

Trace metal cycling in the ocean

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Why study trace elements in the ocean?

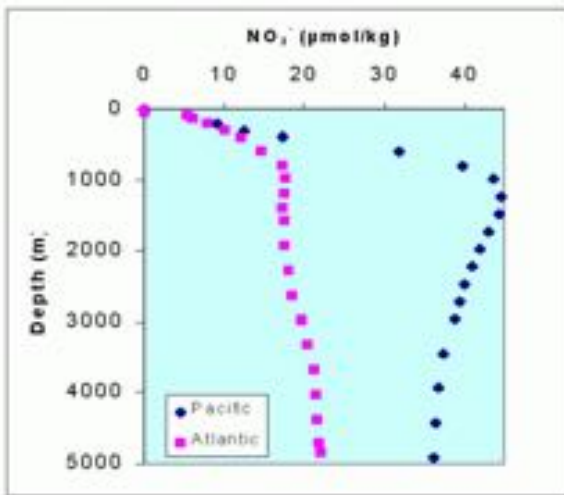
- Some trace elements are essential for marine life.
- Some trace elements are toxic to marine life.
- Some trace elements reveal anthropogenic impacts on the ocean.
- Some trace elements can be used to understand important processes in the ocean.
- Some trace elements might influence climate change.
- Some trace elements can be used to study the geological history of the ocean.

Why study trace elements in the ocean?

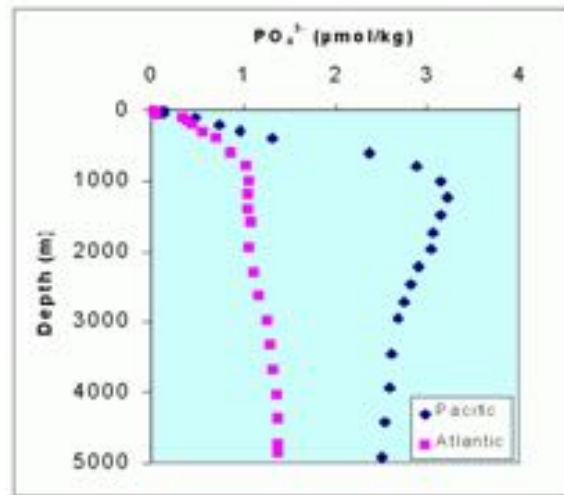
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Some trace metals are
essential building blocks of life

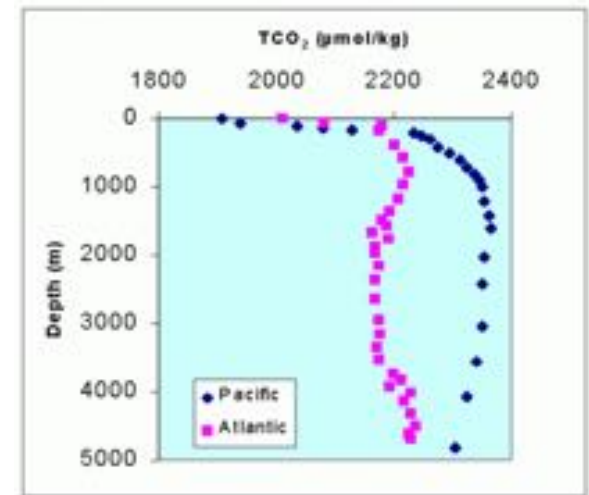
Nitrate



Phosphate

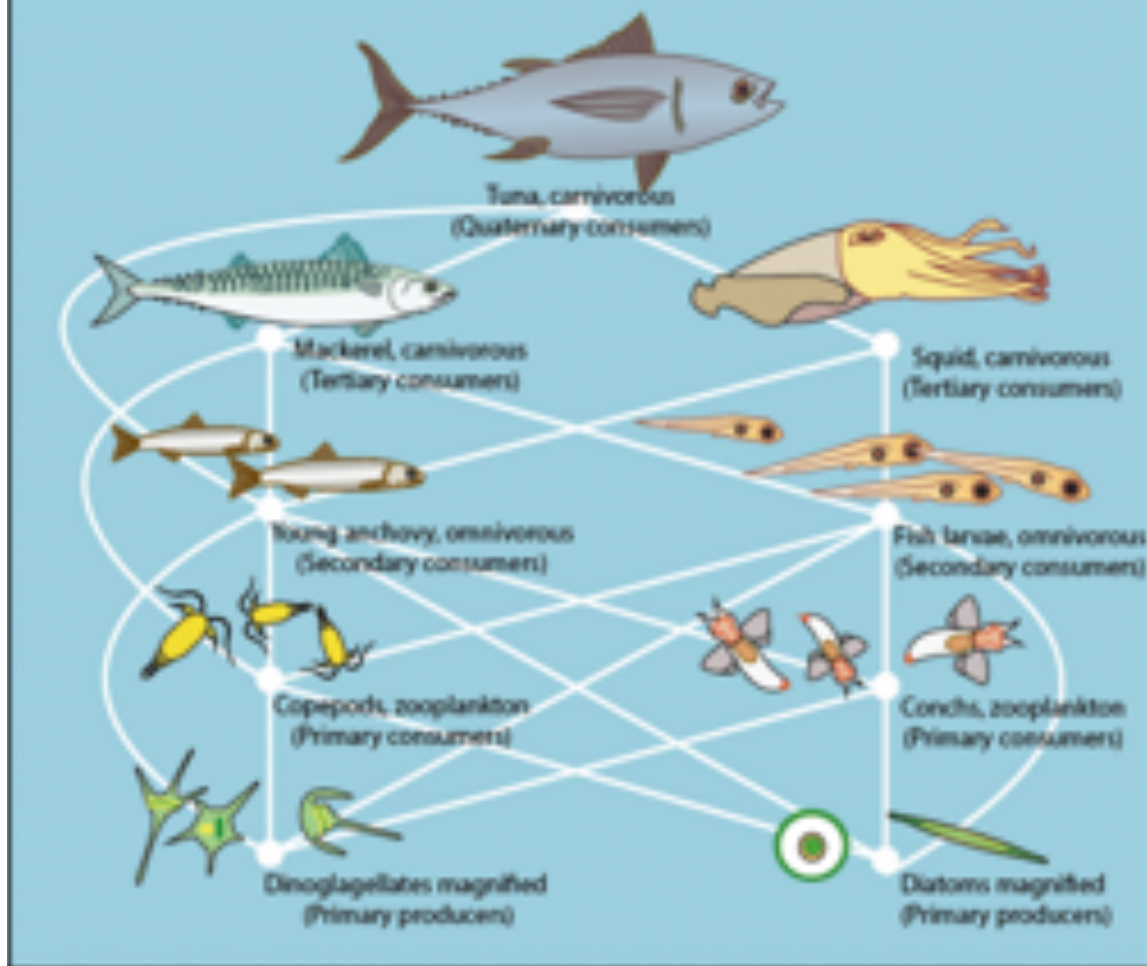


Dissolved inorganic carbon (DIC)

