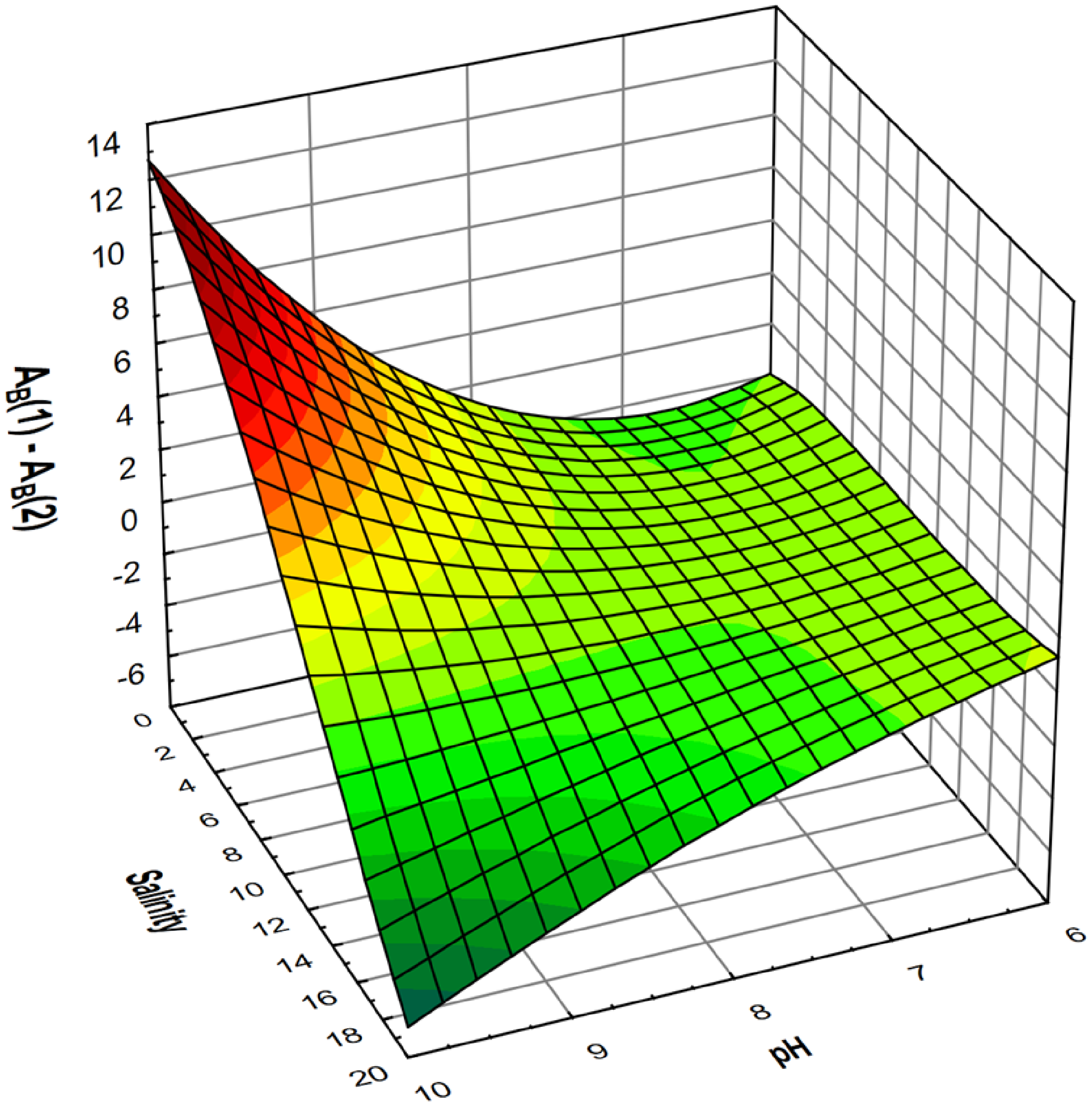




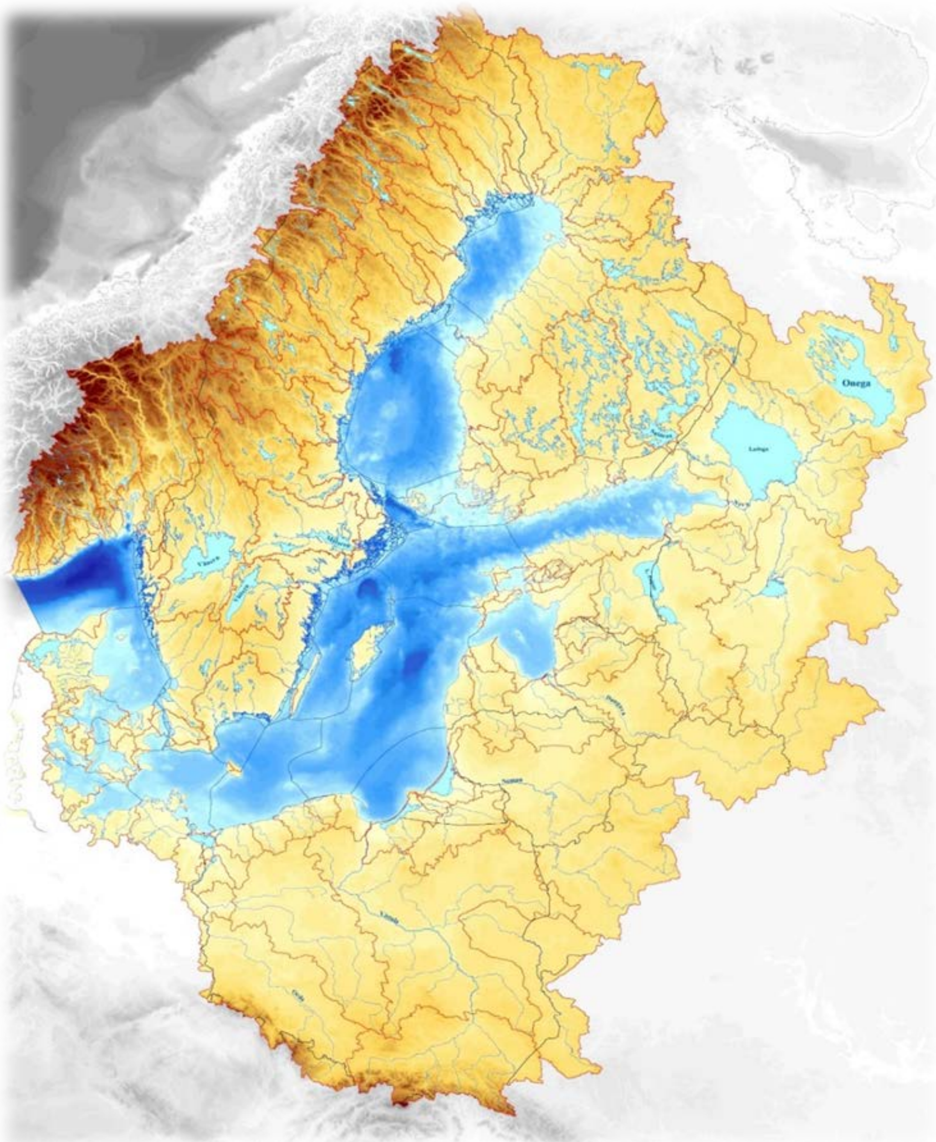
$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] + \ldots + \text{Organics}$$

