Marine Biogeochemistry 1: The chemical constituents of seawater

Winn Johnson

30 July 2018

COESSING at University of Ghana

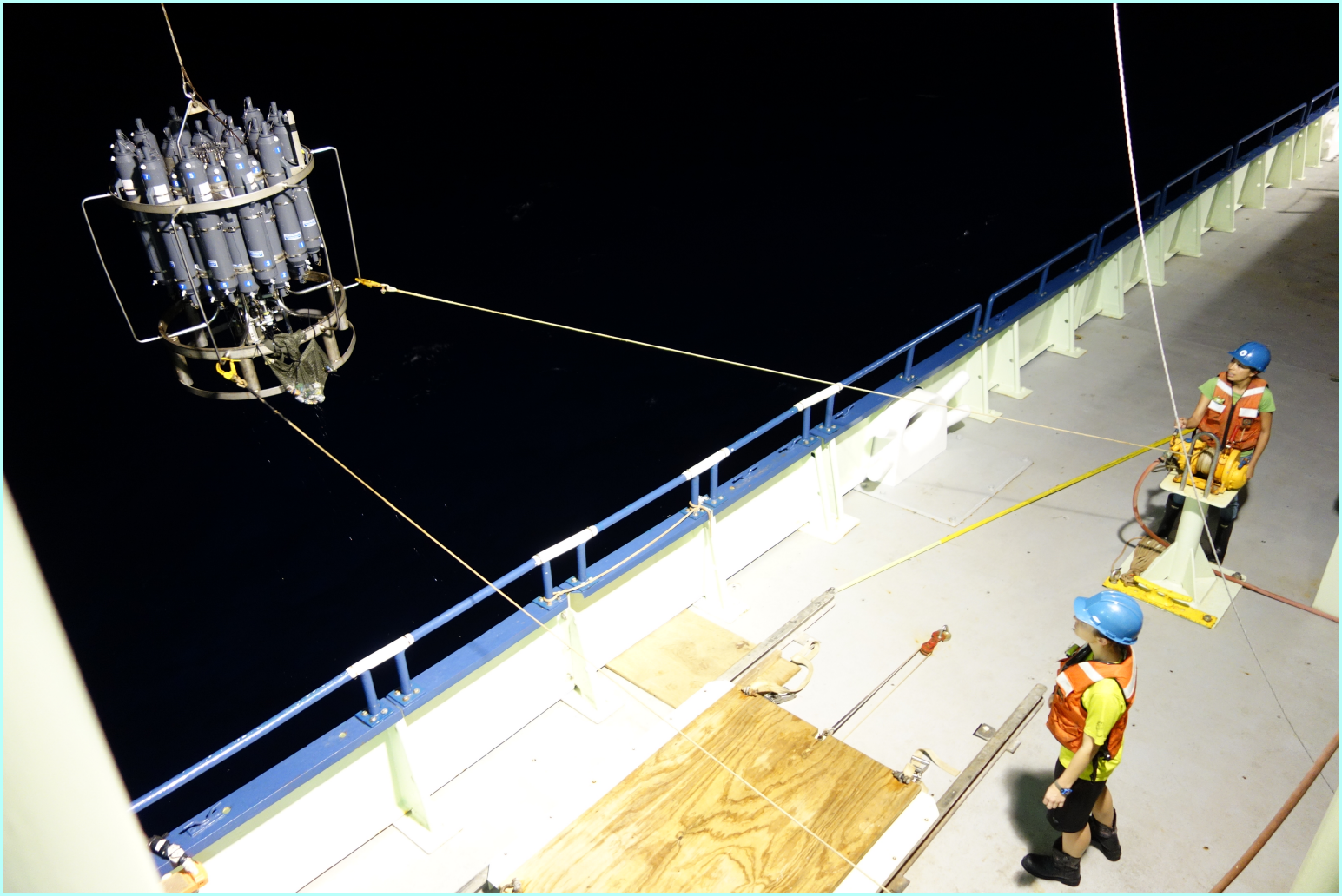
Seawater Chemistry Supports:

- ~50% O_2 production
- Absorbed ~25% CO_2 produced by humans
- 70-100 million tons of fish caught each year

Heading Out to Sea

Zoe Sandwith

Sampling the Ocean



In the Lab

Krista Longnecker

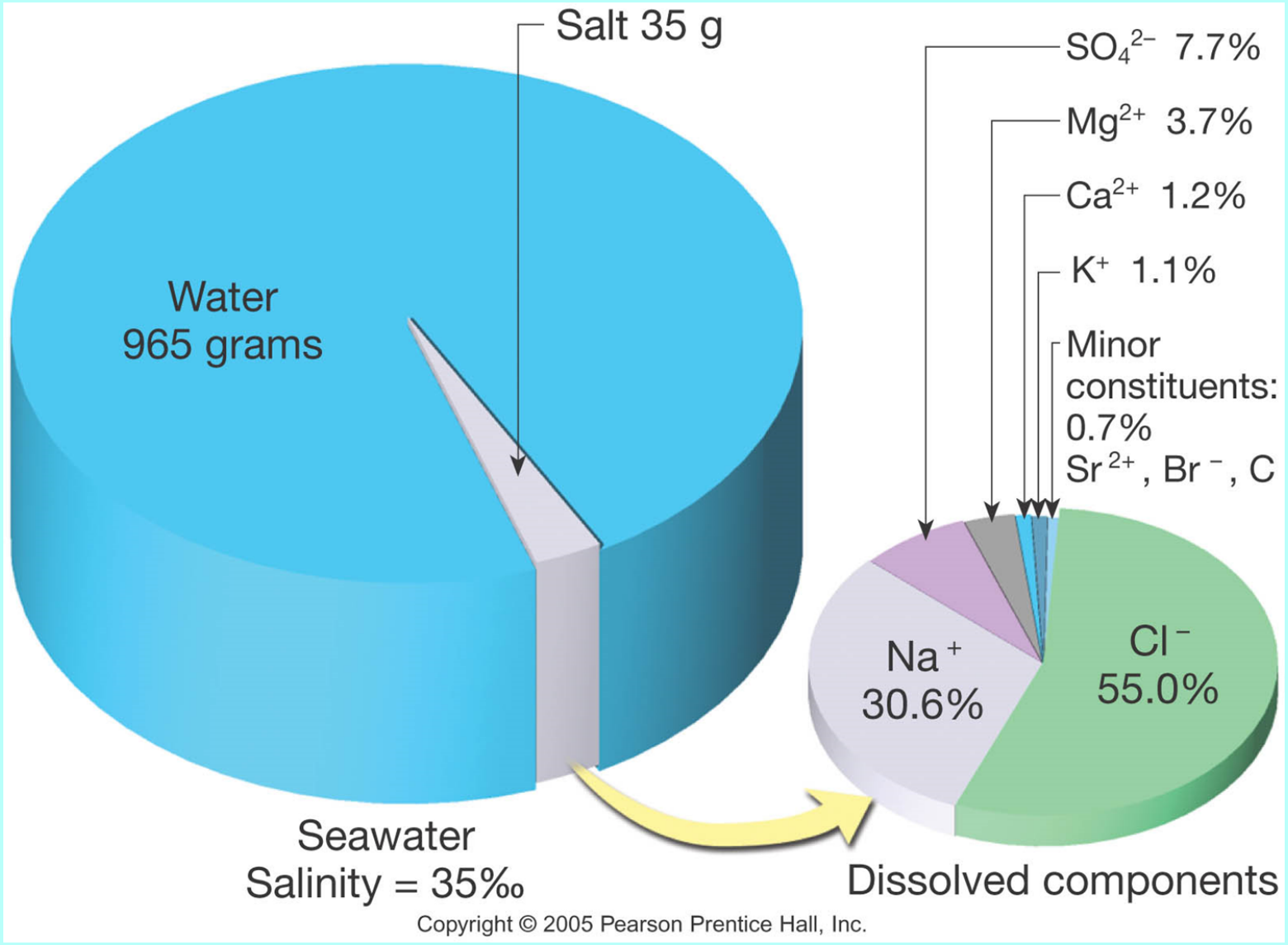
Chemical Constituents of Seawater

- Salts
- Carbonate system
- Nutrients
- Trace Metals
- Organic Matter
- Gases

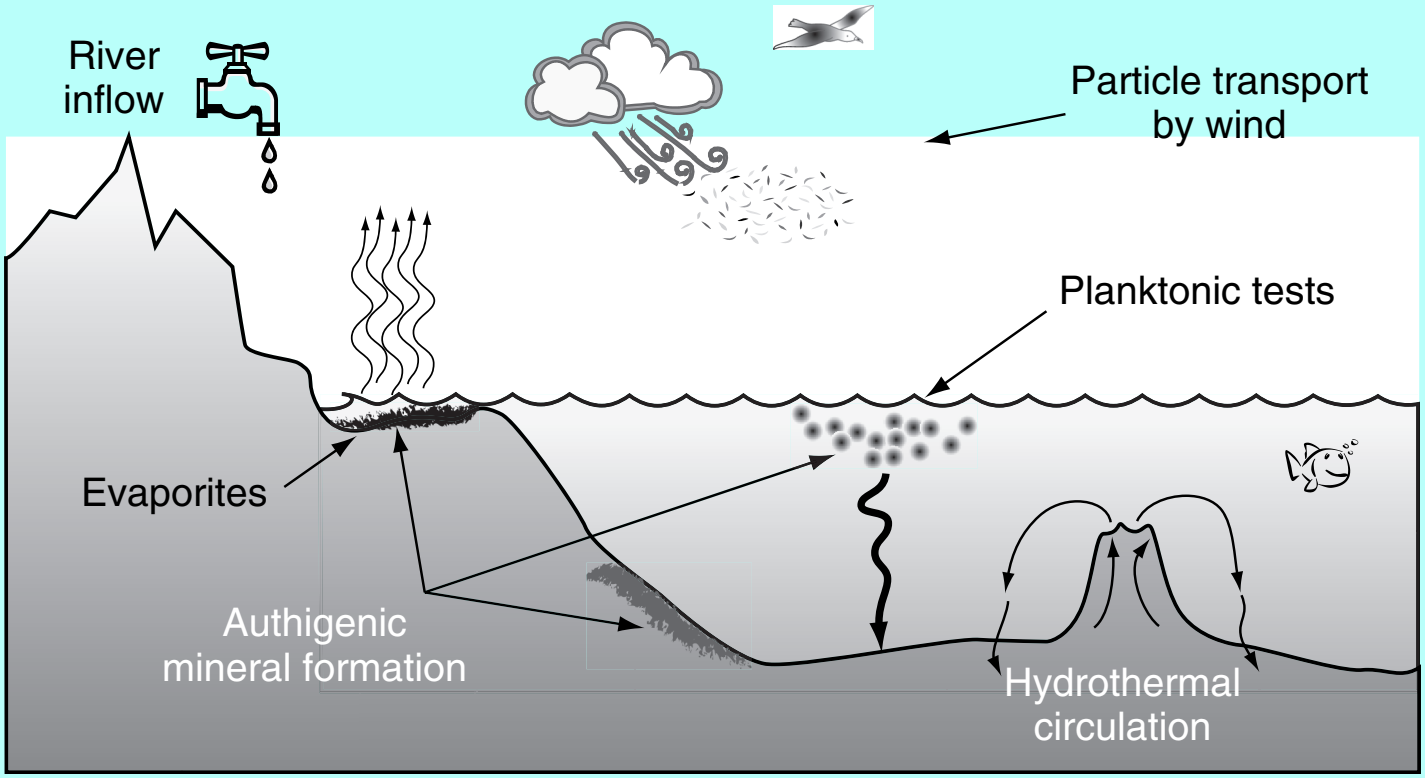
Salts

- Density
- Freezing point
- Ionic strength
- Complexes with other ions
- Analytical challenges

Salt in the Ocean



Sources and Sinks of Chemical Constituents



Emerson & Hedges, 2008

Residence Time

Assume steady state: inputs = outputs

Residence Time (years) = ocean inventory (mol) / river inflow rate (mol y^{-1})
or
τ = reservoir / input or output