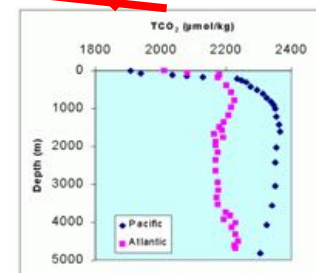
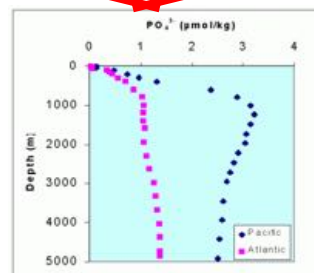
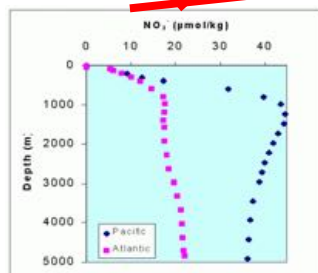
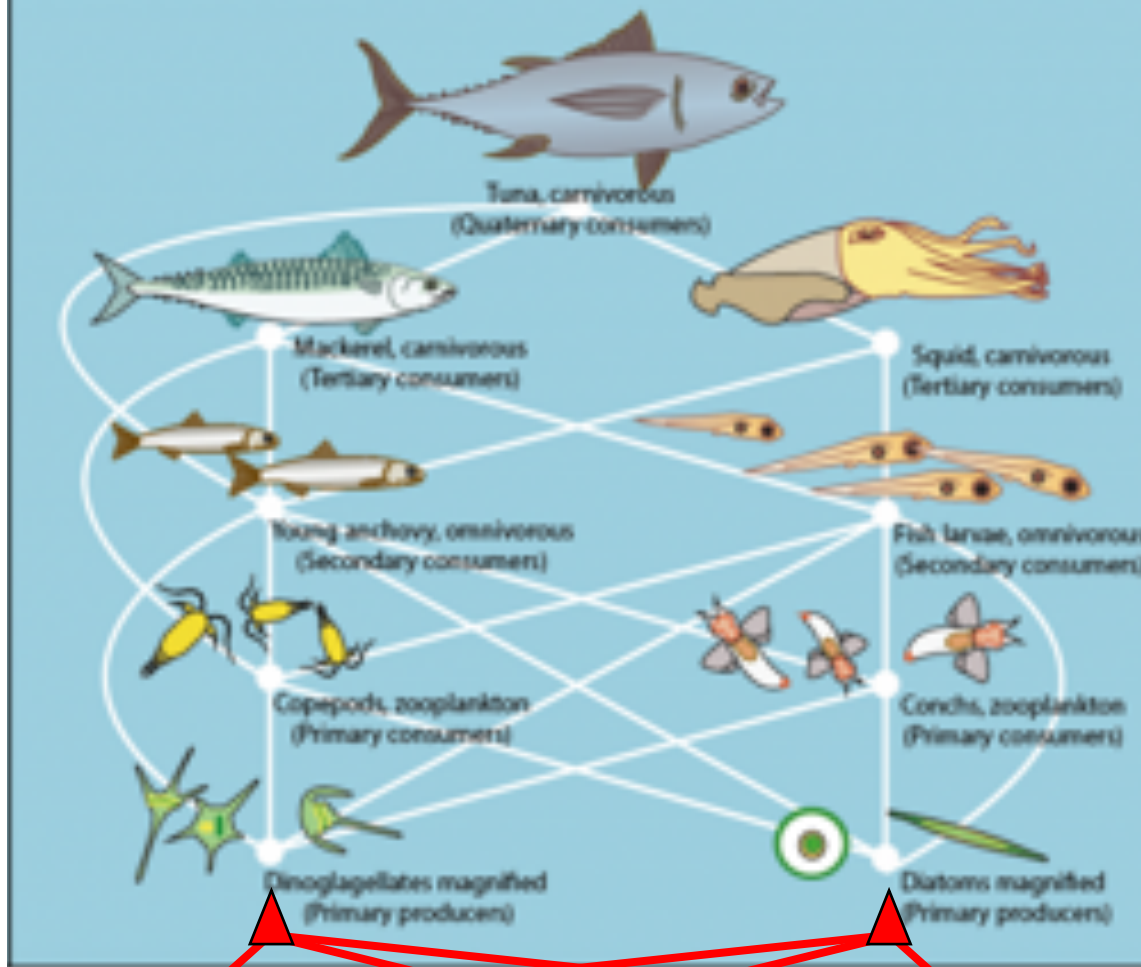