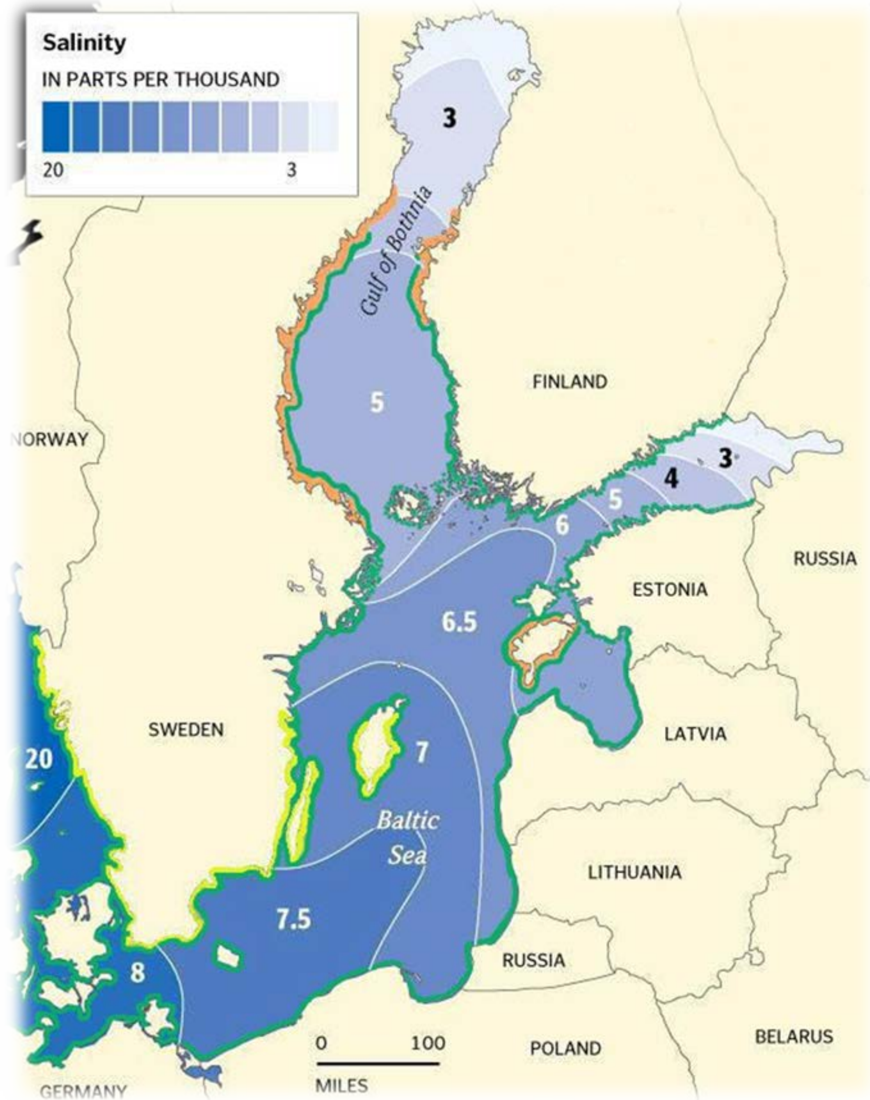
$$- [H^+]_{wolny} - [HSO_4^-] - [HF] - [H_3PO_4] - \ldots$$