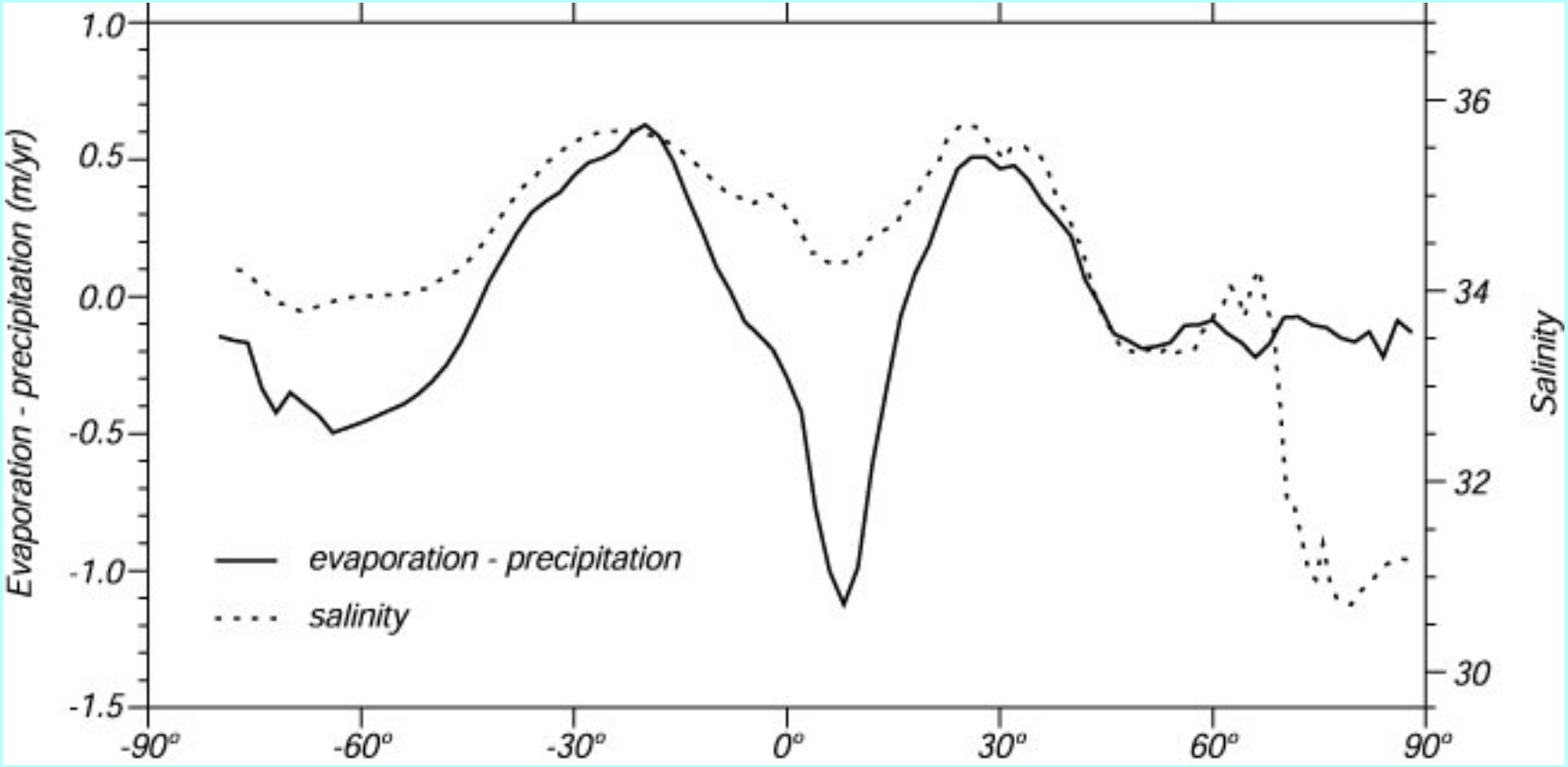
Residence Time of Water = 1.35 x 10^{18} m^3 / 3.5 x 10^{13} m^3 y^{-1} = 40,000 years

Residence Time of Na^+ = 647 x 10^{18} moles / 8.1 x 10^{12} = 80 x 10^6 years

Residence Time of Cl^- = 753 x 10^{18} moles / 7.7 x 10^{12} = 98 x 10^6 years

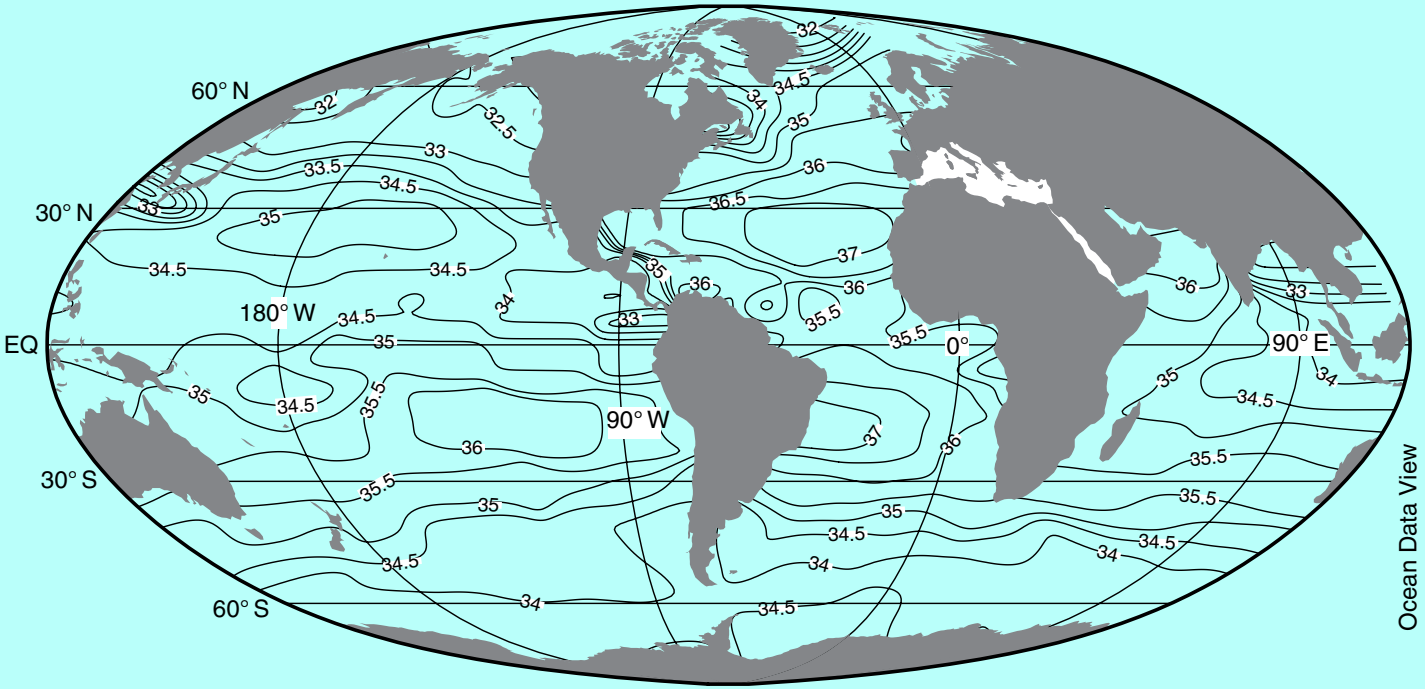
These ions reside in the ocean ~3000 times longer than the water