These are the basic building blocks of all life

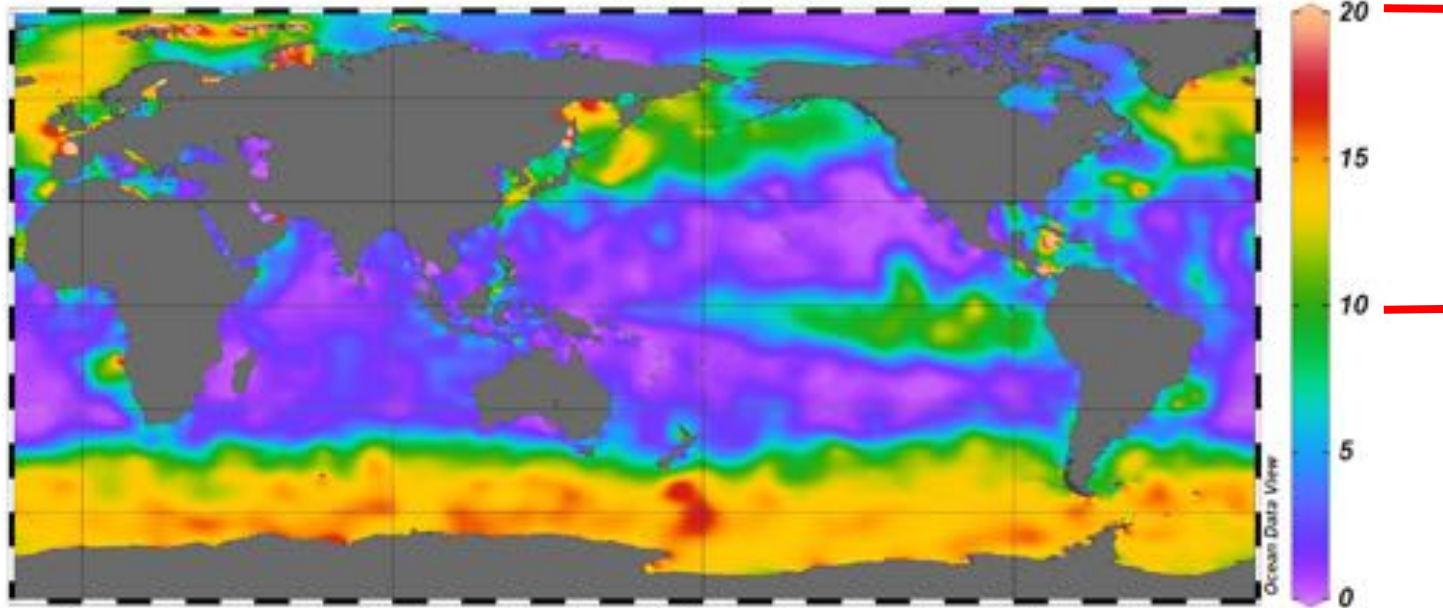
A food web



A food web

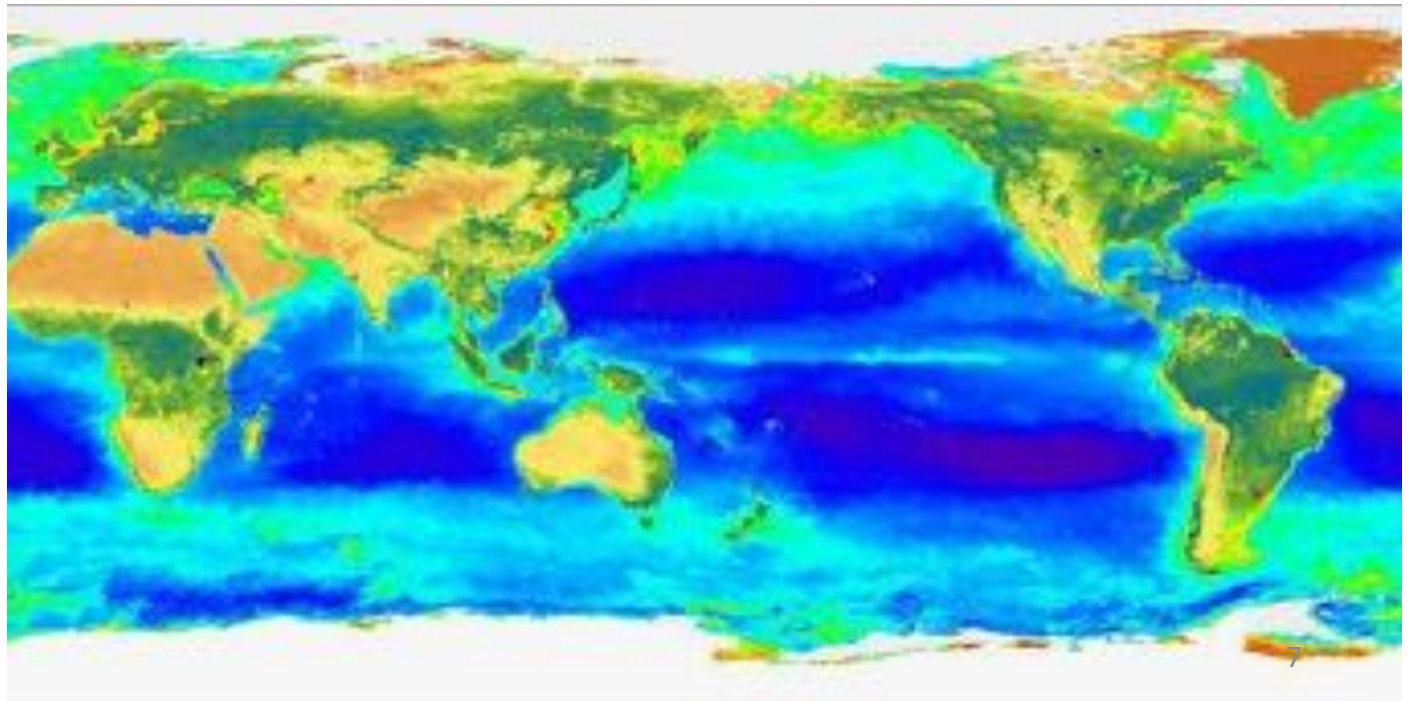


N:P Ratio [molar] @ Depth [m]=first

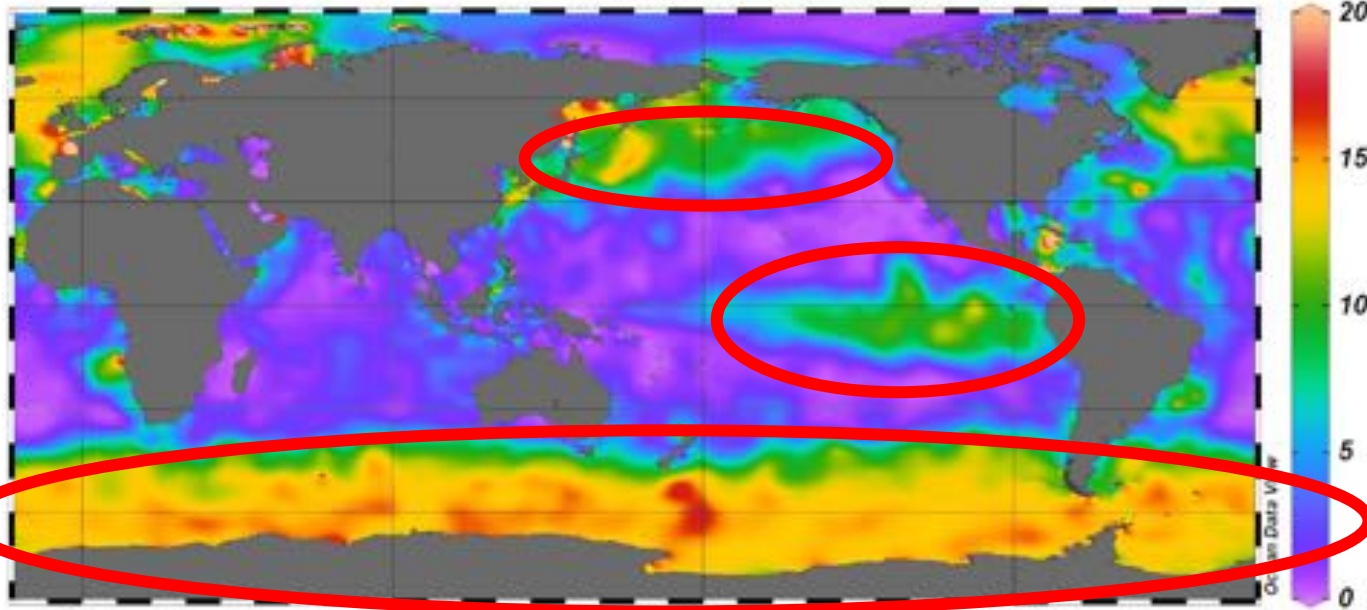


Lots of
nutrients
(nitrogen,
phosphorous)