Source: Kuliński et al., 2018



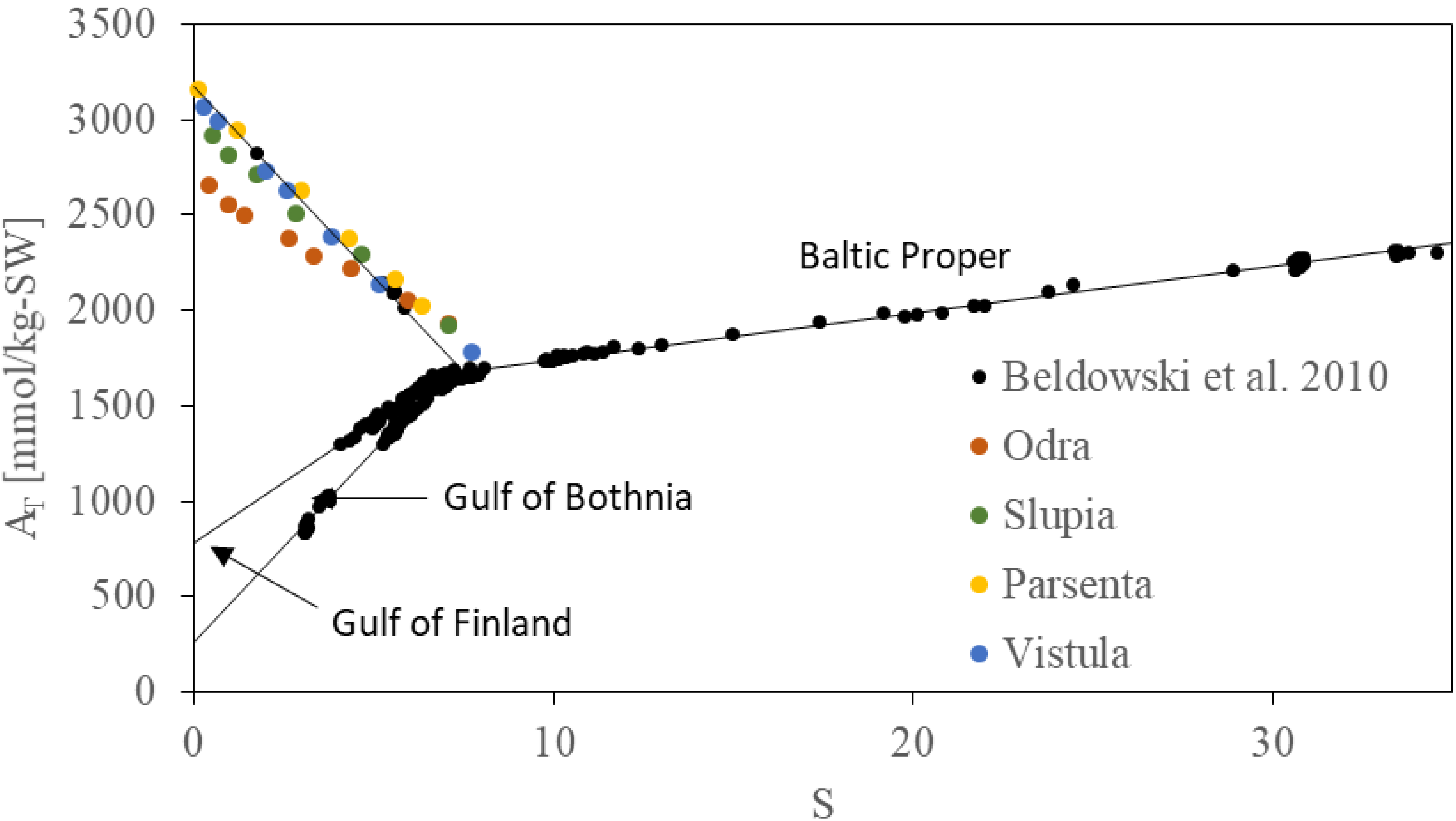
Source: Kuliński et al., 2018



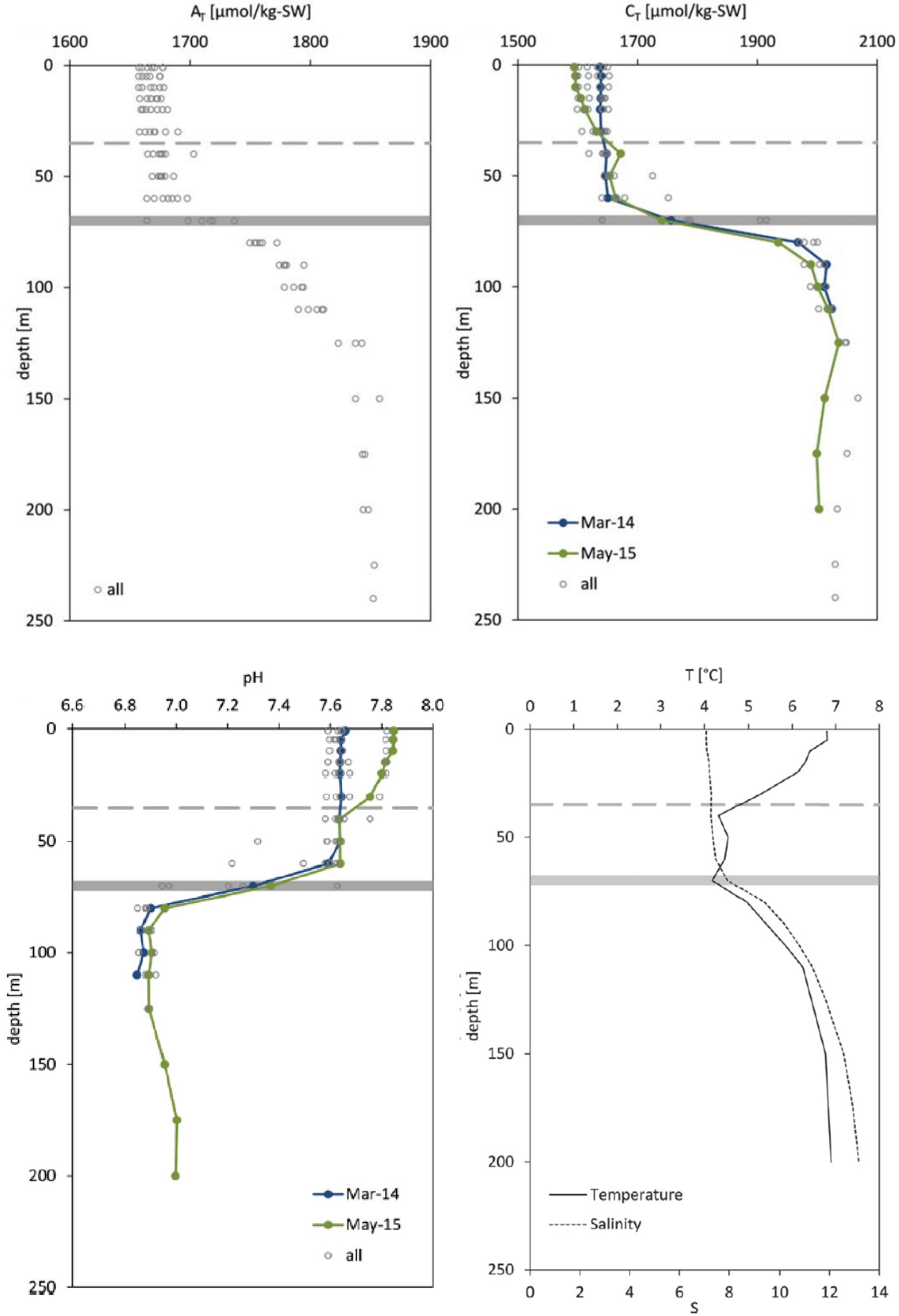


Source: SMHI

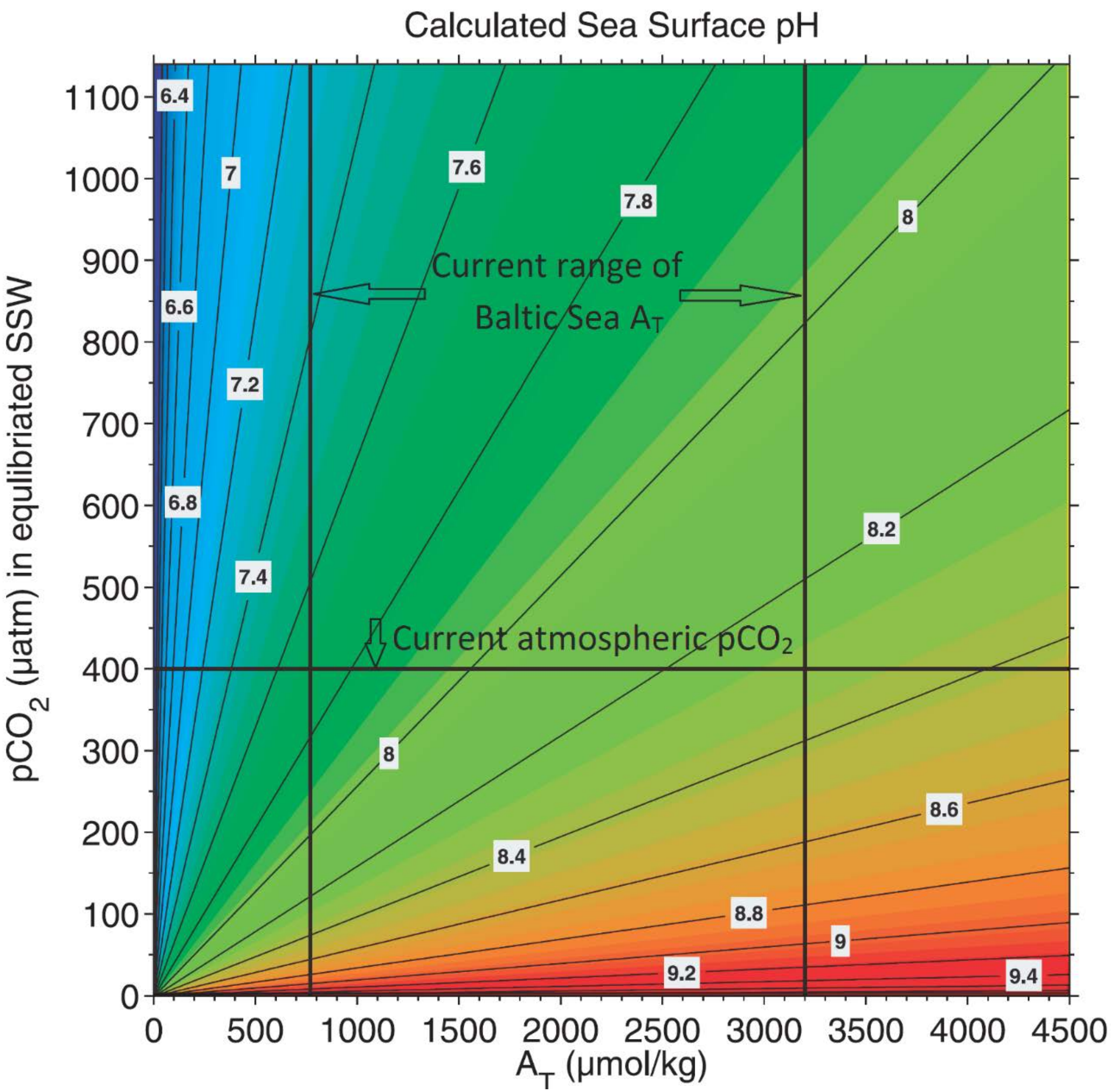
Source: balticseaweed.com



Source: Kuliński et al., in prep.