Evaporation and Precipitation Drive Sea Surface Salinity



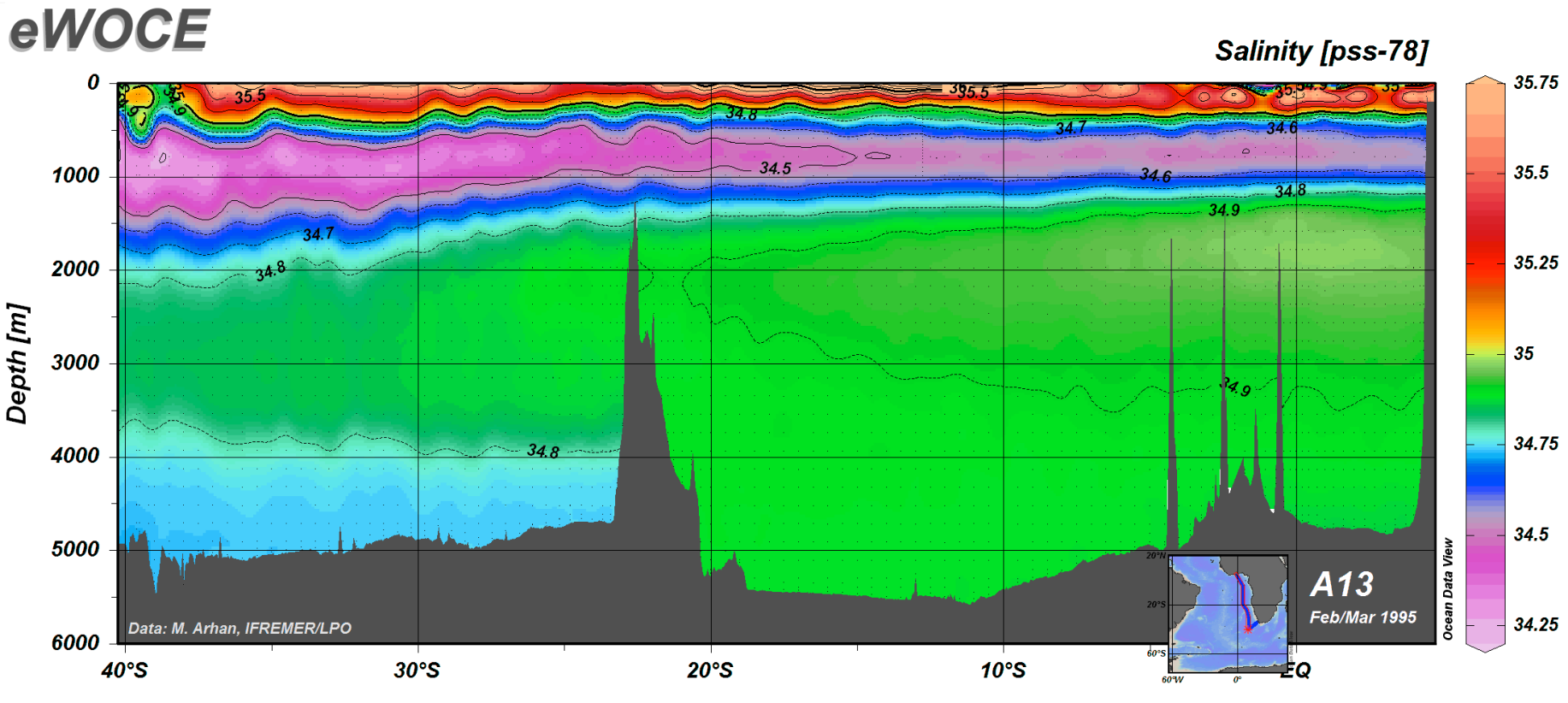
Levitus, 1982

Global Sea Surface Salinity



Emerson & Hedges, 2008

Section View of Salinity



www.ewoce.org

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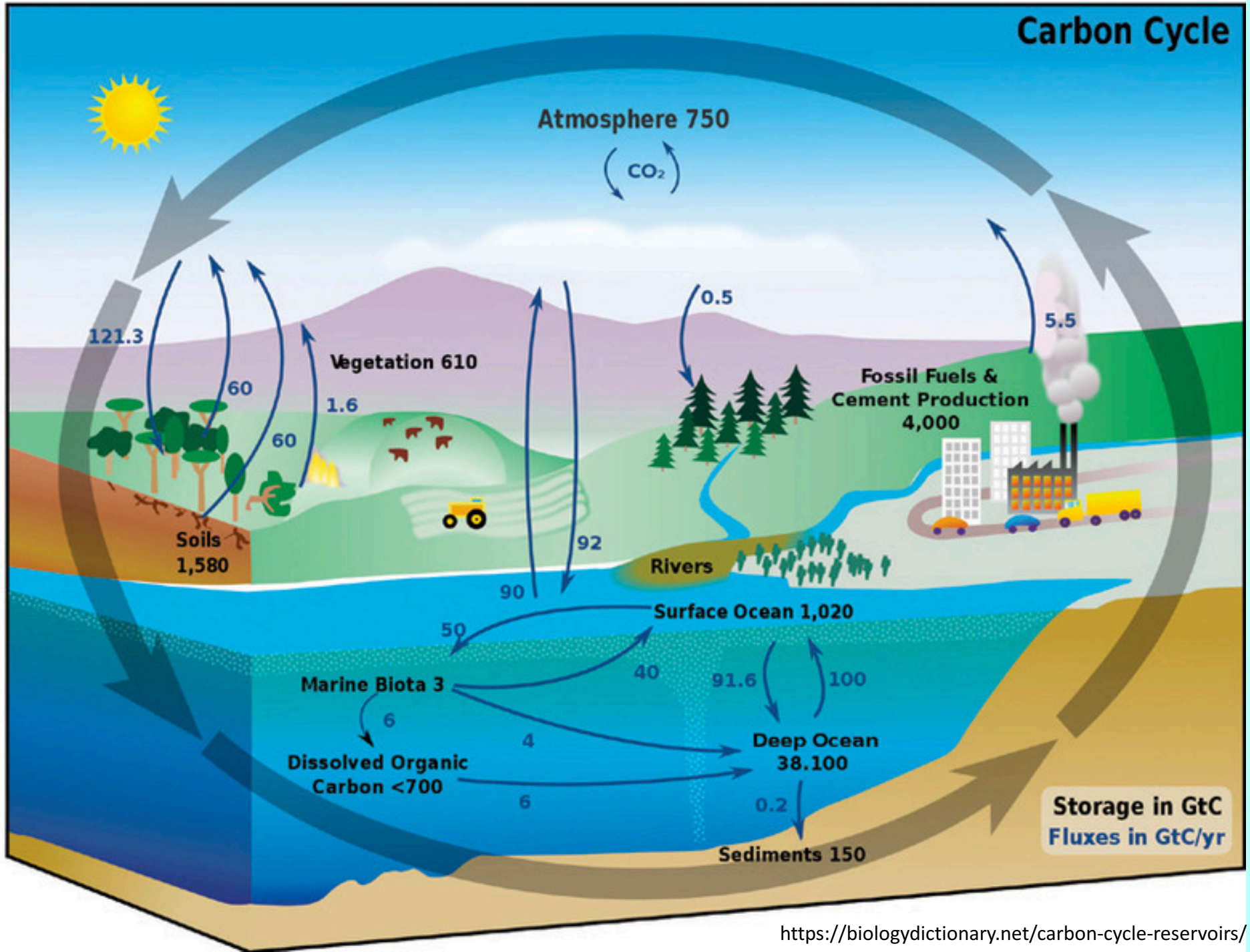
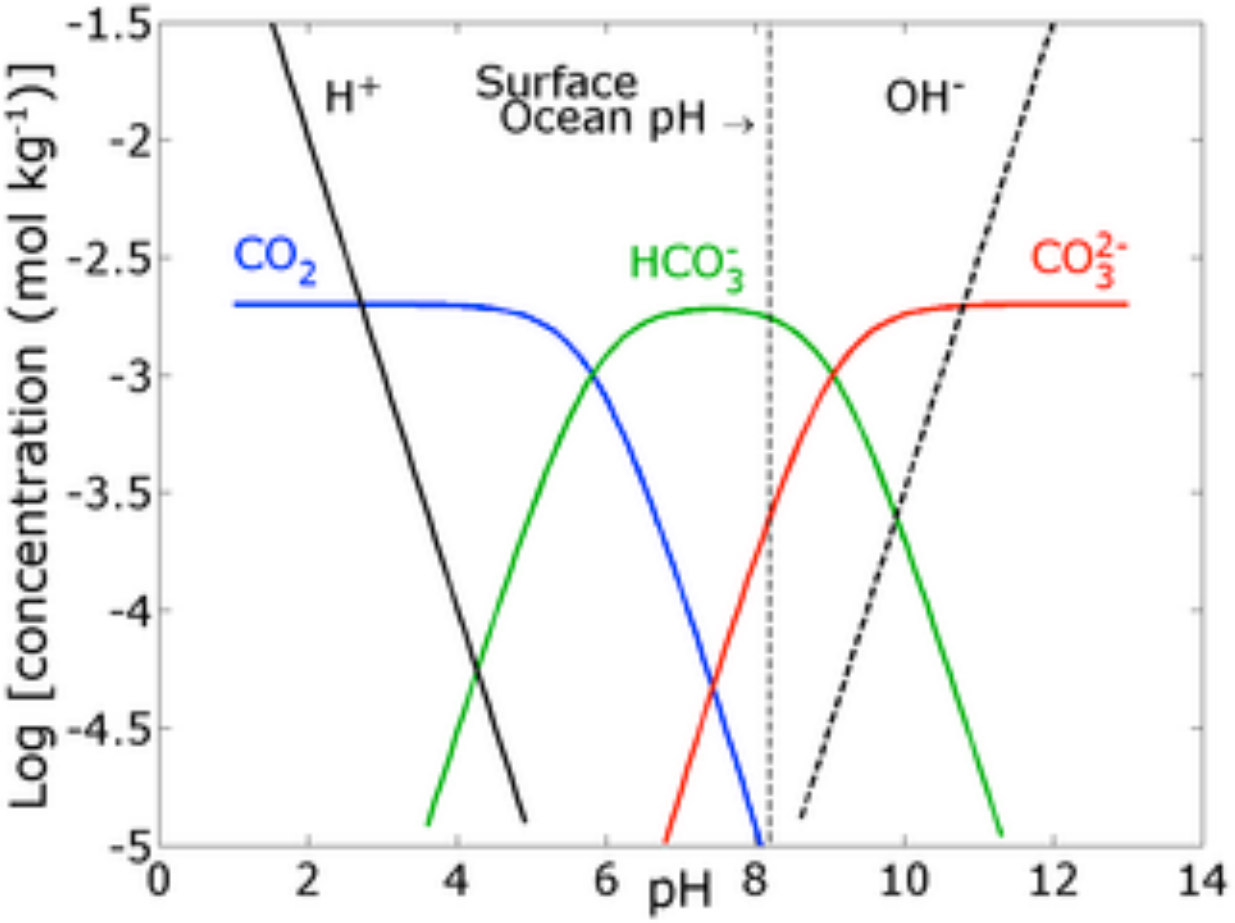
- Carbonate system
- Nutrients
- Trace Metals
- Organic Matter
- Gases



https://biologydictionary.net/carbon-cycle-reservoirs/

Carbonate System: Ocean Storage of Carbon



https://oncirculation.com/the-basics/ocean-processes/carbonate-chemistry/

$CO_2 + H_2O \rightleftarrows H_2CO_3$

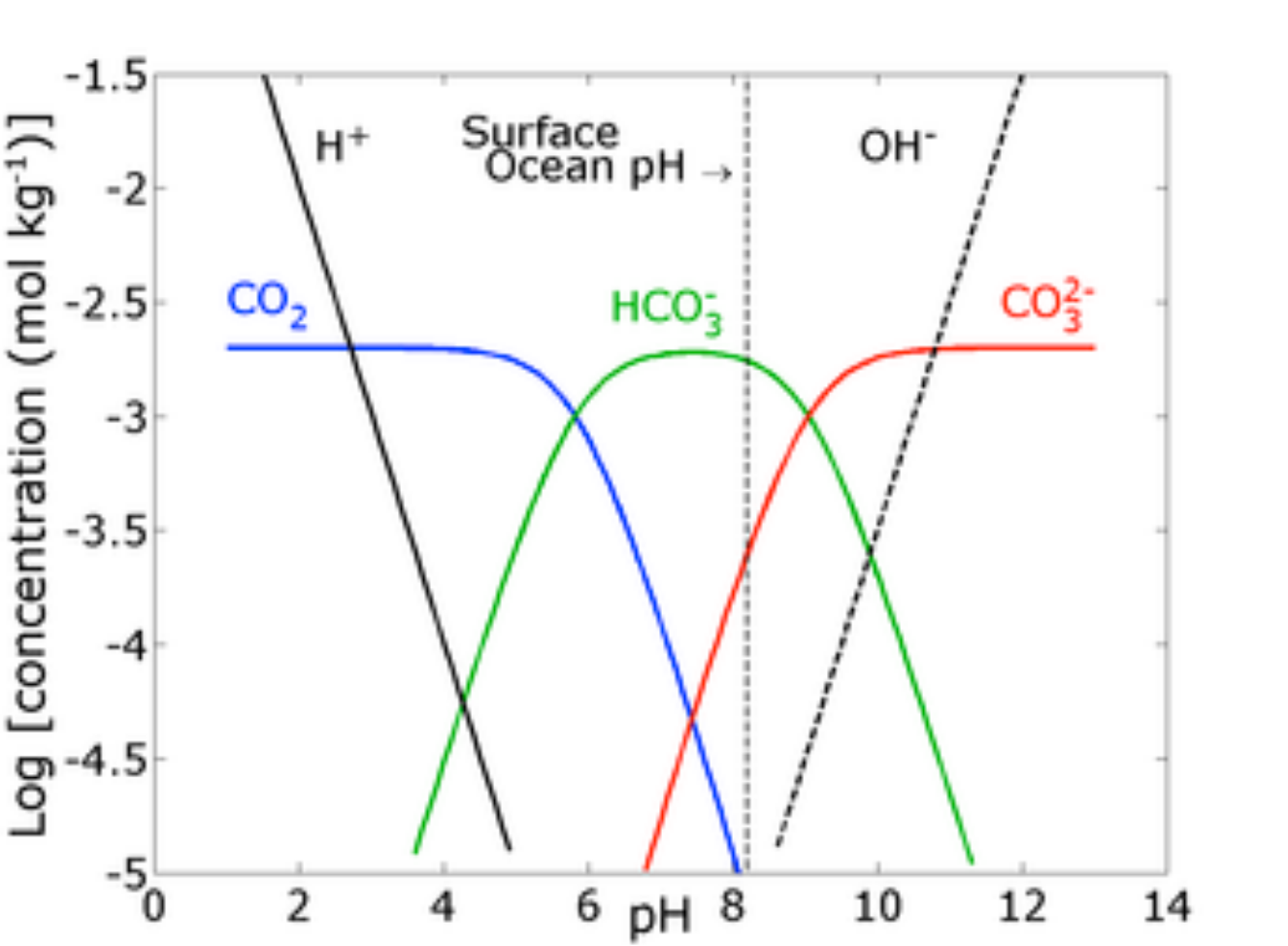
$H_2CO_3 \rightleftarrows HCO_3^- + H^+$

$HCO_3^- \rightleftarrows CO_3^{2-} + H^+$

As Atmospheric CO_2 Increases Ocean Chemistry Responds

NASA

Ocean Acidification



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$HCO_3^- \rightleftarrows CO_3^{2-} + H^+$

Ocean Acidification Can Impact Ocean Life

Physiological response	Major group	Species studied	Response to increasing CO_2 a	b	c	d
Calcification						
	Coccolithophores[1]	4	2	1	1	1
	Planktonic Foraminifera	2	2	–	–	–
	Molluscs	4	4	–	–	–
	Echinoderms[1]	3	2	1	–	–
	Tropical corals	11	11	–	–	–
	Coralline red algae	1	1	–	–	–
Photosynthesis[2]						
	Coccolithophores[3]	2	–	2	2	–
	Prokaryotes	2	–	–	1	–
	Seagrasses	5	–	–	–	–
Nitrogen Fixation						
	Cyanobacteria	1	–	1	–	–
Reproduction						
	Molluscs	4	4	–	–	–
	Echinoderms	1	1	–	–	–

1) Increased calcification had substantial physiological cost; 2) Strong interactive effects with nutrient and trace metal availability, light, and temperature; 3) Under nutrient replete conditions.

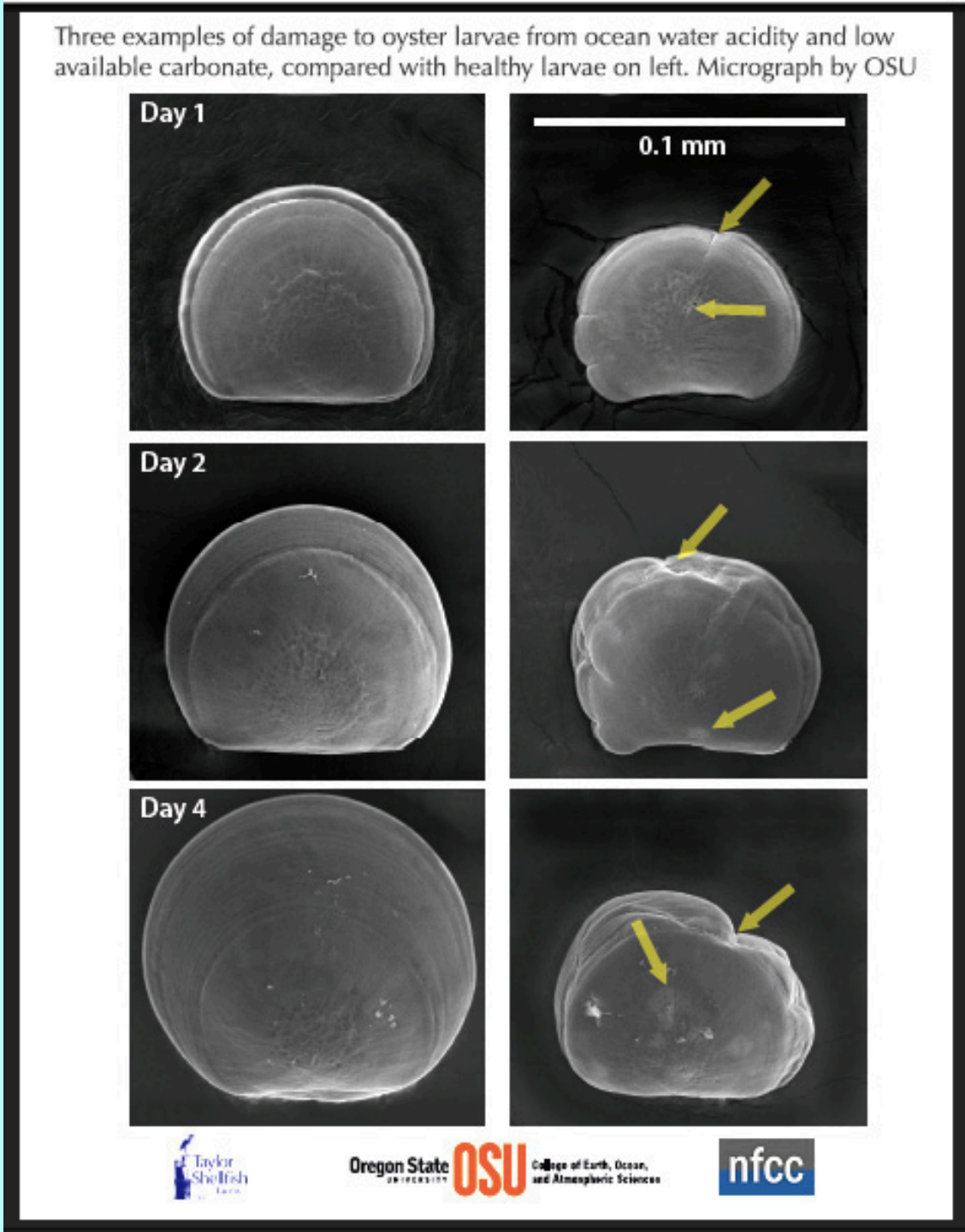
Doney et al., 2009

$CaCO_3$ ➔ $Ca^{2+} + CO_3^{2-}$

Oysters

-affects development of oysters

-already a problem on Northwest Coast of U.S.