Chlorophyll a

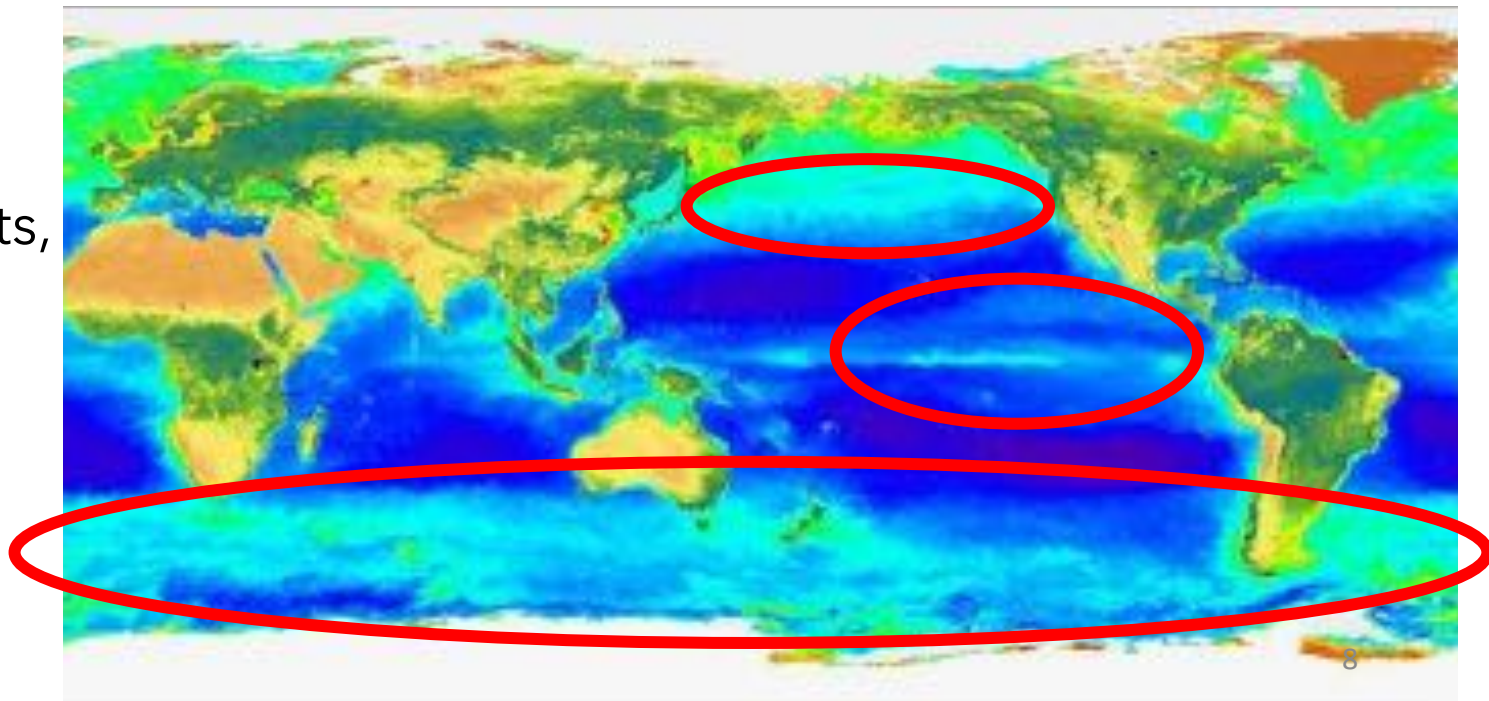


N:P Ratio [molar] @ Depth [m]=first



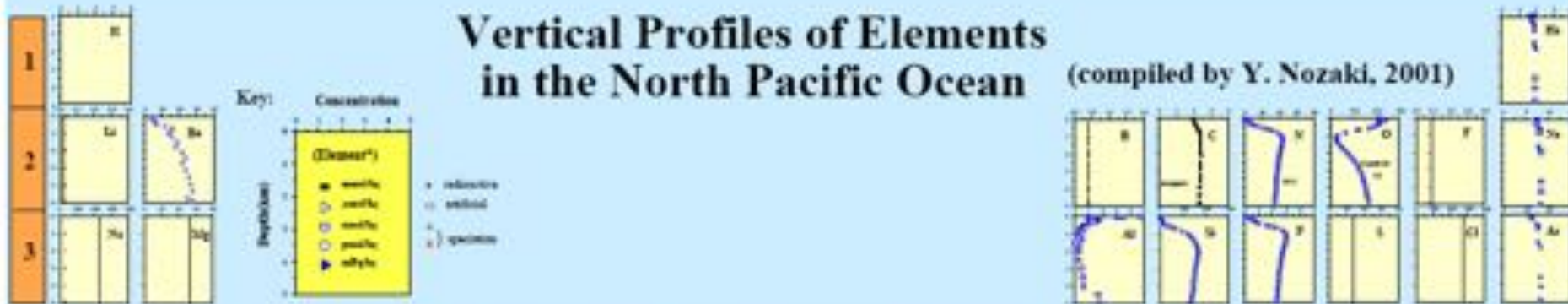
**High Nutrient
Low Chlorophyll
regions (HNLCs)**

Lots of nutrients,
but not much
primary
productivity



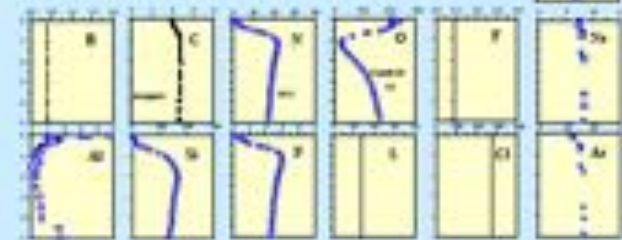
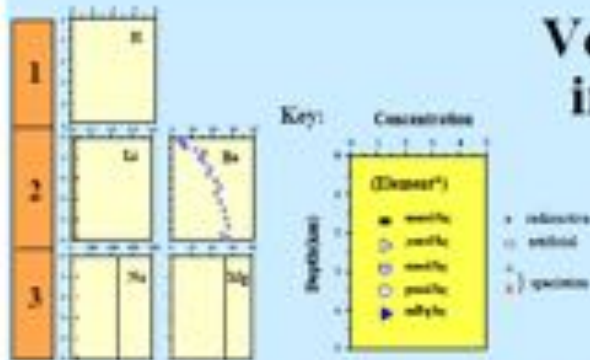
Vertical Profiles of Elements in the North Pacific Ocean

(compiled by Y. Nozaki, 2001)



Vertical Profiles of Elements in the North Pacific Ocean

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1A 2A 3A 4A 5A 6A 7A 8 1B 2B 3B 4B 5B 6B 7B 0



Karl Turekian, on the field of Marine Trace Metal Chemistry (1930-1980)

Quoted in L-G. Daniellson's Ph.D thesis "Trace metals in marine waters: analytical investigations on Cadmium, Cobalt, Copper, Iron, Lead, Nickel and Zinc

"Indeed one has the feeling that the whole field of trace metal marine geochemistry would have been a completely dull one over the past fifty years if it weren't for analytical errors."

NOTE: "analytical errors" includes both **errors in laboratory handling and measurement methods** and **contamination during sampling and analysis**.

Karl Turekian, on the field of Marine Trace Metal Chemistry



methods and contamination during sampling and analysis.

Karl Turekian, on the field of Marine Trace Metal Chemistry



Geochimica et Cosmochimica Acta 1965, Vol. 29, pp. 259 to 313. Pergamon Press Ltd. Printed in Northern Ireland

**The investigation of the geographical and vertical
distribution of several trace elements in sea water
using neutron activation analysis**

DONALD F. SCHUTZ* and KARL K. TUREKIAN
Department of Geology, Yale University, New Haven, Connecticut

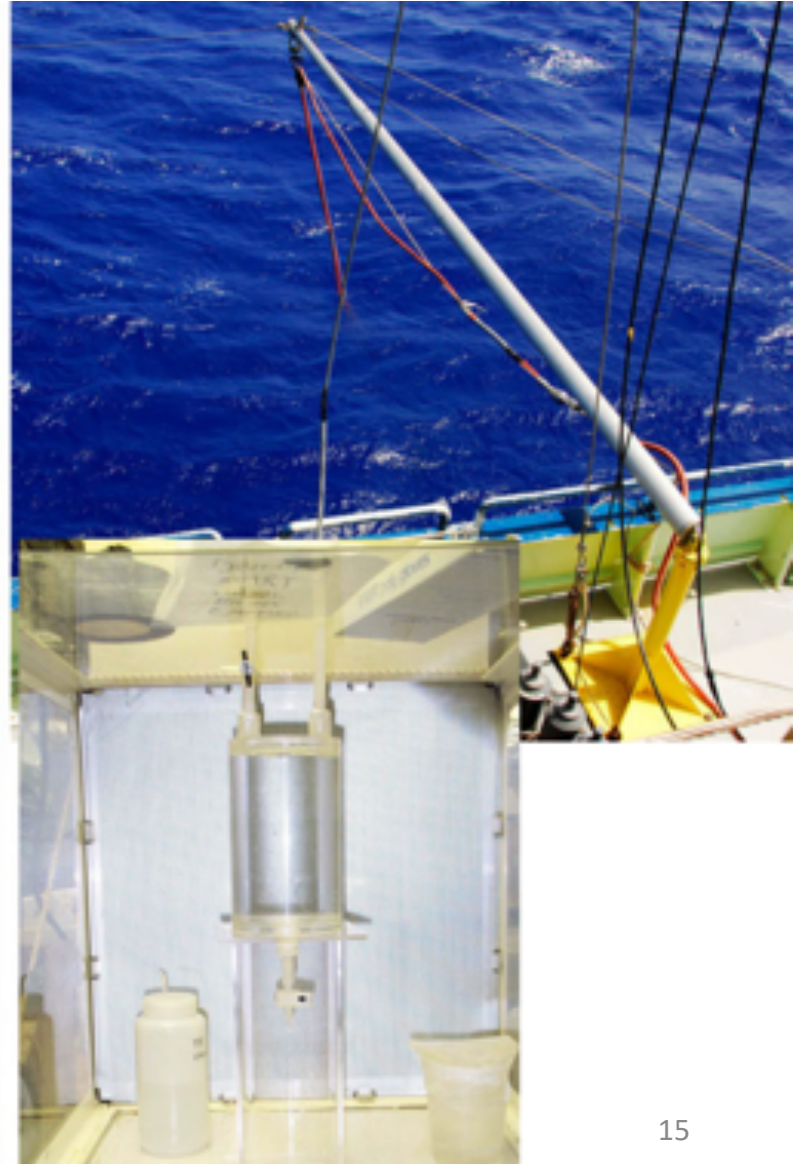
As indicated in Table 4, some samples were taken with an unlined 50 gal galvanized barrel and some surface samples were taken from the surface pump used for cooling the hydrowinch.

Trace metals were notoriously difficult to measure because...