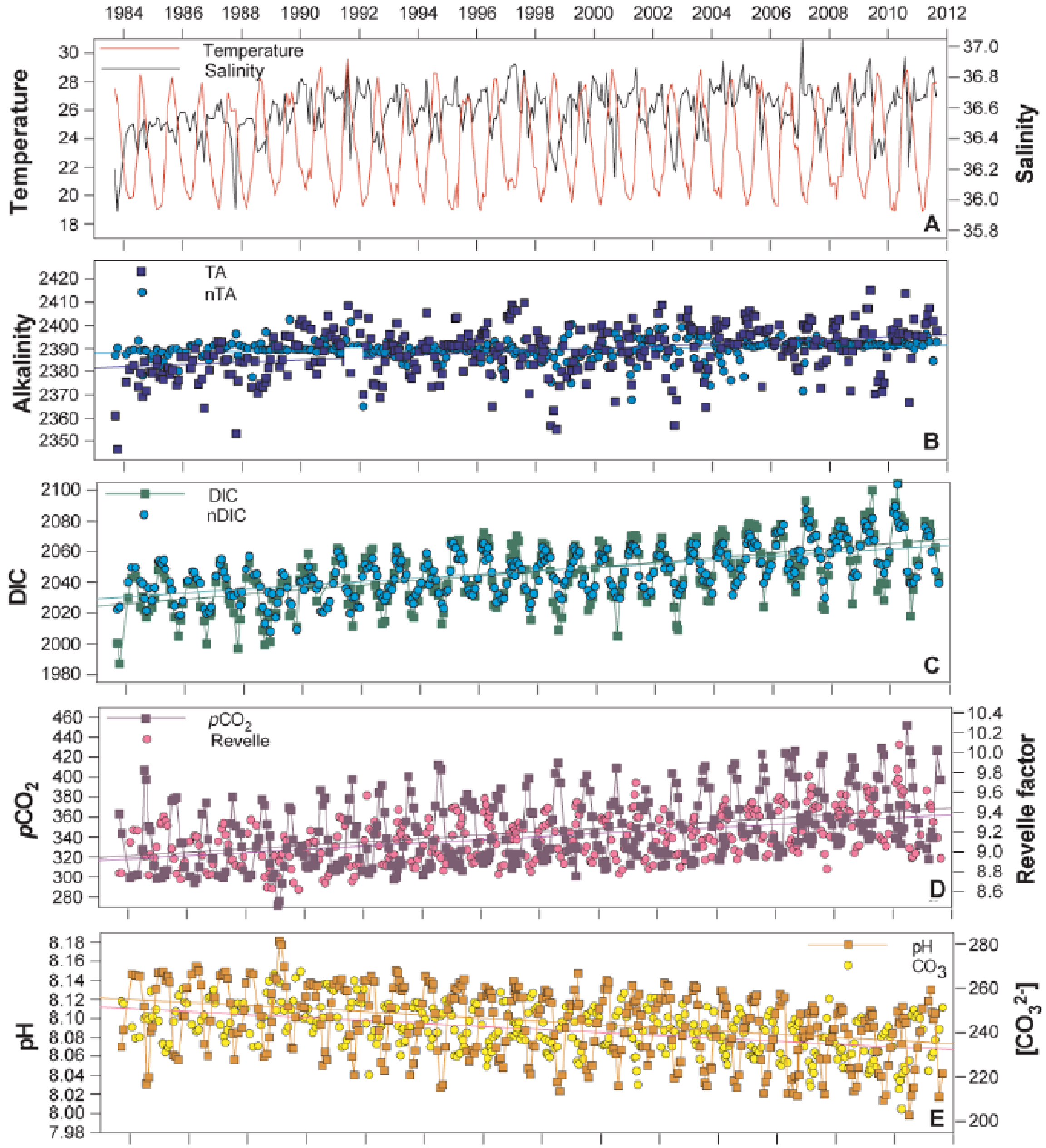


Source: Hammer et al., 2017

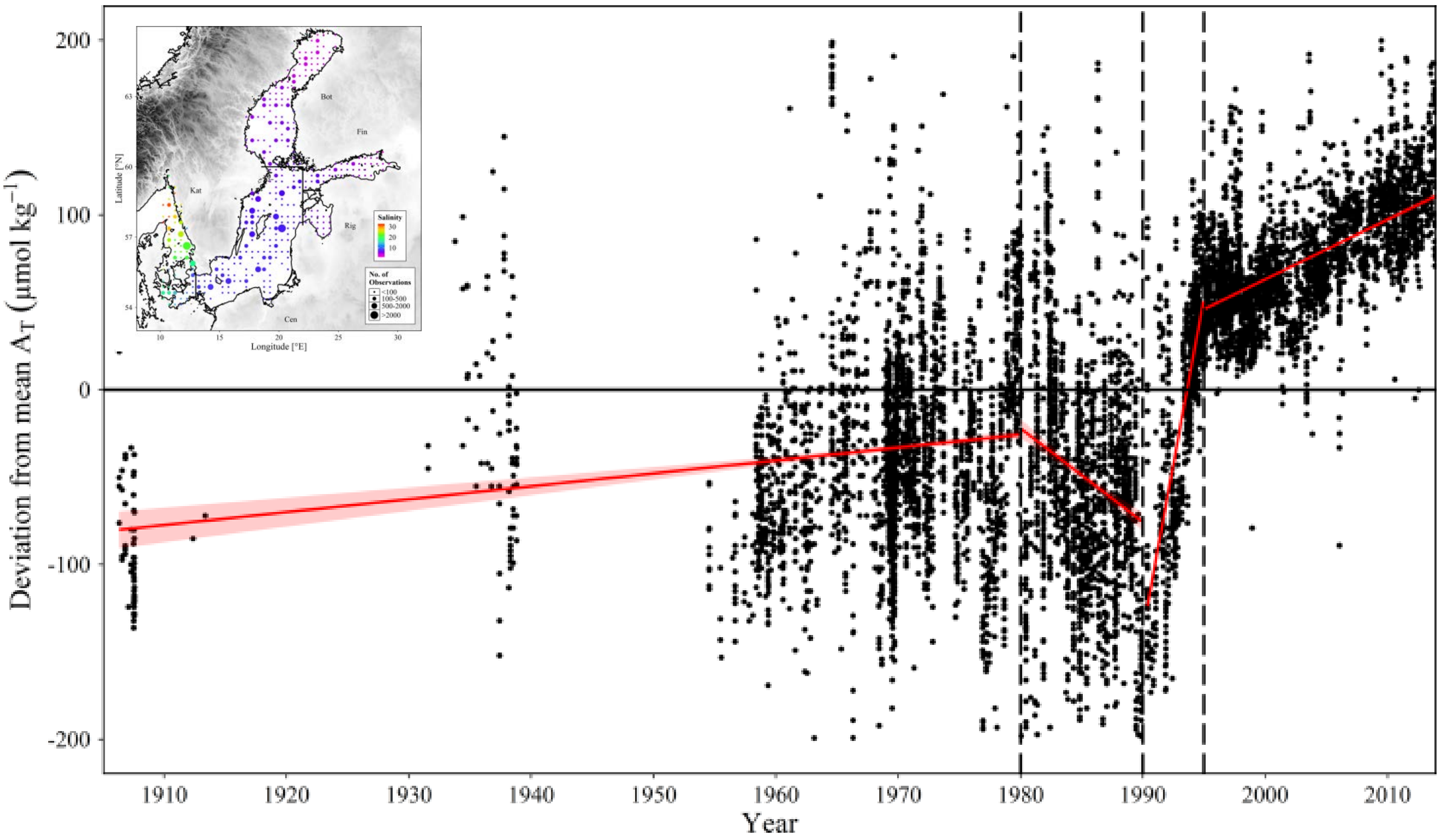


Source: Kuliński et al., 2017 modified after Omstedt et al., 2010

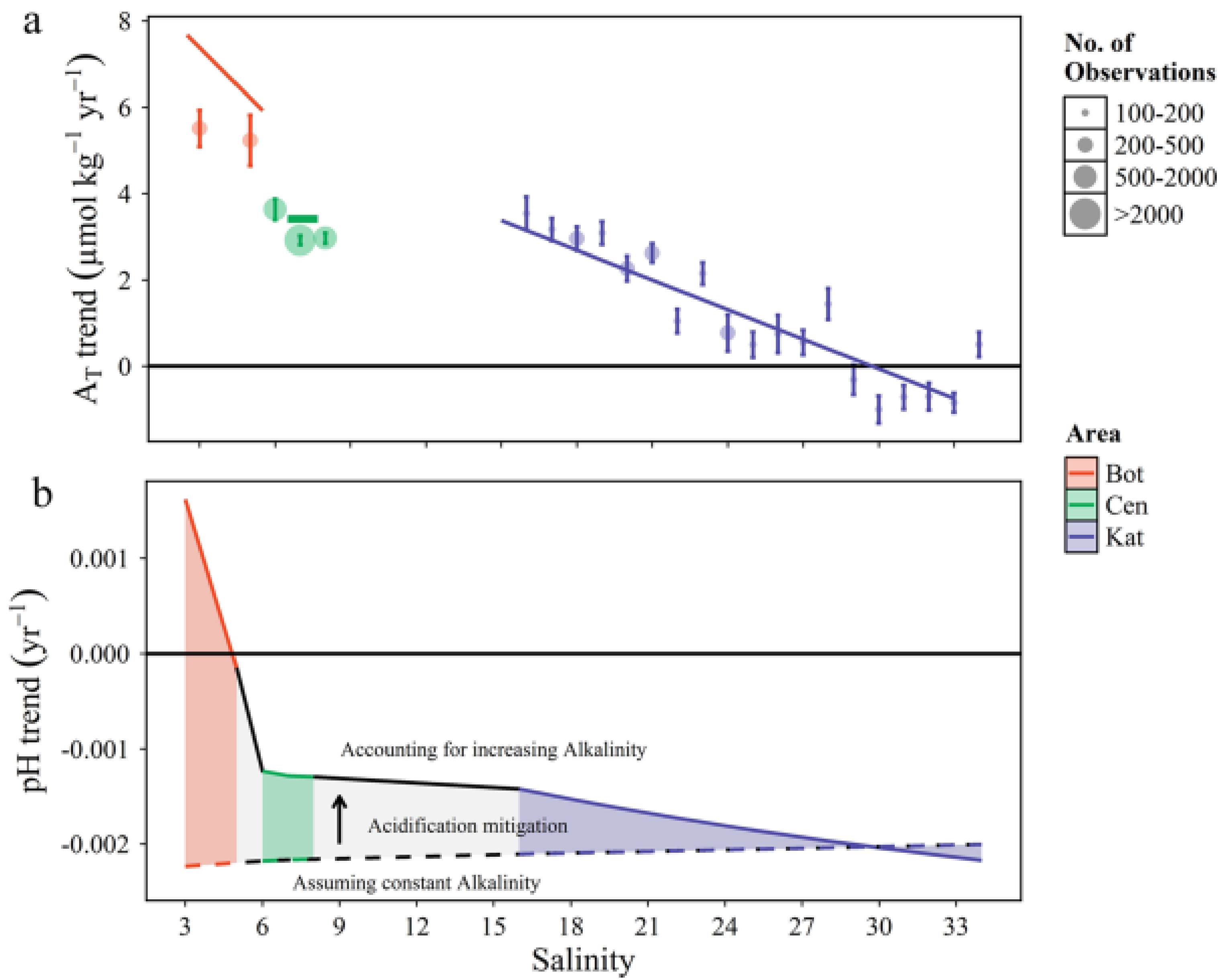
BATS - Bermuda Atlantic Time-series Study