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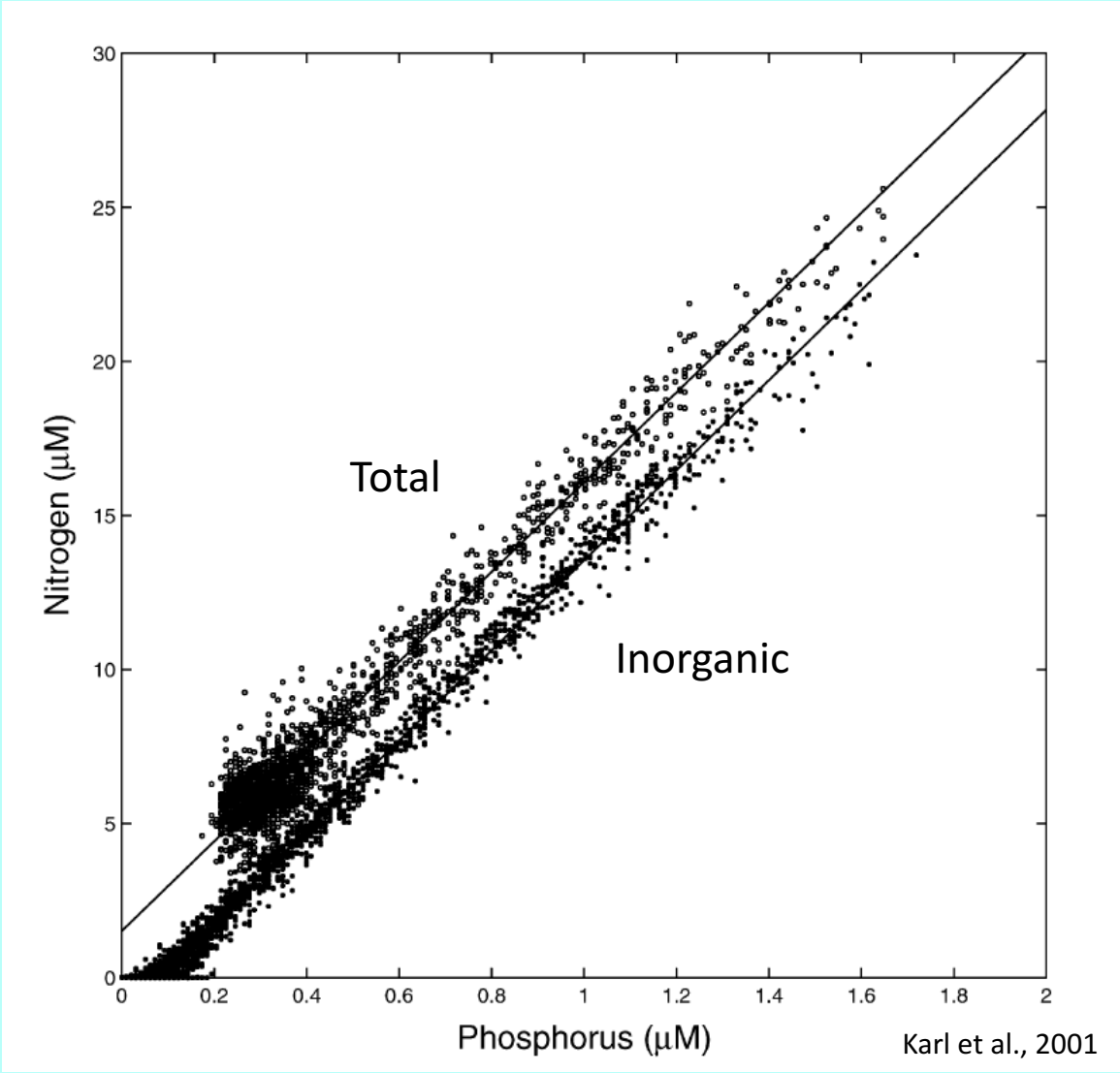
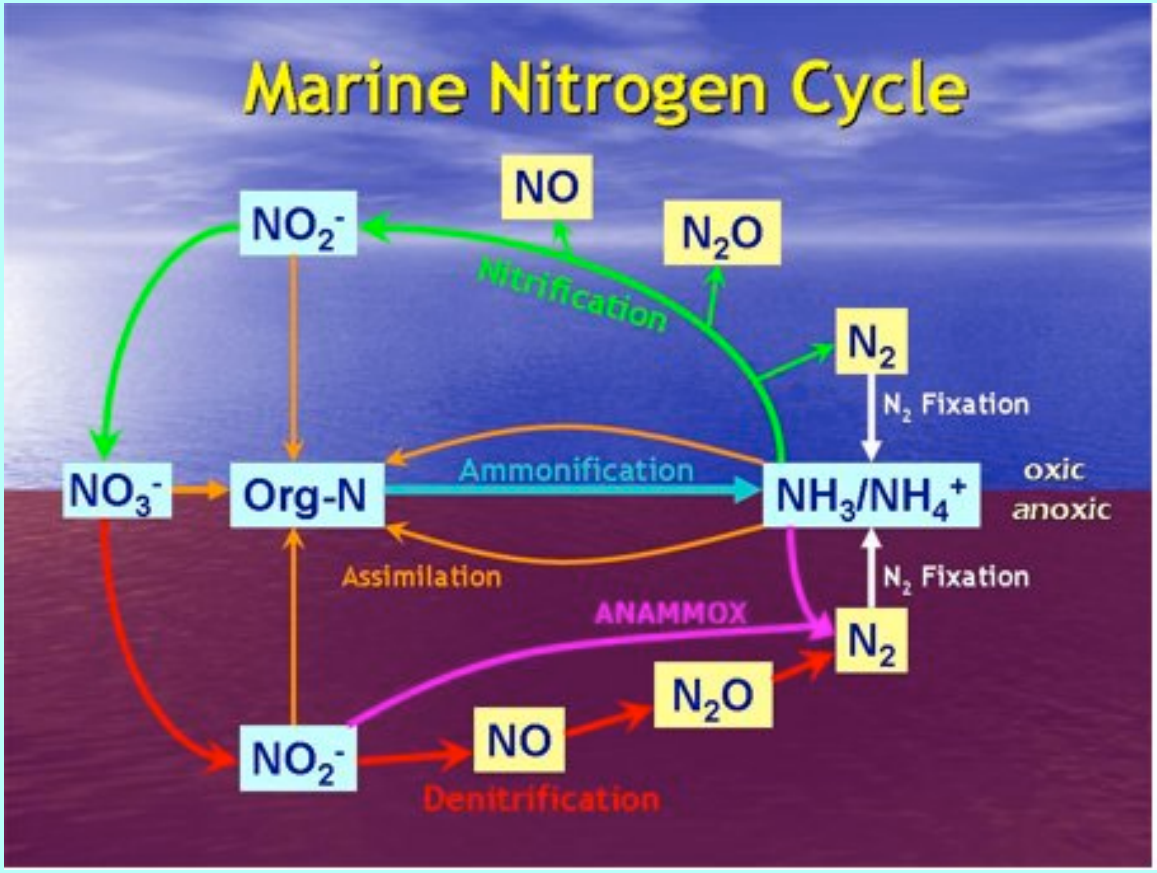
Nitrogen vs. Phosphorus Limitation



Karl et al., 2001

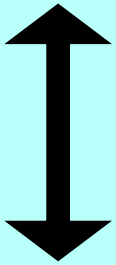
Nitrogen Cycle



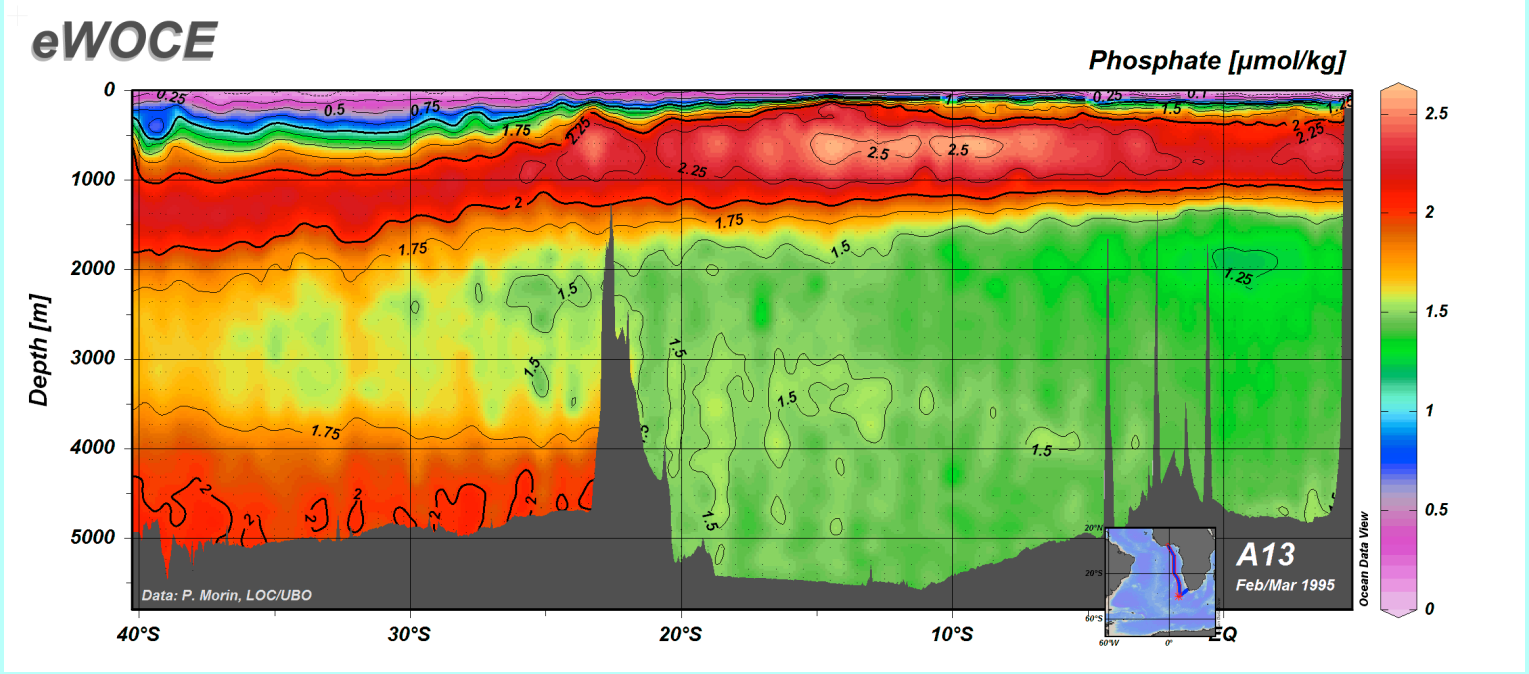
https://wordsinmocean.com/2012/09/18/challenger-2012-selected-keynote-lectures-phyllis-lam-max-planck-institute-microbial-nitrogen-cycling-in-oxygen-minimum-zones/