- Ships are painted with marine paints that contain metals (e.g. copper, lead, tin)
- Ships pump out bilge water and let off exhaust, contaminating the water near the ship
- Old sampling techniques used bottles either made entirely of metal or using metal joints

Working toward better sampling techniques in the surface

Towed FISH (1974)



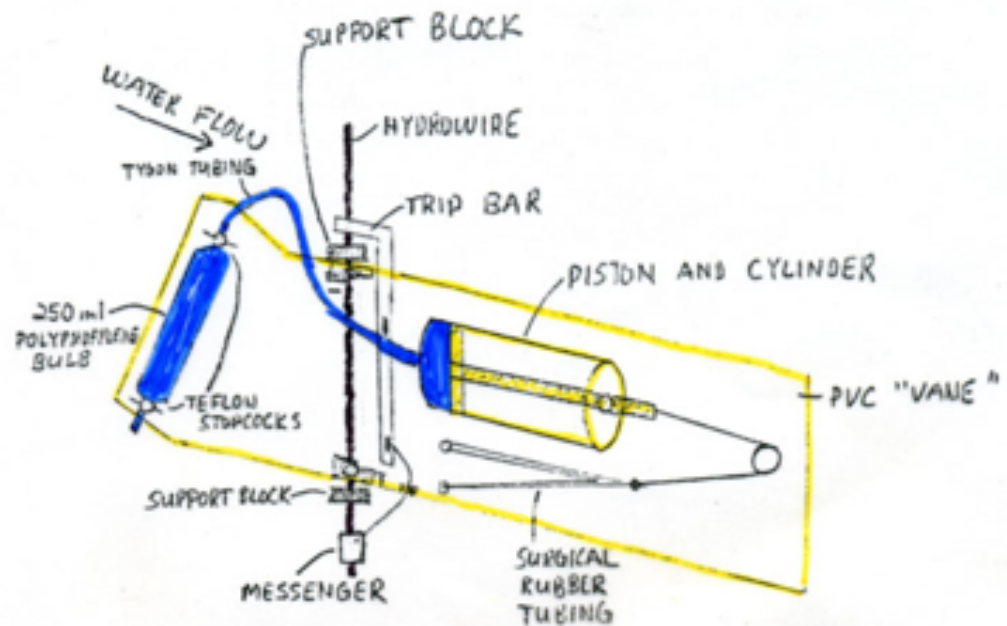
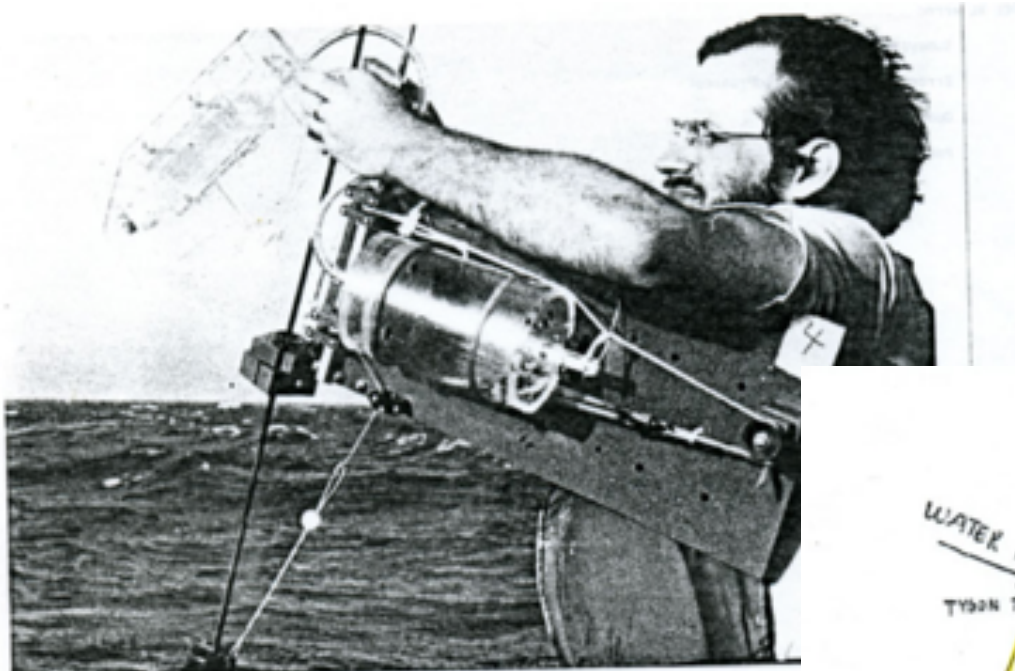
Working toward better sampling techniques in the surface

MIT pole (1978)



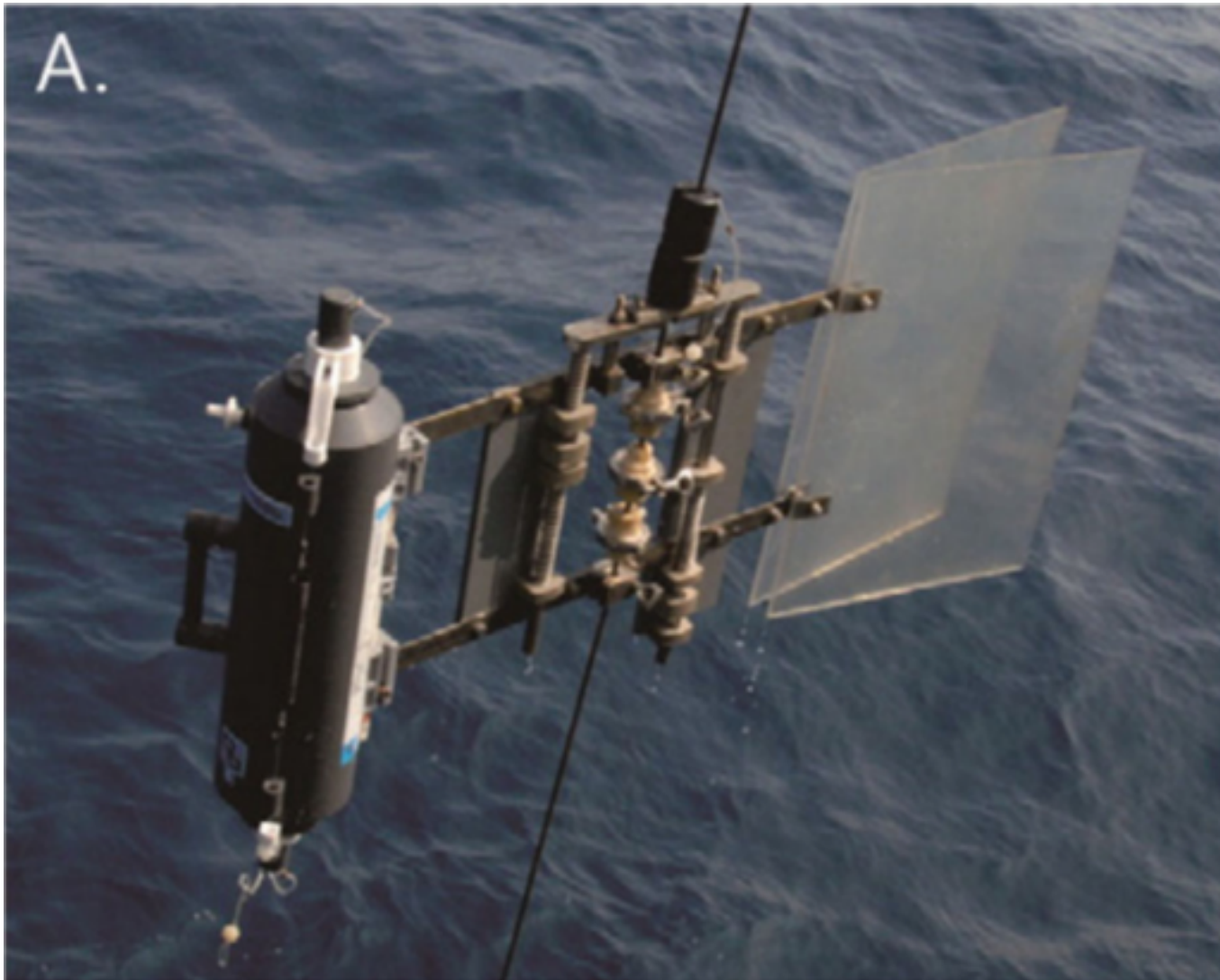
Working toward better sampling techniques through the water column