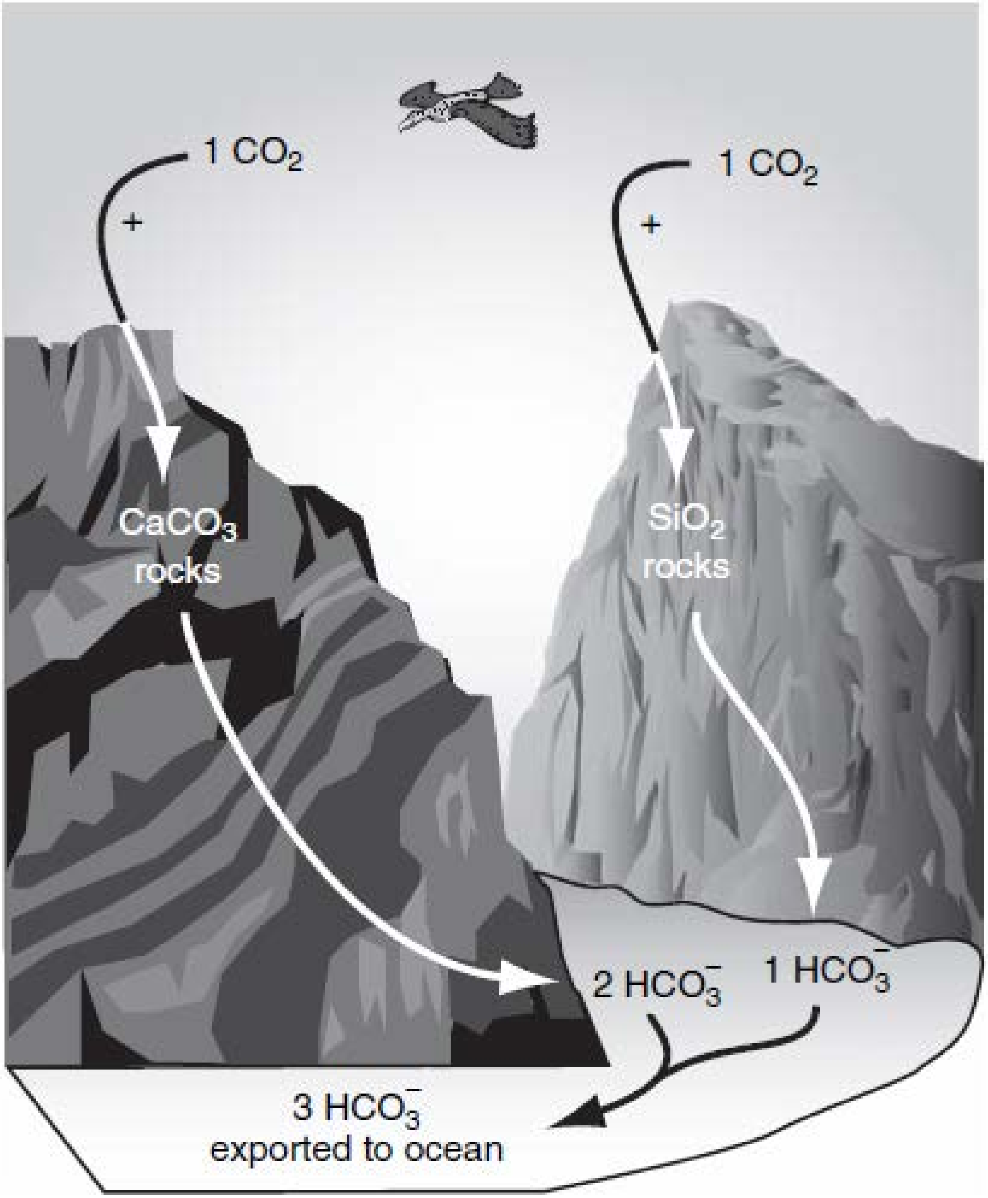
Source: Bates et al., 2012



Source: Müller et al., 2016



Source: Müller et al., 2016



Source: Emerson & Hedges, 2008

Sediments – source of alkalinity

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2 \rightarrow 106CO_2 + 16H^+ + 16NO_3^- + 122H_2O + H_3PO_4$$

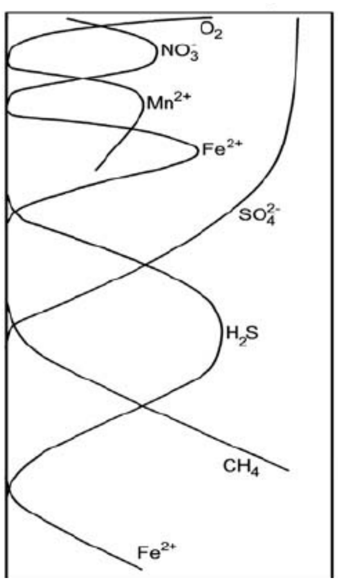
ΔA_T **= -16**

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 236MnO_2 + 472H^+ \rightarrow 236Mn^{2+} + 106CO_2 + 8N_2 + 366H_2O + H_3PO_4$$

ΔA_T **= +472**

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 84.8H^+ + 84.8NO_3^- \rightarrow 106CO_2 + 42.4N_2 + 16NH_3 + 148.4H_2O + H_3PO_4$$

ΔA_T **= +100.8**



$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 212Fe_2O_3 + 848H^+ \rightarrow 424Fe^{2+} + 106CO_2 + 16NH_3 + 530H_2O + H_3PO_4$$