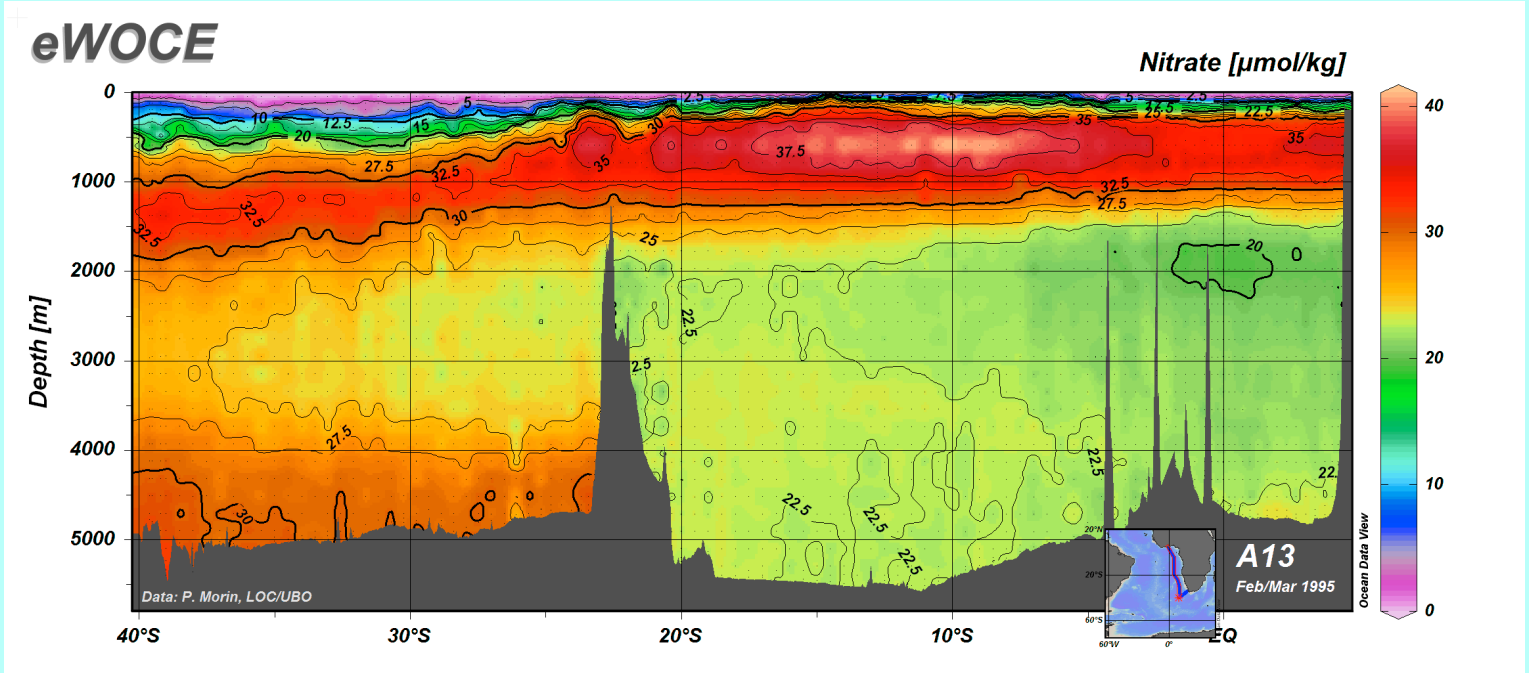
Phosphorus Cycle

PO_4^{3-}

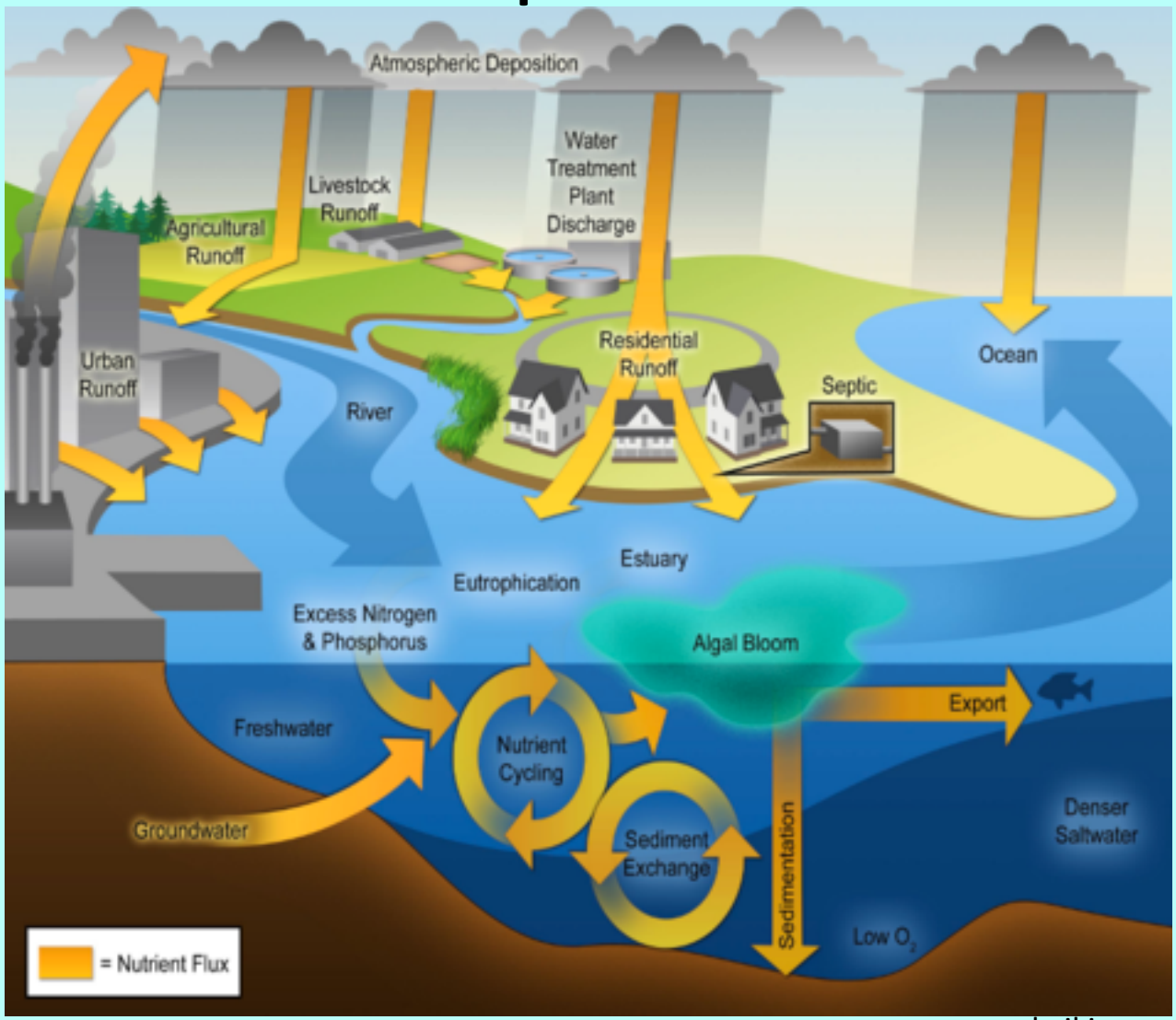


Organic
Phosphorus


eWOCE
Phosphate [µmol/kg]
Depth [m]
0
1000
2000
3000
4000
5000
40°S
30°S
20°S
10°S
EQ
Data: P. Morin, LOC/UBO
A13
Feb/Mar 1995
Ocean Data View
2.5
2
1.5
1
0.5
0


eWOCE
Nitrate [µmol/kg]
Depth [m]
0
1000
2000
3000
4000
5000
40°S
30°S
20°S
10°S
EQ
Data: P. Morin, LOC/UBO
A13
Feb/Mar 1995
Ocean Data View
40
30
20
10
0

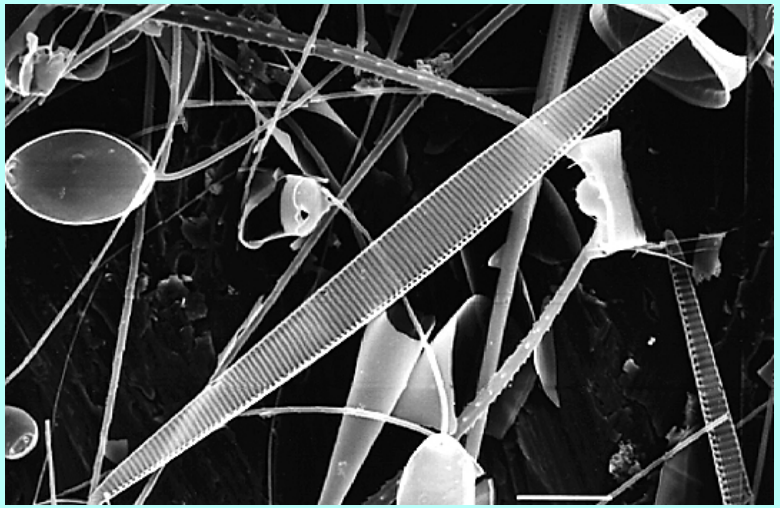
Increased Inputs of Nutrients: Eutrophication



coastalwiki.org

Harmful Algal Blooms

- Toxins
  - Shellfish poisoning
  - Fish kills
- Hypoxia
  - Blooms drawdown oxygen so quickly that an area becomes anoxic driving organisms away or killing them

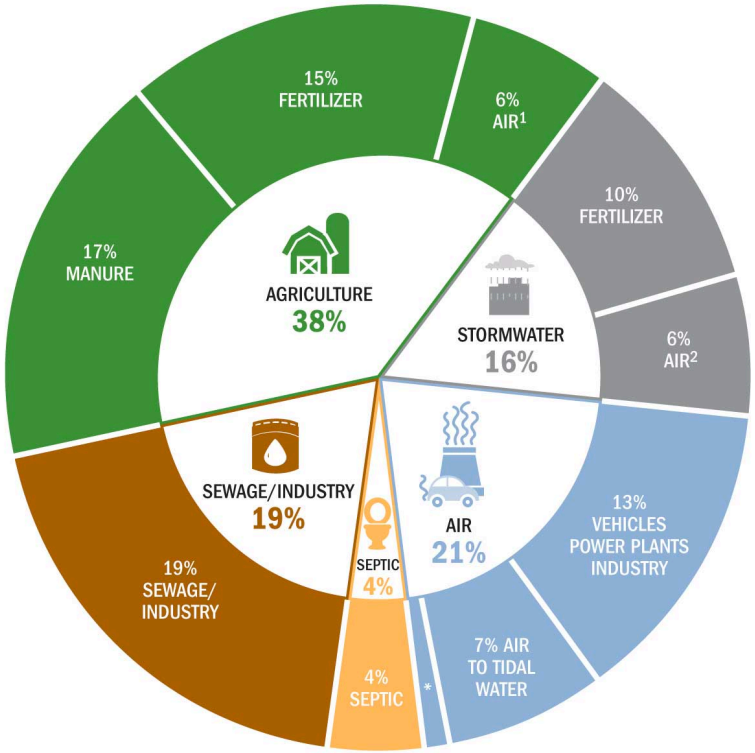


Pseudo-nitzschia australis. (J. Rines)

A Noctiluca bloom in Union Bay, British Columbia. (Lisa M. Holm)