MIT Vanes sampler (1983-1995)



Working toward better sampling
techniques through the water column

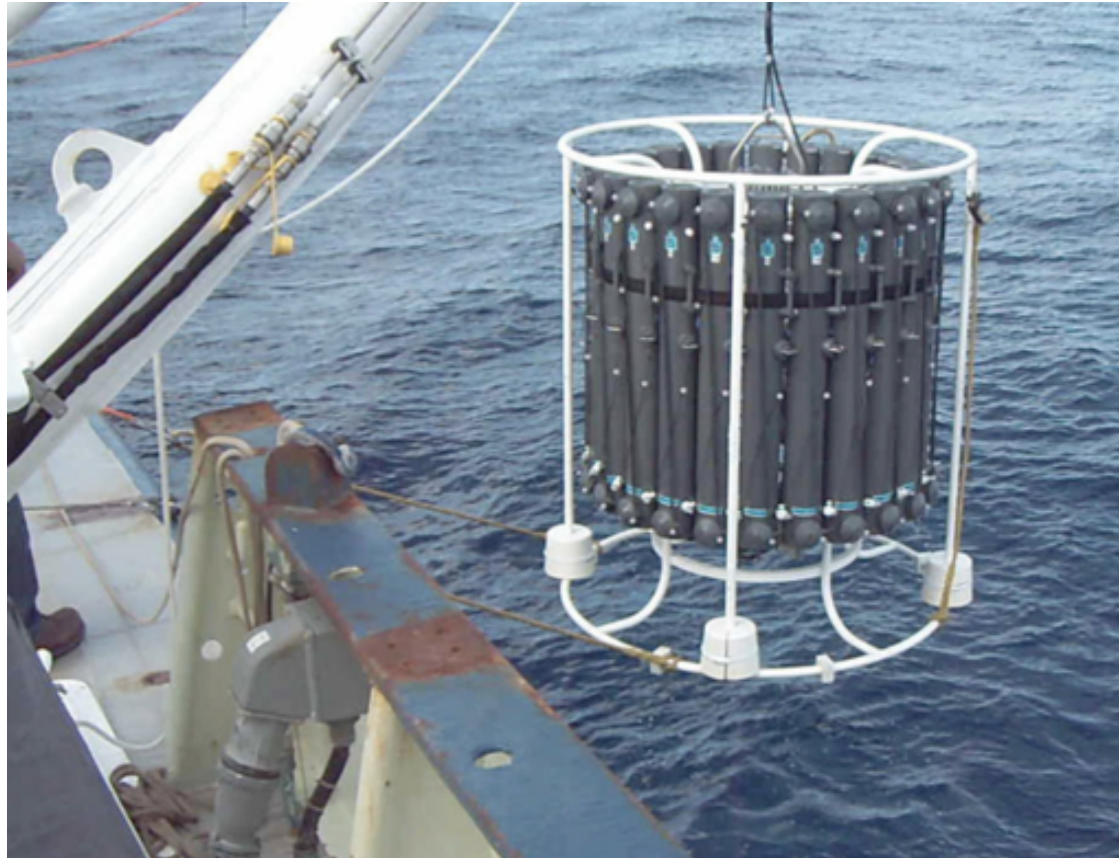
Niskin-X Vane Sampler
(2015)



Zhang (2015) Mar. Chem. 177: 653

Current gold-standard sampling techniques

GEOTRACES
GOFlo Carousel



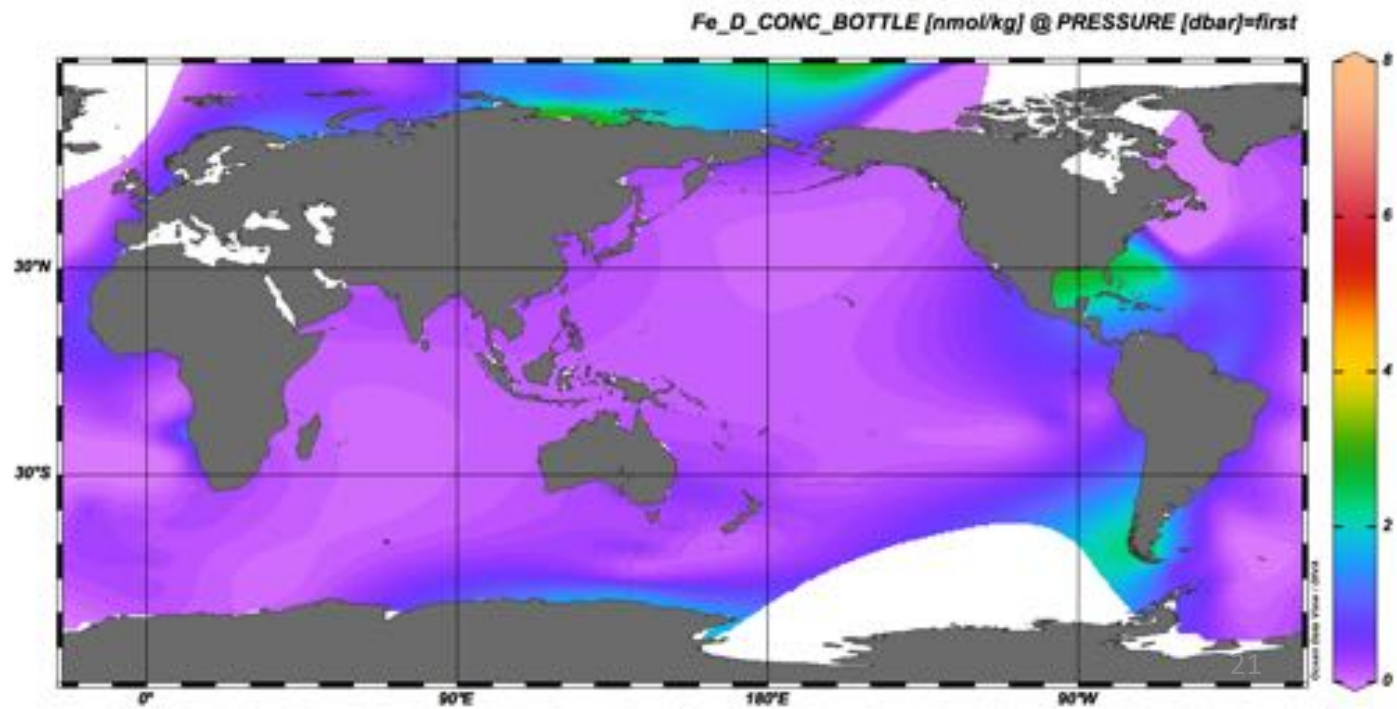
Kevlar conducting cable deployed, polyurethane powder-coated carousel, teflon-coated Niskin bottles with no internal metal.

Sampling is done while moving up through the water column to avoid CTD contamination.