ΔA_T **= +864**

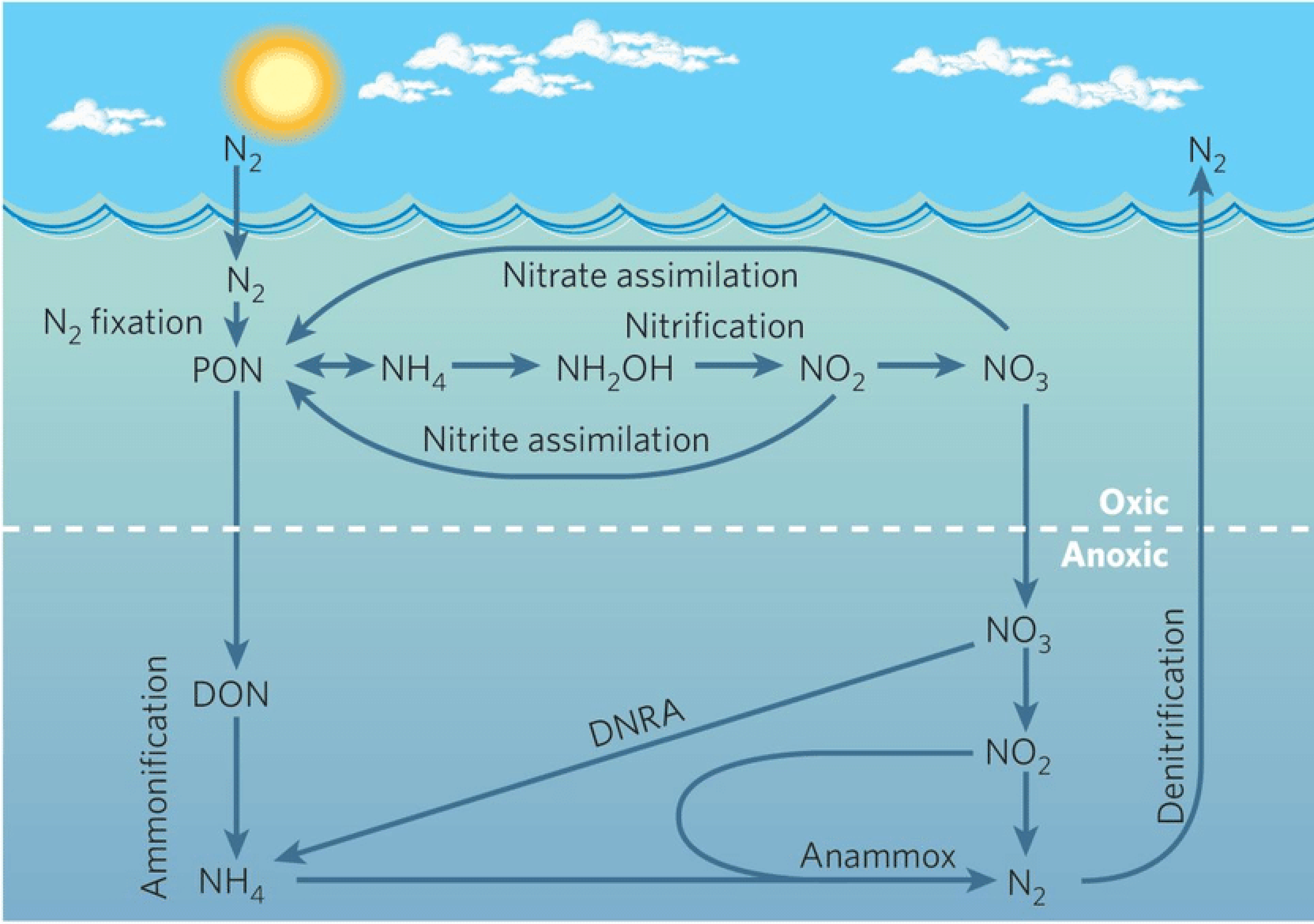
$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53SO_4^{2-} \rightarrow 106CO_2 + 16NH_3 + 53S^{2-} + 106H_2O + H_3PO_4$$

ΔA_T **= +122**

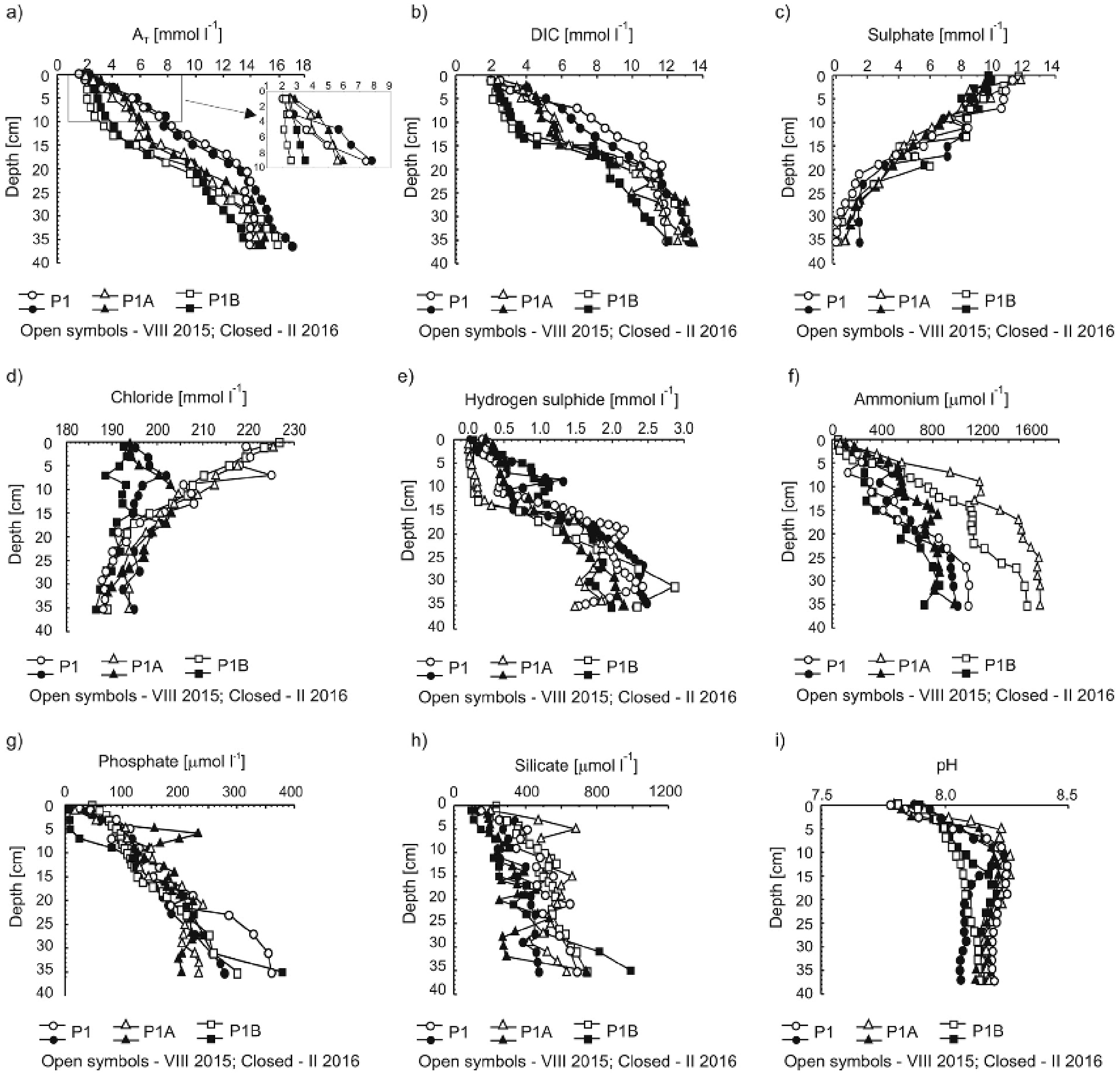
$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) \rightarrow 53CO_2 + 53CH_4 + 16NH_3 + H_3PO_4$$