Nitrogen Pollution to the Chesapeake Bay

By Sector



SOURCE: CHESAPEAKE BAY PROGRAM

* 1% NATURAL AIR POLLUTION

[1] AGRICULTURAL EMISSIONS OF AIR POLLUTION

[2] ASSUMING THAT ROUGHLY 40% OF TOTAL STORMWATER NITROGEN COMES FROM THE AIR

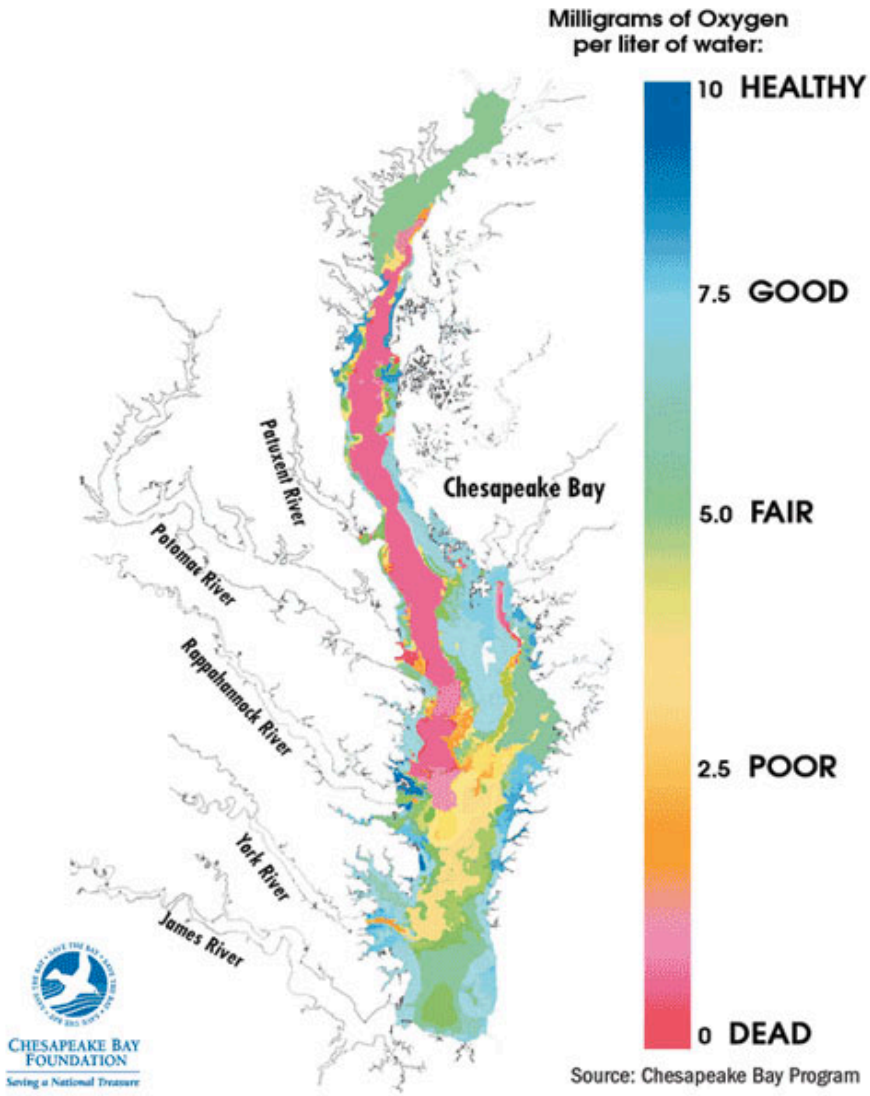
December 2012

CHESAPEAKE BAY FOUNDATION | cbf.org

Saving a National Treasure

CHESAPEAKE BAY RECORD DEAD ZONE

AUGUST 2005



Source: Chesapeake Bay Program

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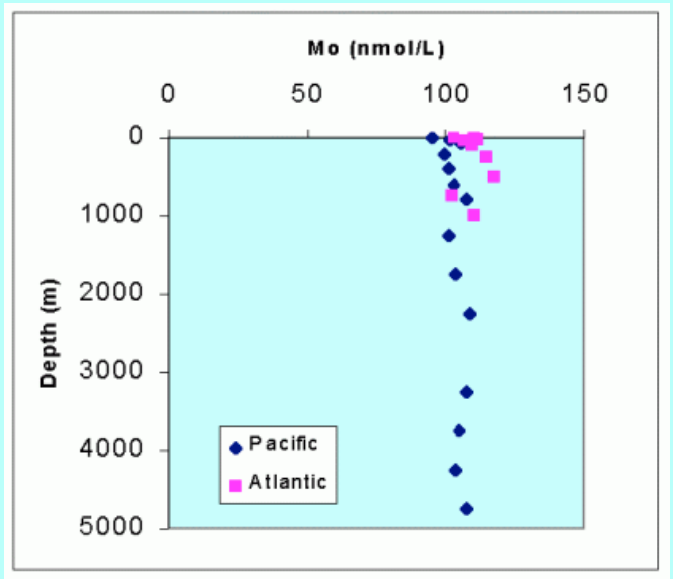
Trace Metals

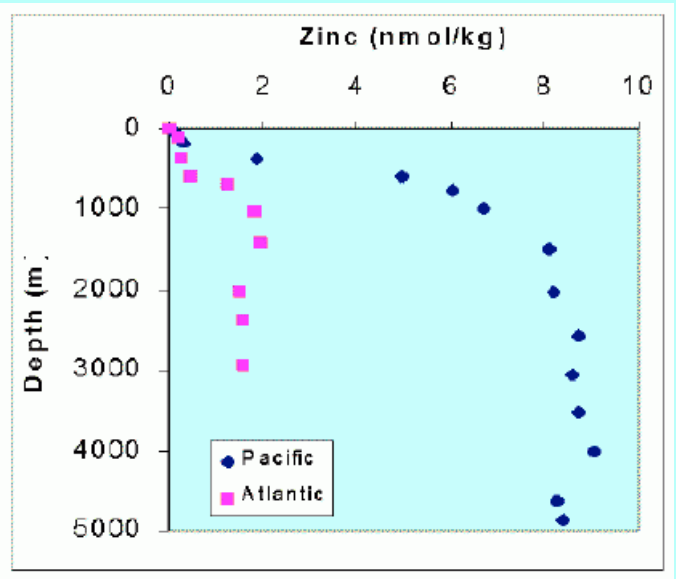
- Micronutrients
- Iron can limit nitrogen fixation
- Human contamination

Trace Metal Profiles

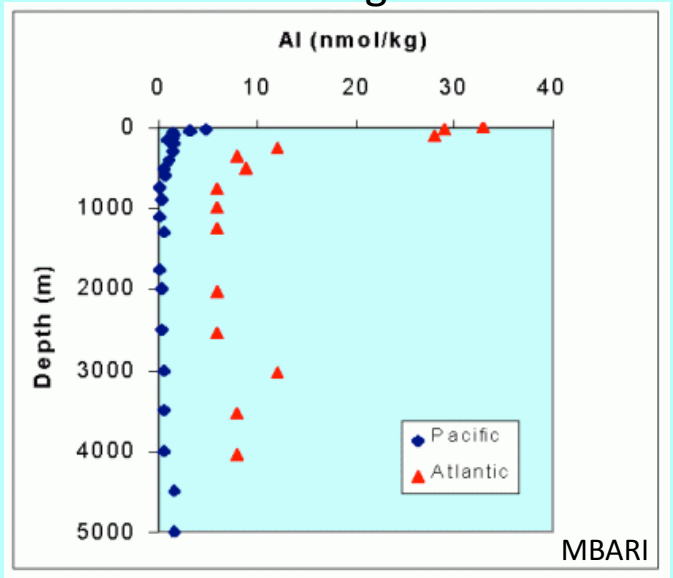
1. Conservative



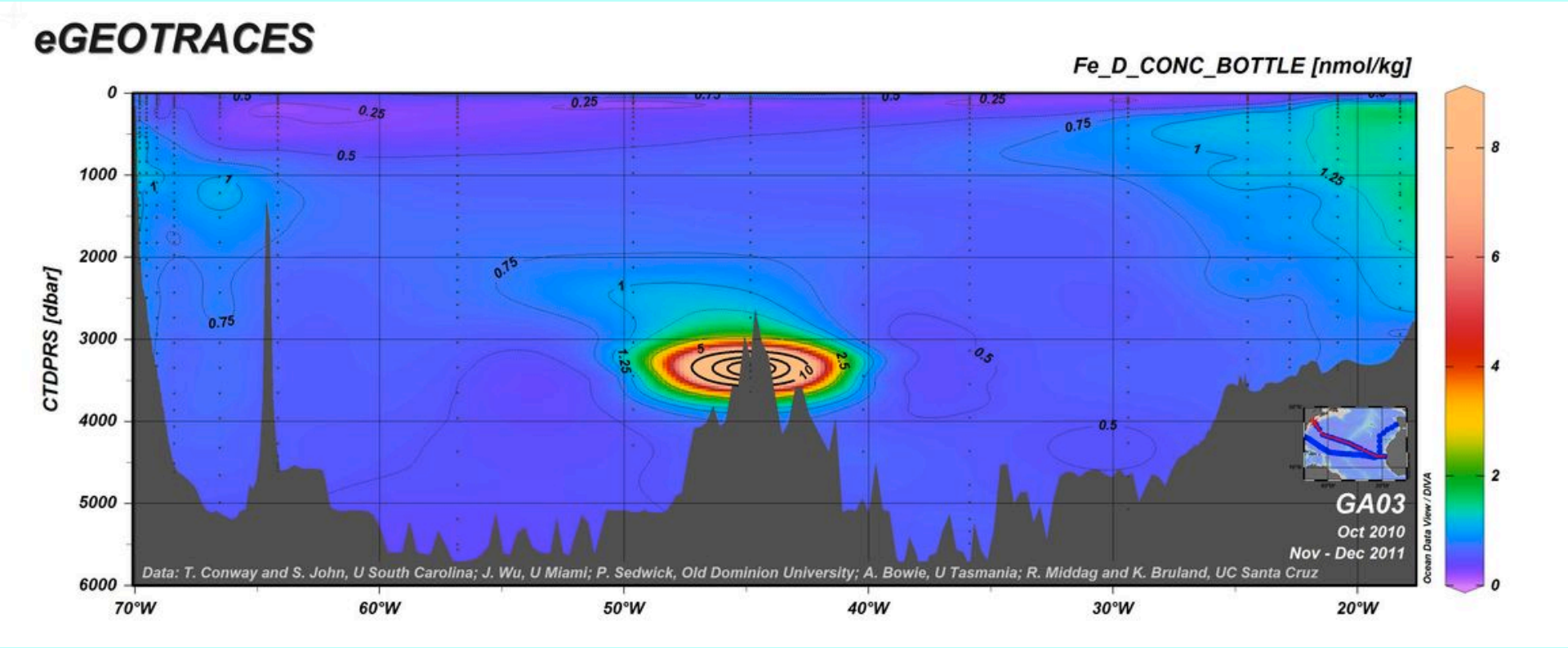
2. Nutrient-like Profile



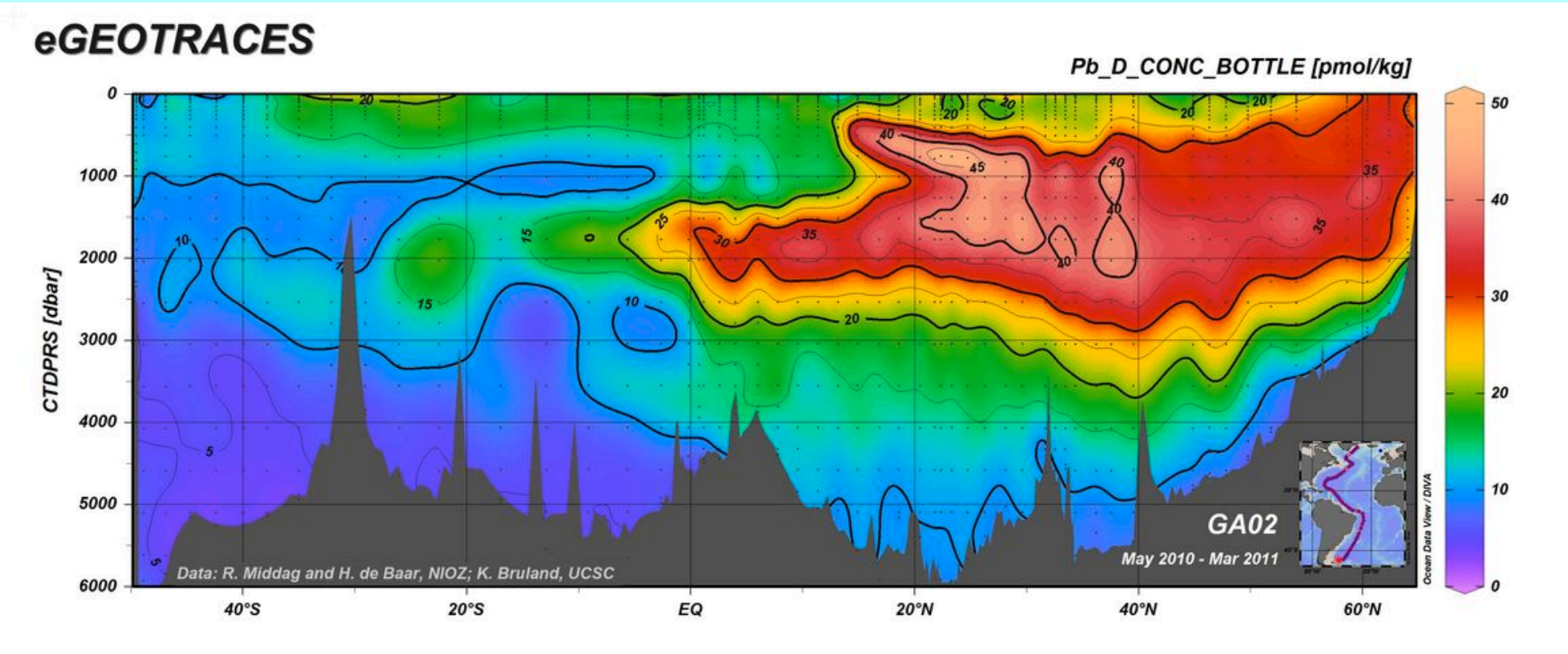
3. Particle-scavenged



Also hydrothermal sources of metals: iron coming off a hydrothermal vent on the mid-Atlantic ridge



Human Contributions to Trace Metal Concentrations also Detectable: Higher Concentrations of Lead in North Atlantic Deepwater