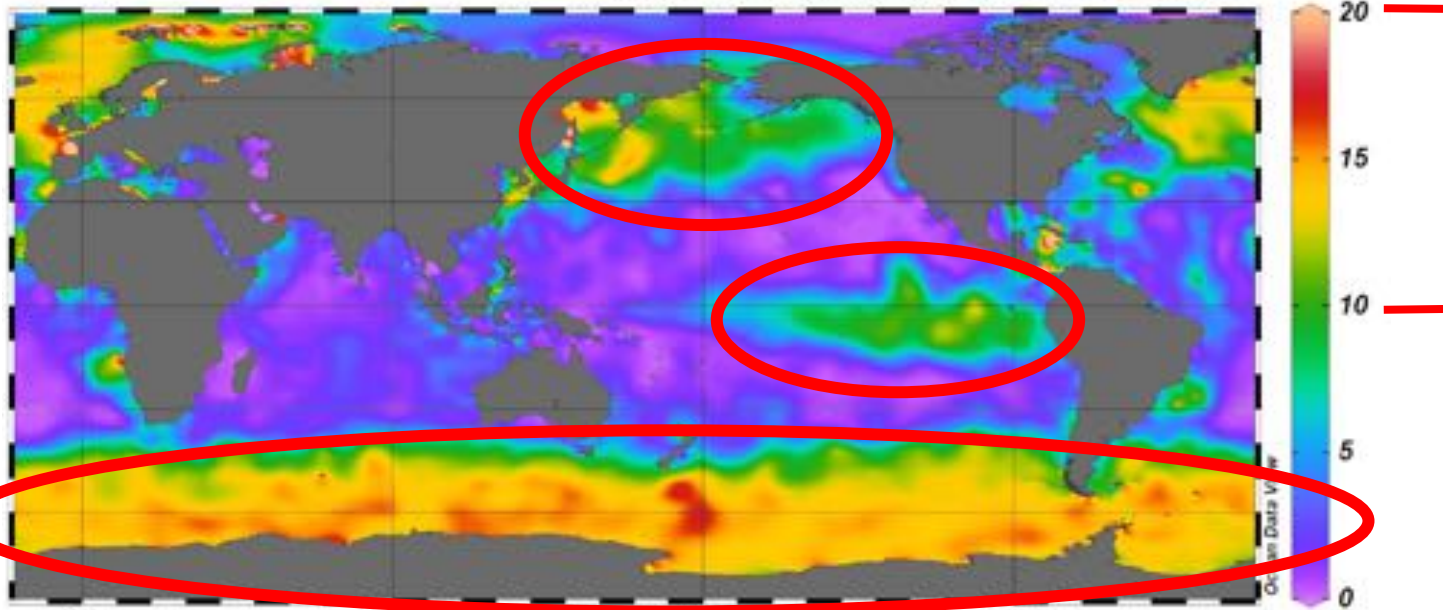


Must process samples in a clean lab to prevent contamination

Dissolved Iron

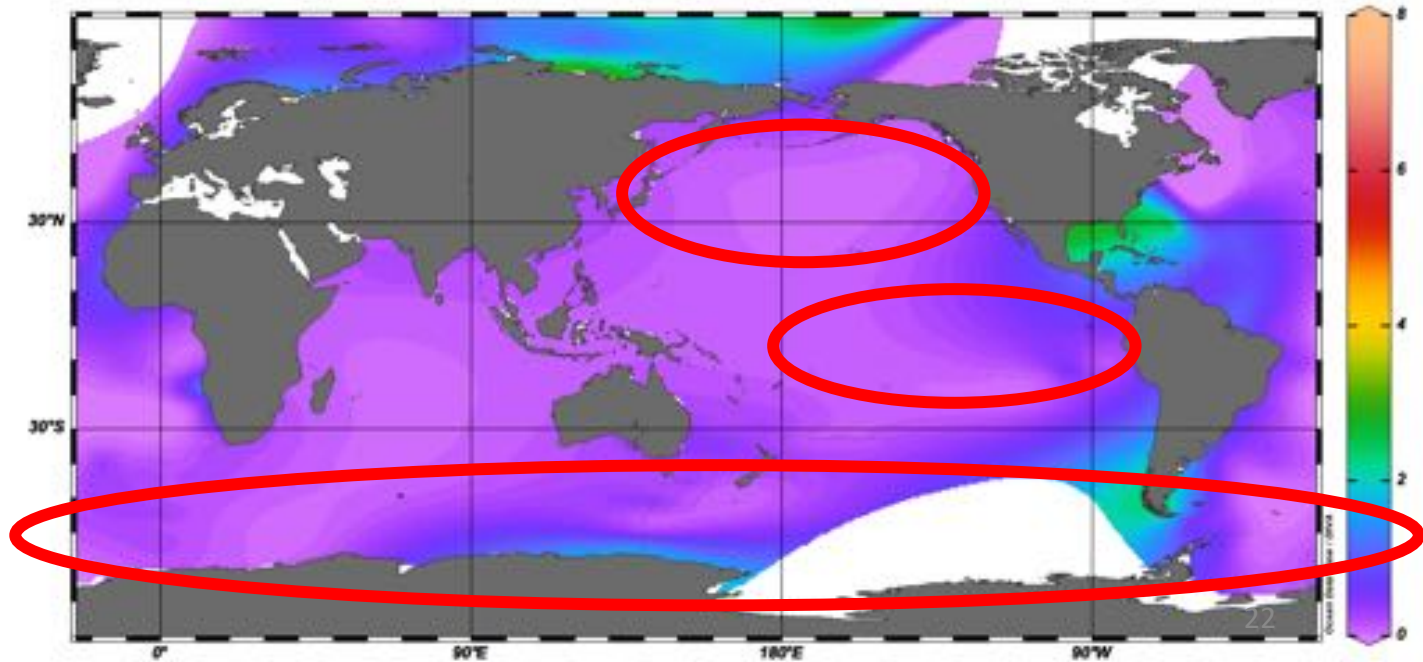


N:P Ratio [molar] @ Depth [m]=first



Lots of
nutrients
(nitrogen,
phosphorous)

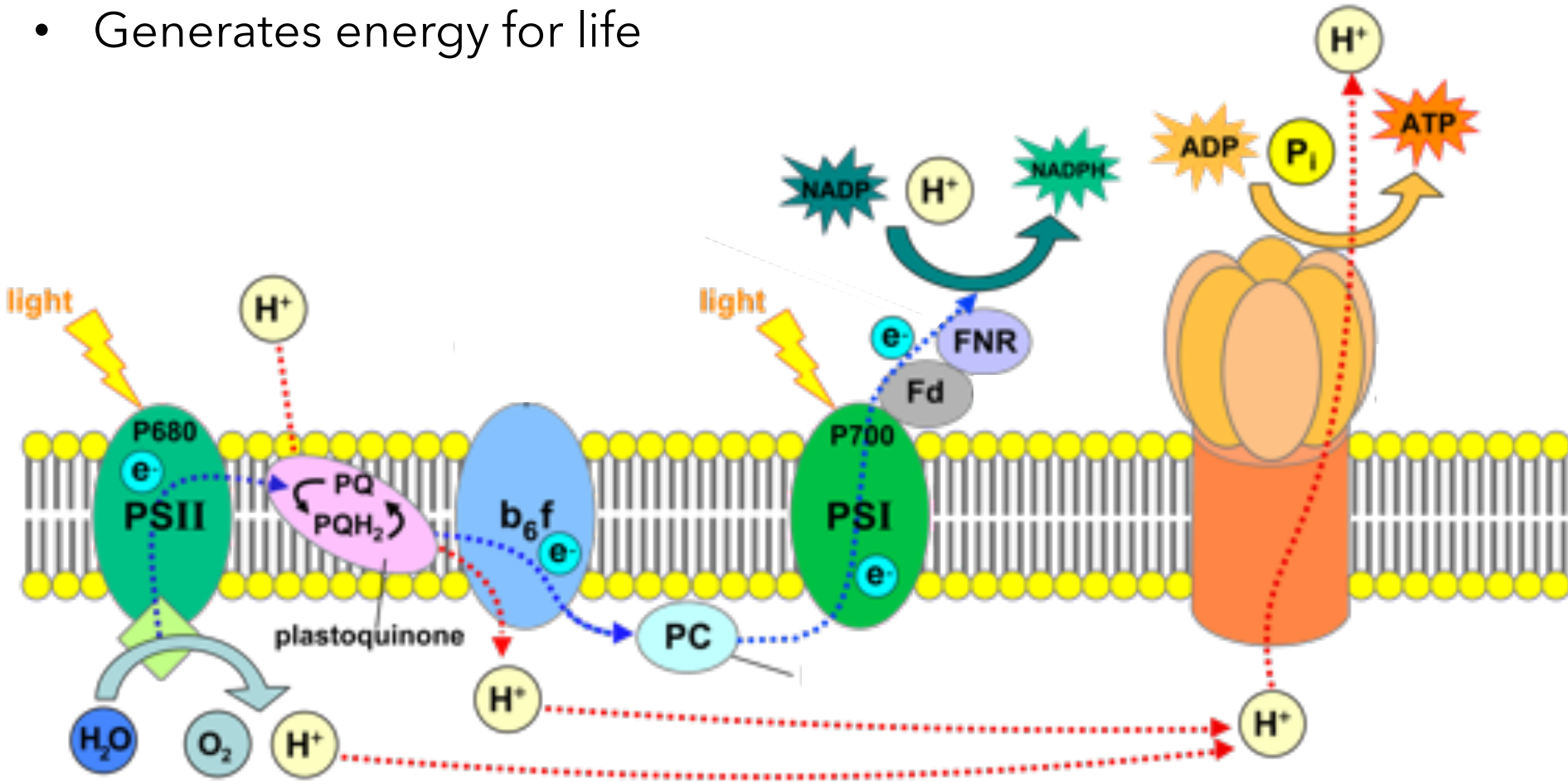
Fe_D_CONC_BOTTLE [nmol/kg] @ PRESSURE [dbar]=first