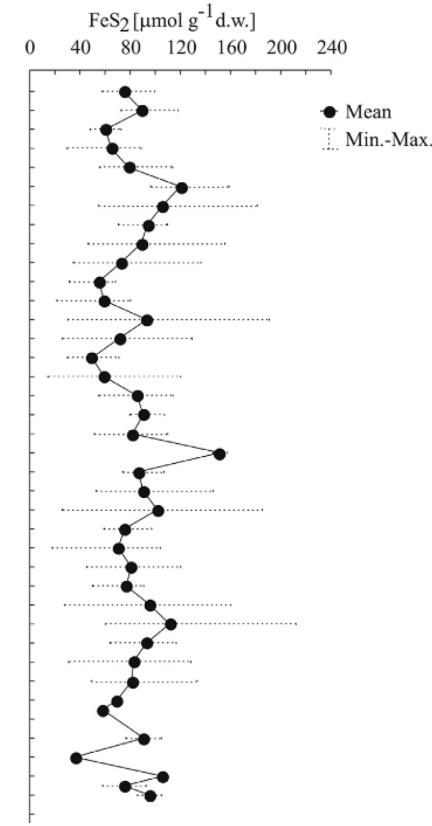
ΔA_T **= +16**

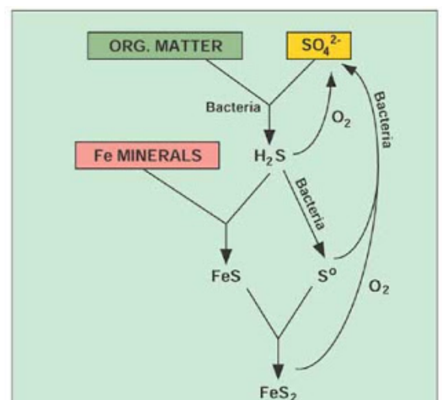
Source: Kuliński et al., 2017



Source: Arrigo, 2005

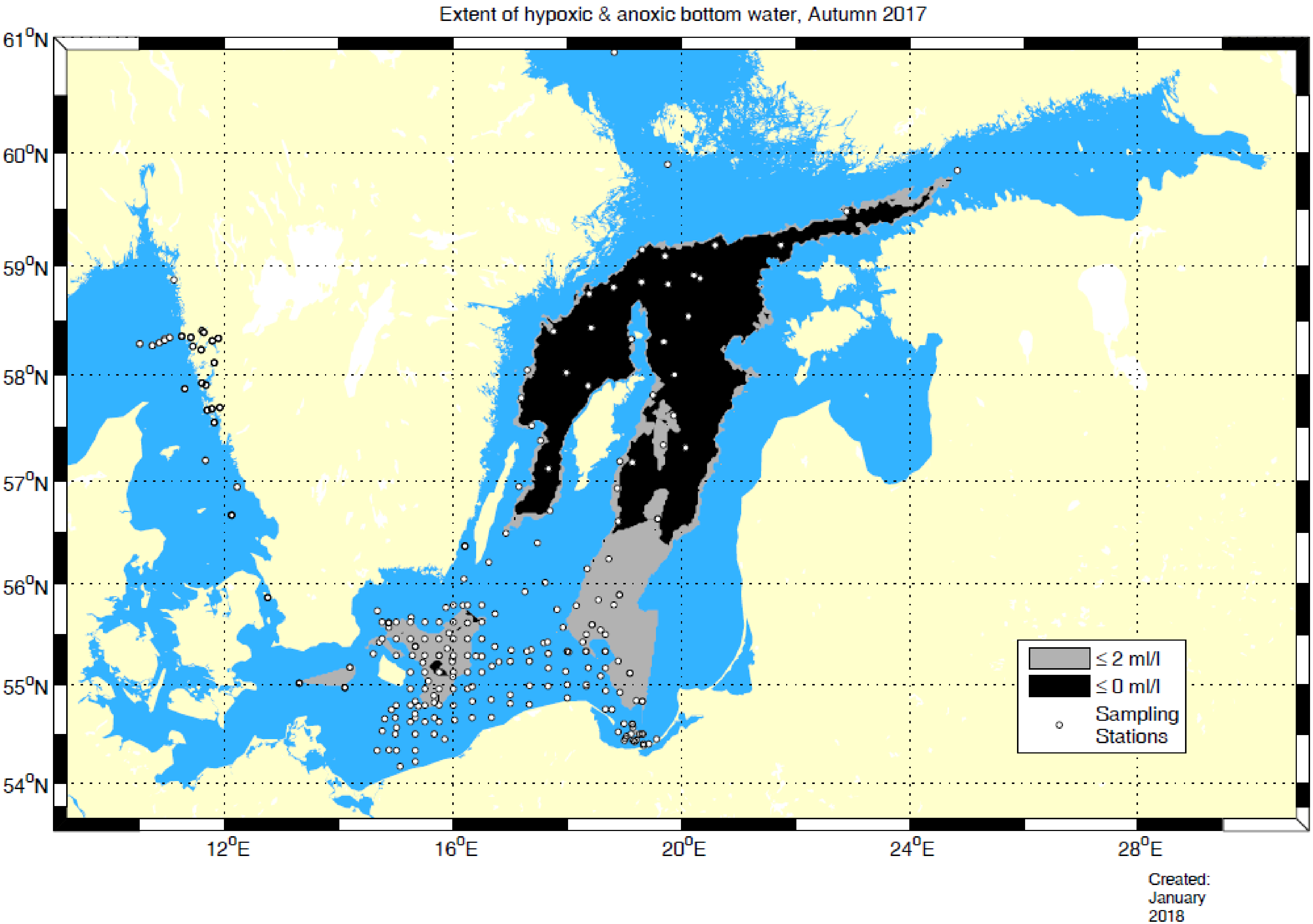




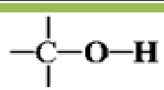
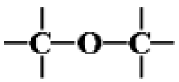
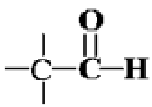
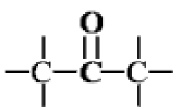
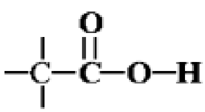
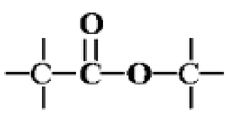
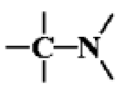
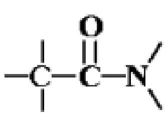