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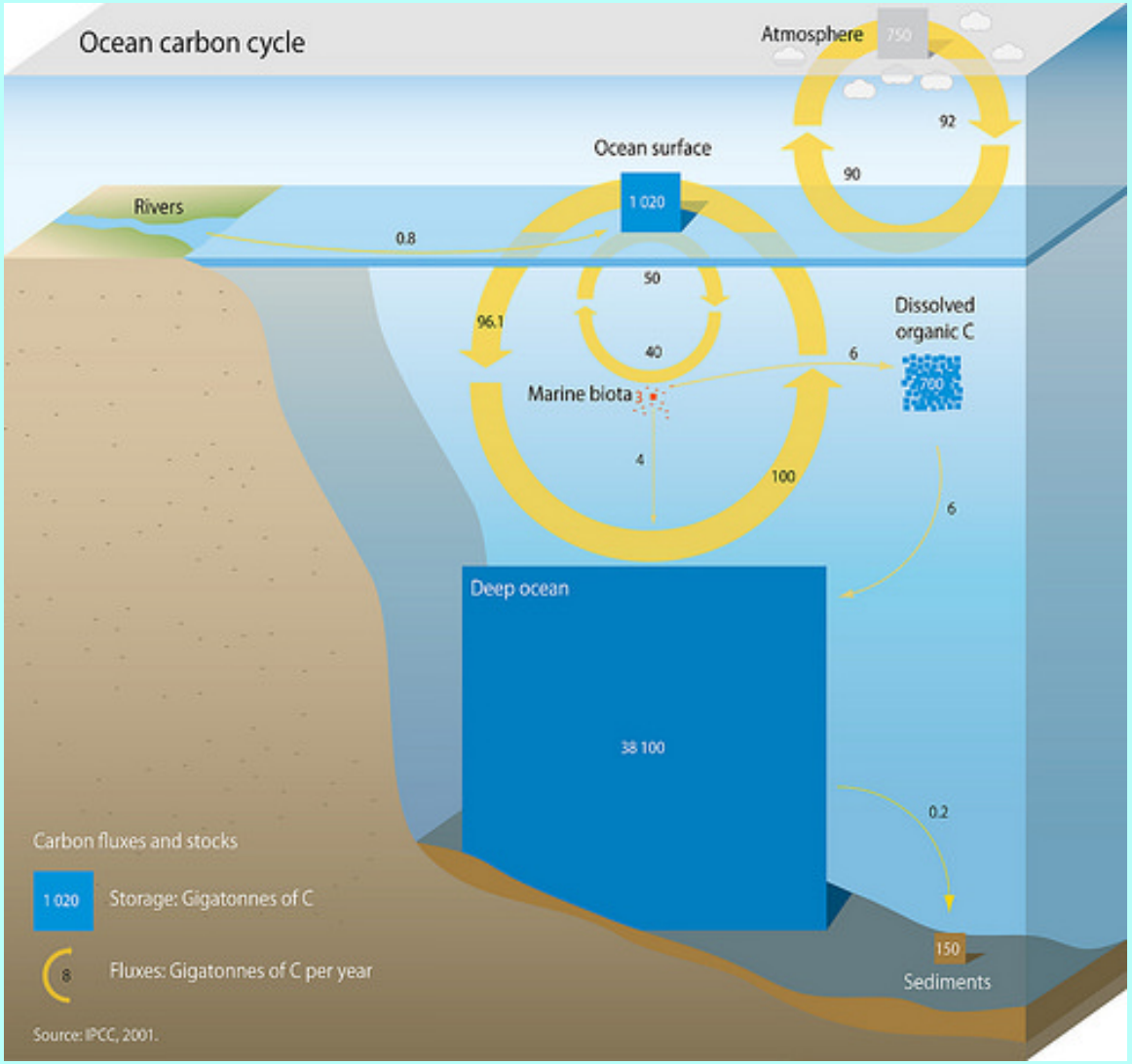
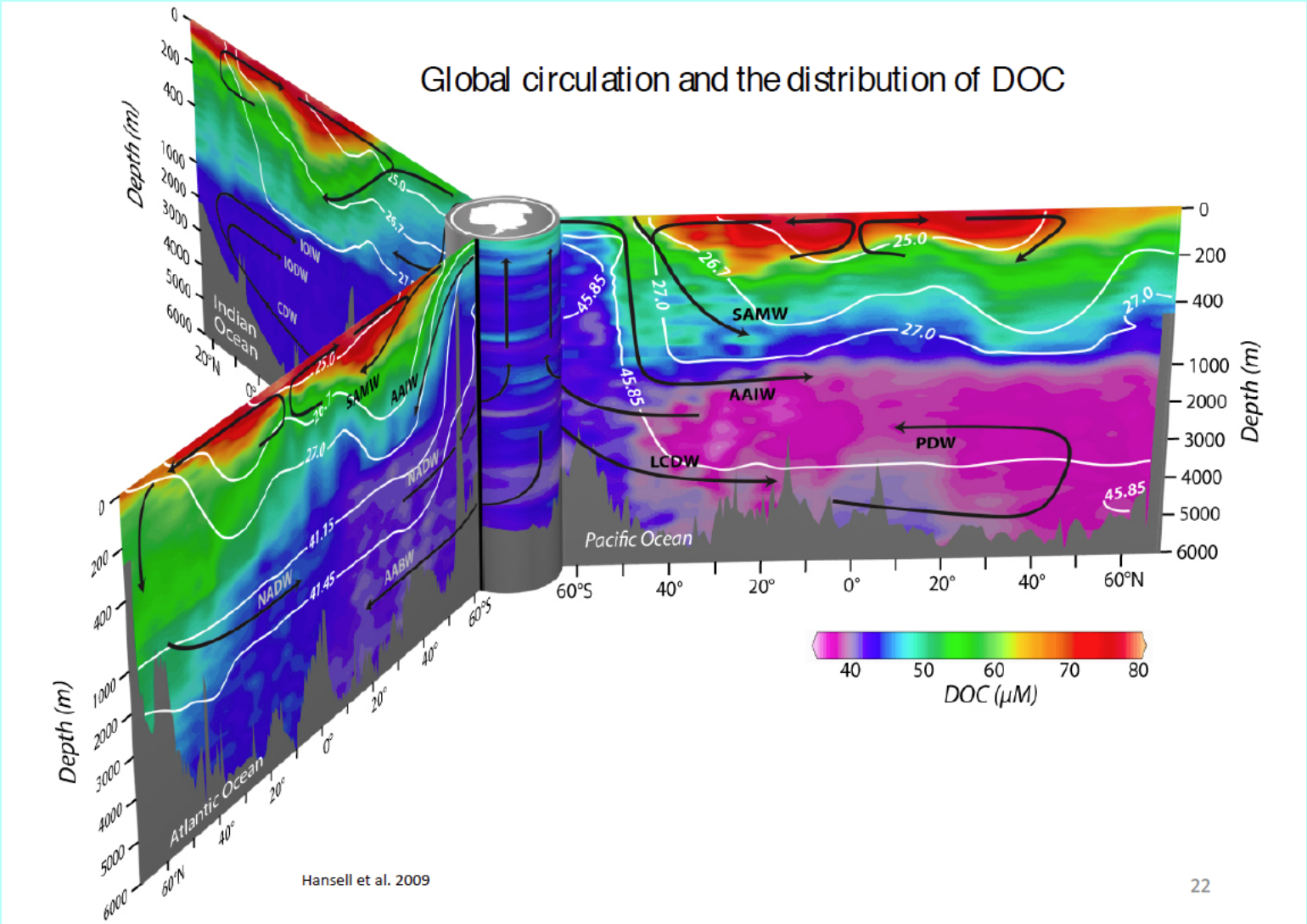
Marine Organic Carbon Reservoir ~= Atmospheric Carbon Reservoir



Global Distributions of Dissolved Organic Carbon

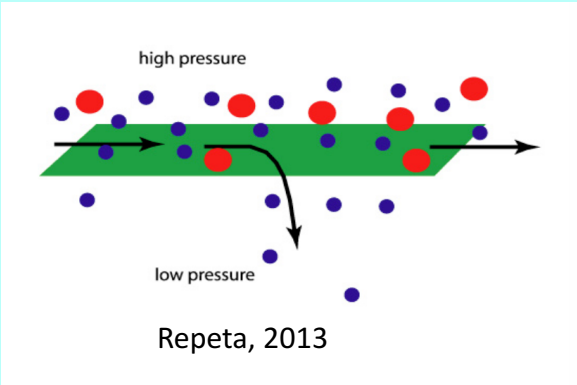


Hansell et al. 2009

Marine Organic Matter

- Operationally defined:
  - High molecular weight organic matter
  - Low molecular weight organic matter

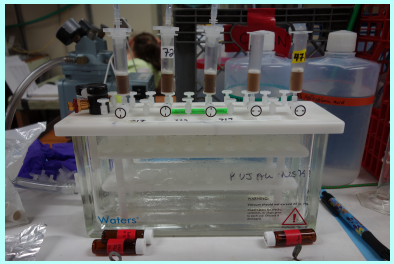
- Ultrafiltration (> 1000 Da)



Repeta, 2013

- Solid phase extraction

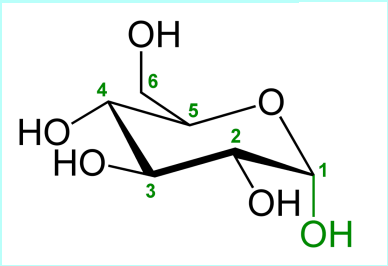
(< 1000 Da)