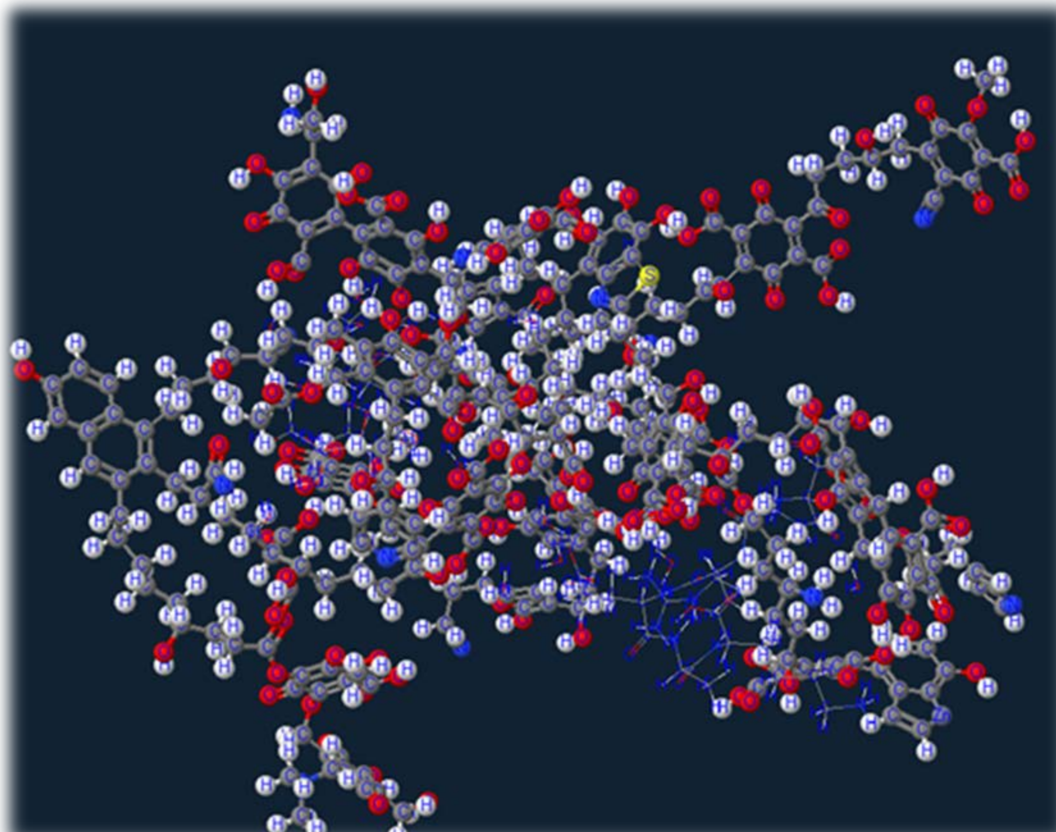
Source: Berner, 1983

Source: Łukawska-Matuszewska & Graca, 2018

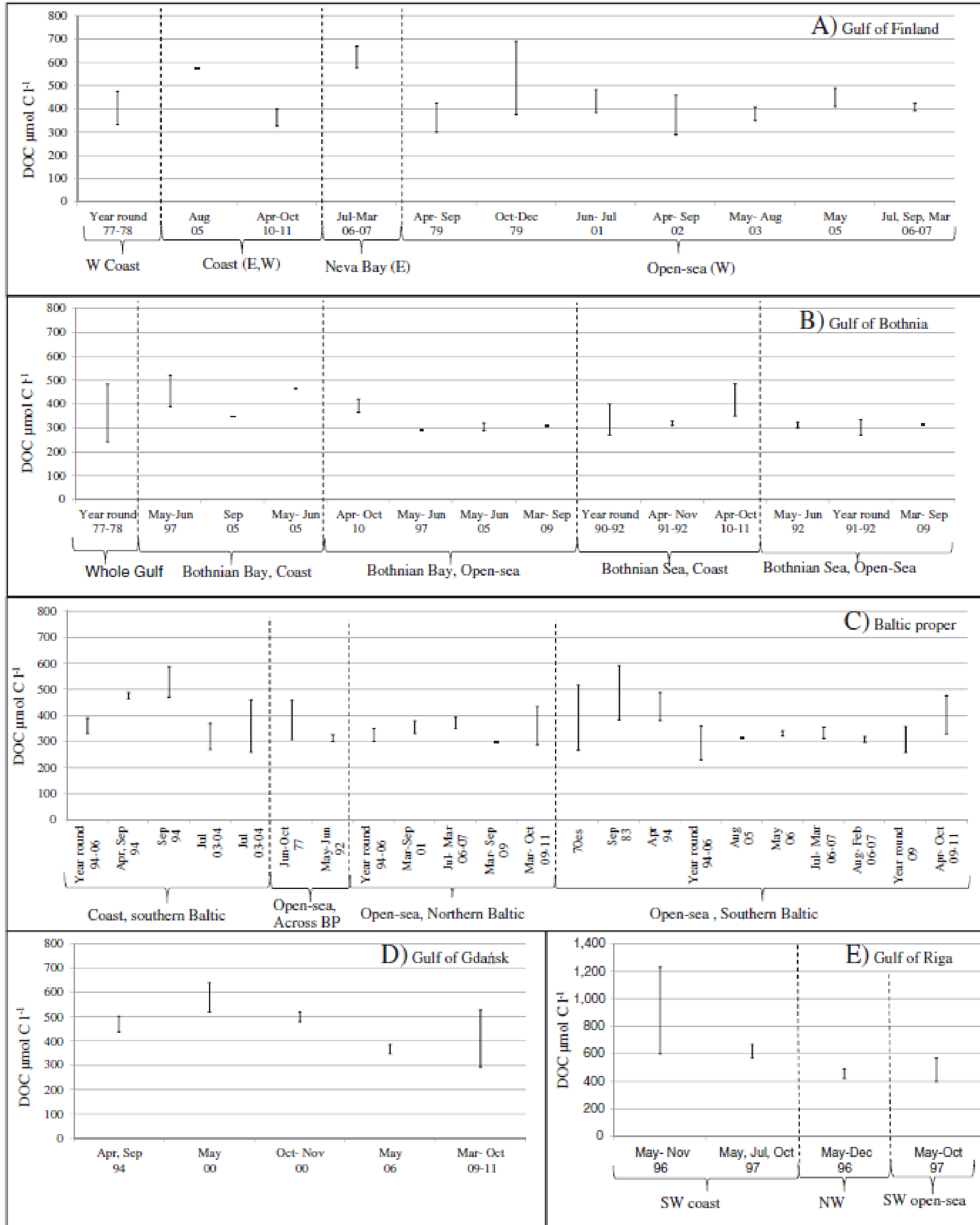


Source: HELCOM

Group	Structure	Exchange H ?
Alcohol		Yes
Phenol		Yes
Ether		
Aldehyde		No
Ketone		
Carboxyl		Yes
Ester		
Amine		Yes
Amide		Yes

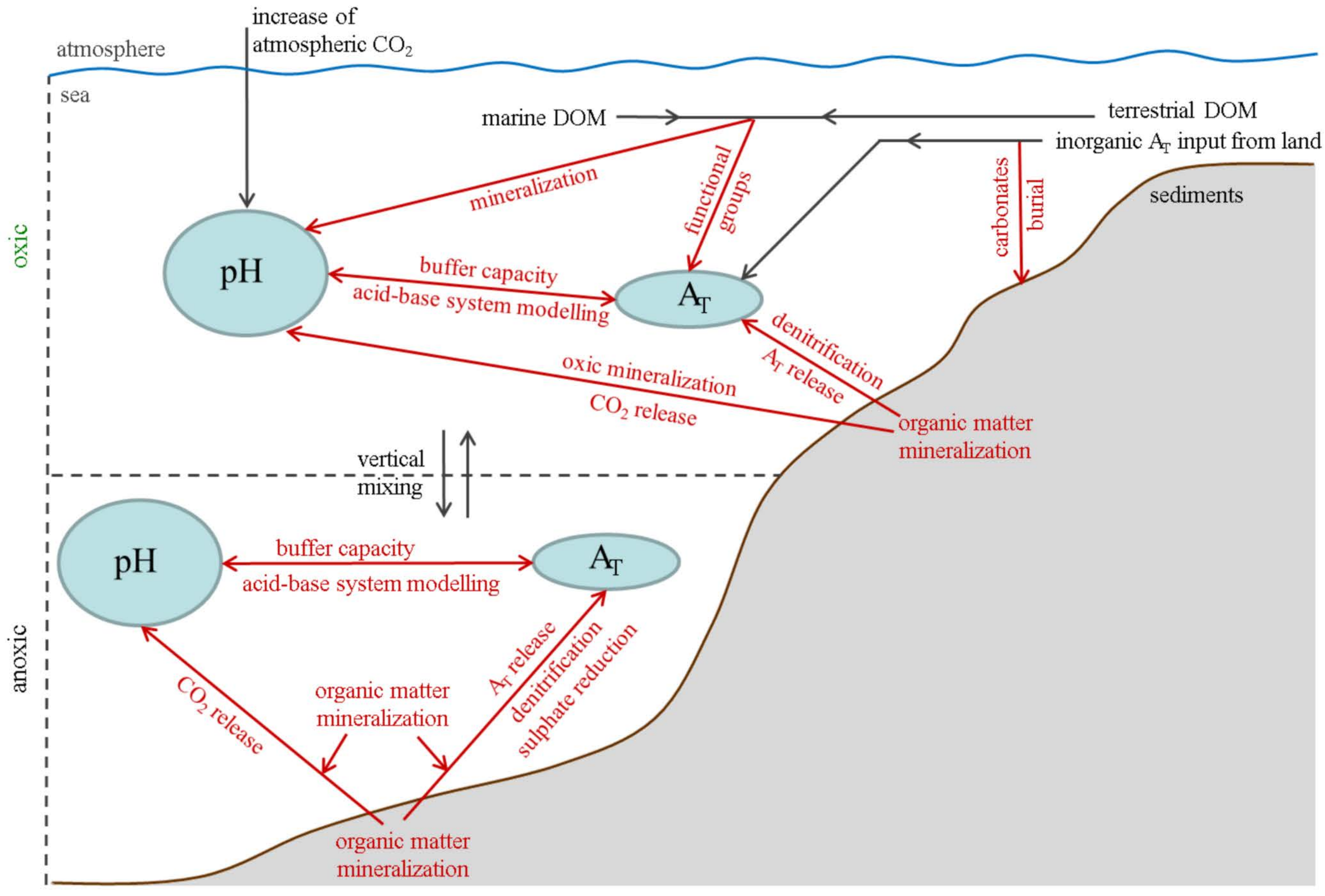


hypothetical structure of humic-like substances



Source: Hoikkala et al., 2015

Peculiarities of the acid-base system in the Baltic Sea



Question:

Name the nation we all hate?

Answer:

Exami-Nation

😂😨😂