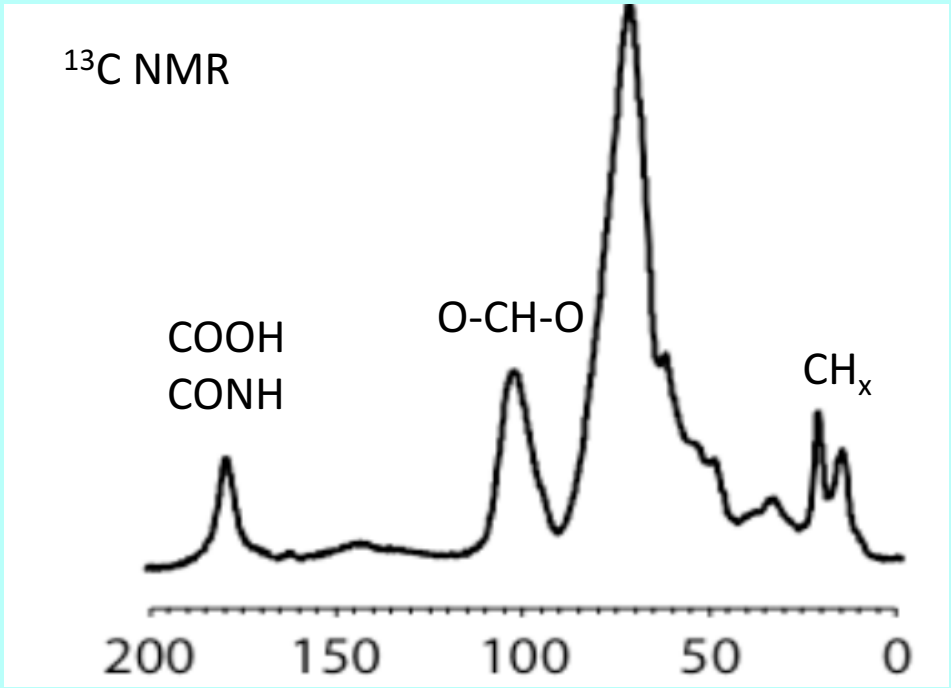


High Molecular Weight Organic Matter Composition

Surface, North Pacific Subtropical Gyre

Carboydrate Example:
Glucose



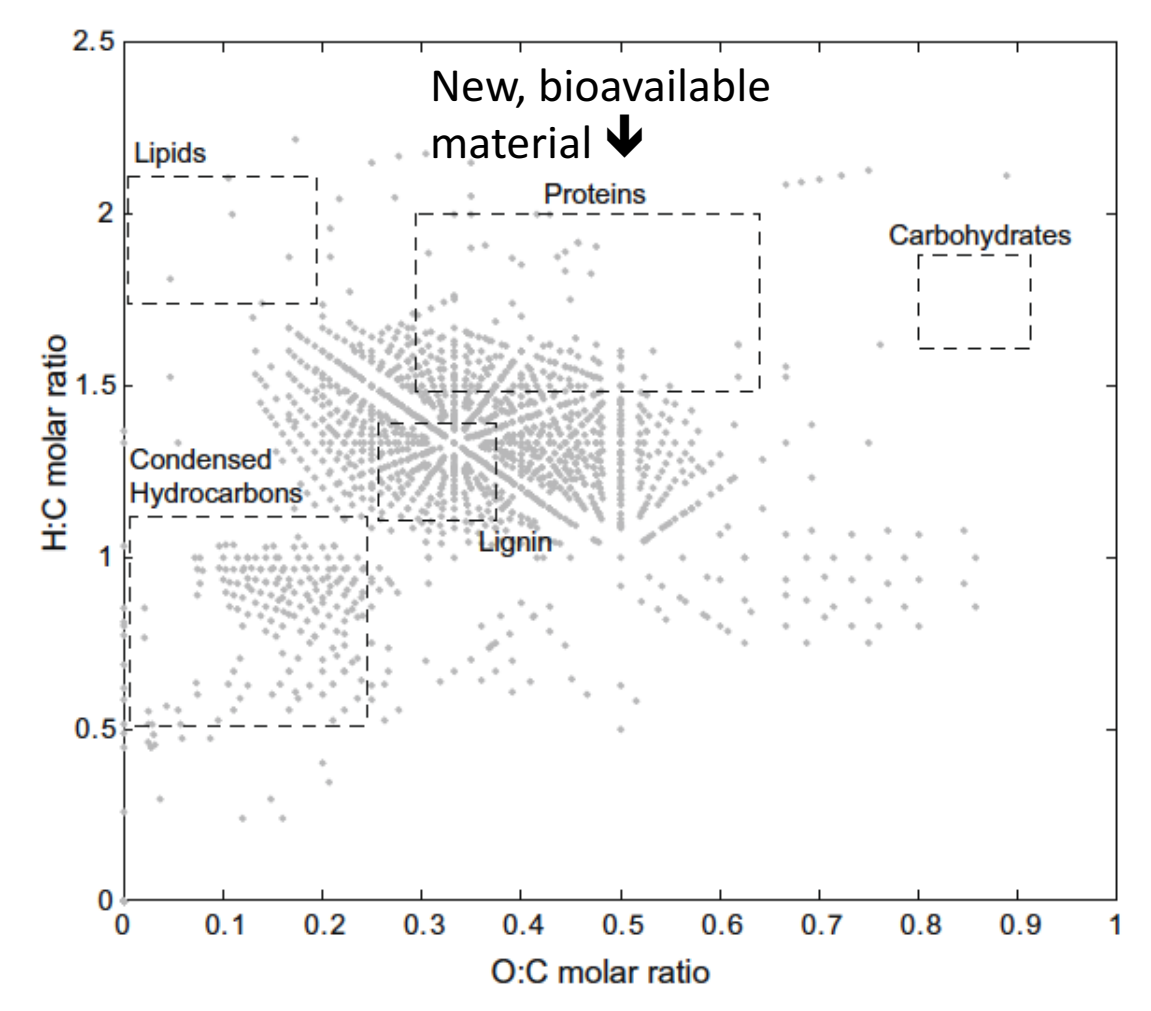


Major peaks are from carbohydrate functional groups (70-90%)

Repeta, 2013

Low Molecular Weight Organic Matter Composition

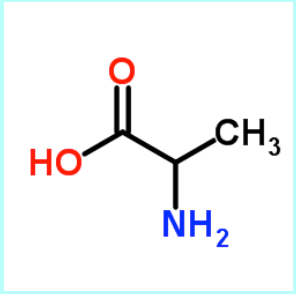
Old, refractory material ➔



Kujawinski et al., 2009

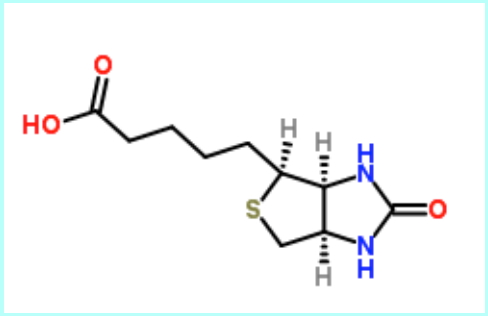
Metabolites

Amino Acids



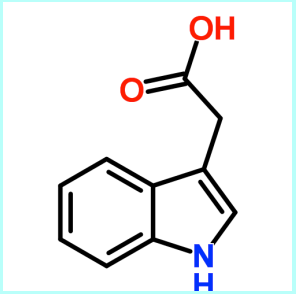
alanine

Vitamins/cofactors



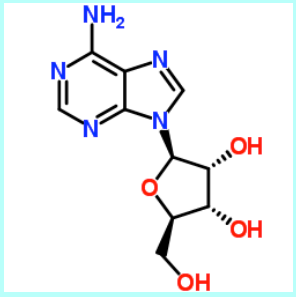
biotin (Vitamin B_7)

"Secondary" Metabolites: defense, signaling



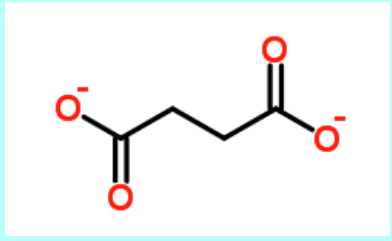
indole-3-acetic acid

Nucleic Acids



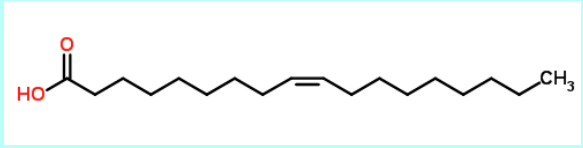
adenosine

Intermediates in Metabolic Pathways



succinic acid

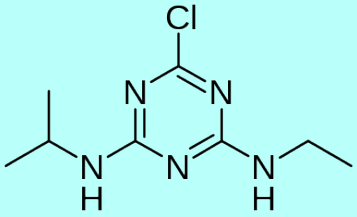
Lipids



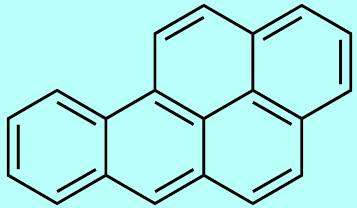
oleic acid

Organic Pollutants

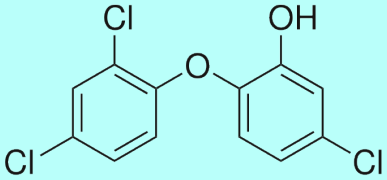
DEET
Insect repellent



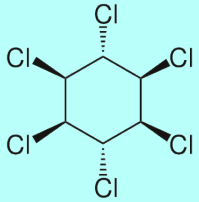
Atrazine
herbicide



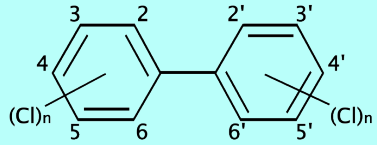
Polycyclic Aromatic
Hydrocarbons (PAHs)
Oil or incomplete combustion



Triclosan
Anti-bacterial



Lindane
pesticide



Polychlorinated biphenyls (PCBs)
Various industrial applications

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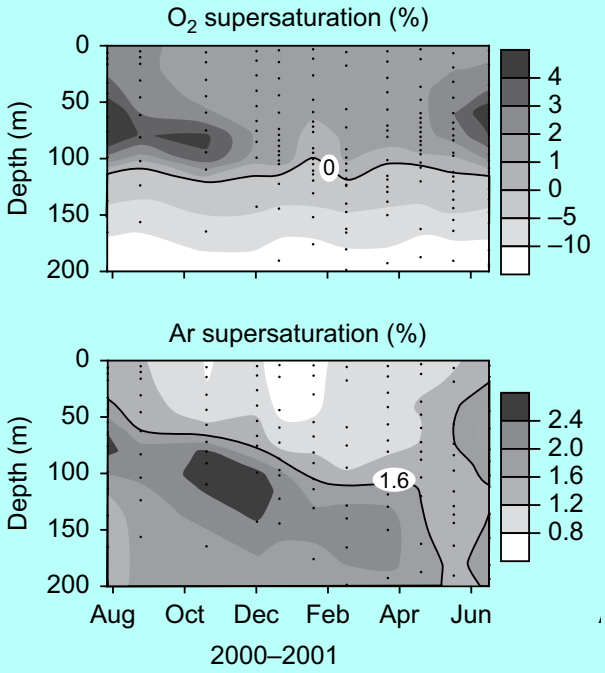
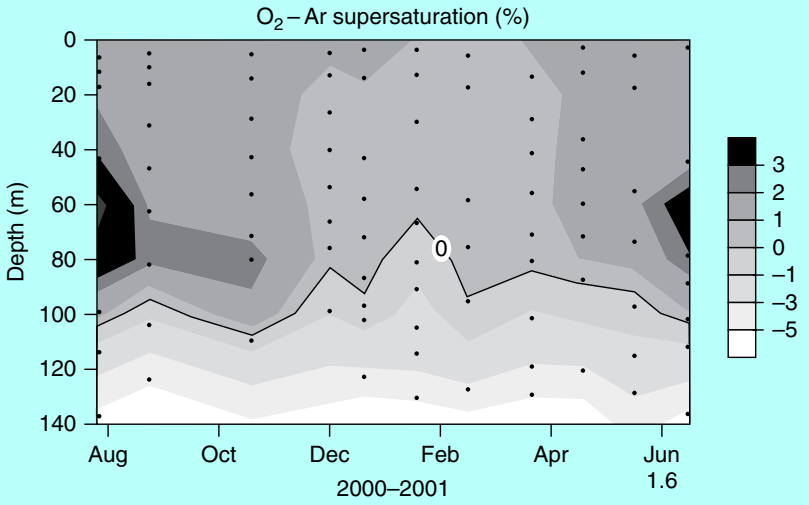
Oxygen-Argon: Measuring the balance of between photosynthesis and respiration

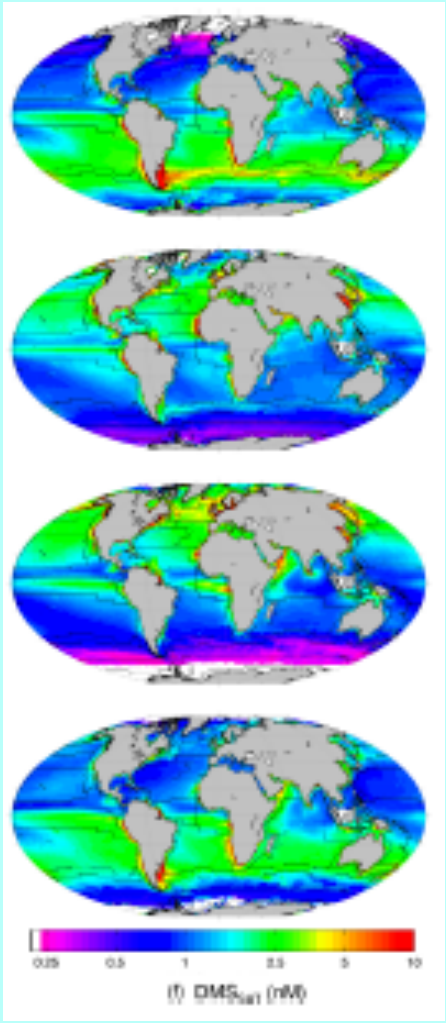




Emerson & Hedges, 2008

Dimethylsulfide: Climatically active

- Gas produced by the degradation of a common phytoplankton-produced molecule
- Can oxidize in the atmosphere providing cloud nucleation sites

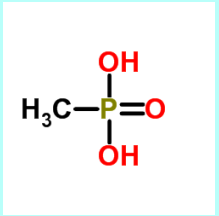


Galí et al., 2018

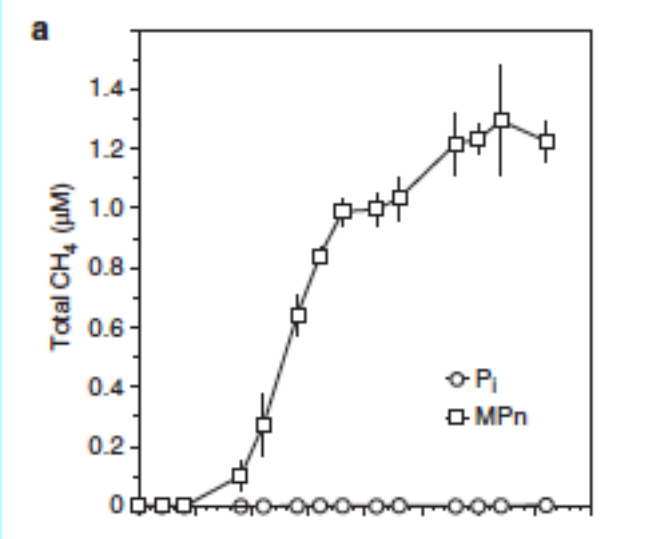
Methane

- Potent greenhouse gas
- Originally thought to exclusively be produced in anoxic sediments
- Now known to be produced in the surface ocean by marine bacteria degrading

Marine archaea



SAR11 Isolate → CH_4



Carini et al. 2014

Conclusions

- Many marine chemical constituents including trace metals, nutrients, and the carbonate system underlie a delicate a balance that supports the productivity of the ocean

- Chemicals also act as tracers of physical processes occurring in the ocean including deep water circulation, inputs from hydrothermal vents, and upwelling

- The chemistry of the ocean is influenced by humans in many ways

Questions?