Dissolved Iron

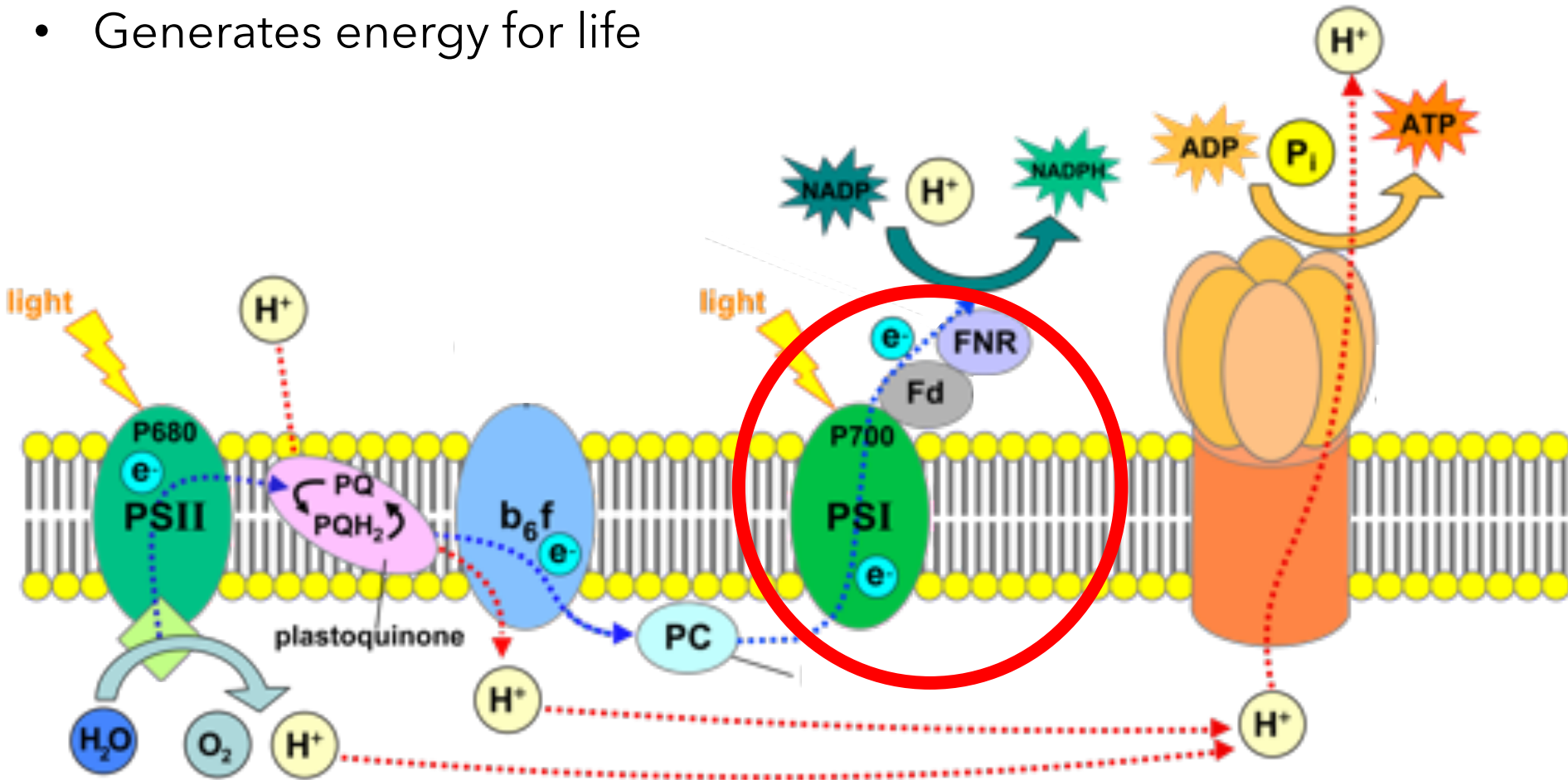
Electron export chain in plants

- Generates energy for life



Electron export chain in plants

- Generates energy for life

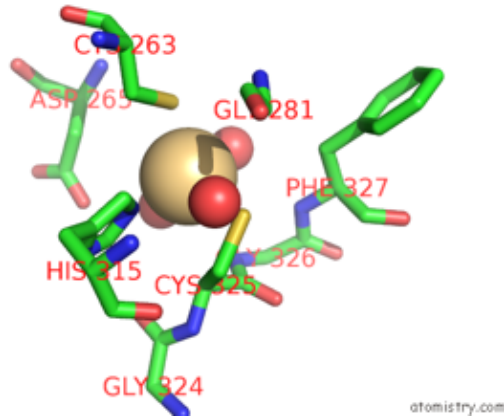


Photosystem I

- must** have iron to function properly and generate energy

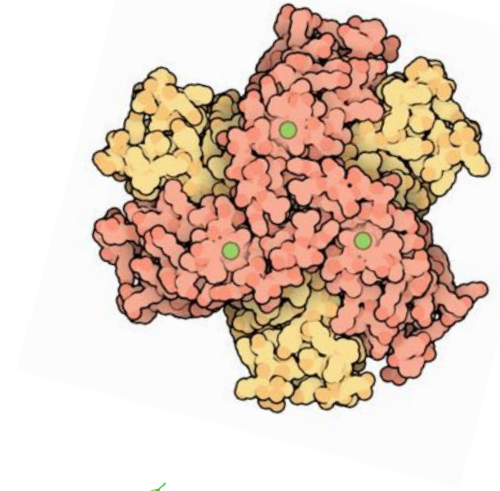
Cadmium carbonic anhydrase

- Catalyzes the conversion of $\text{CO}_2(\text{aq})$ to $\text{HCO}_3^-(\text{aq})$



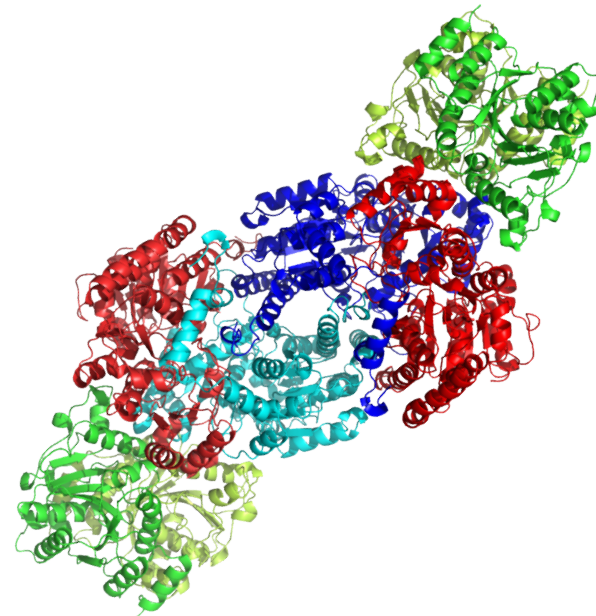
Nickel super oxide dismutase

- Catalyzes the conversion of Superoxide to oxygen or peroxide



Iron nitrogenase

- Catalyzes the reduction of N_2 to NH_3 , allowing nitrification in the oceans



Why study trace elements in the ocean?

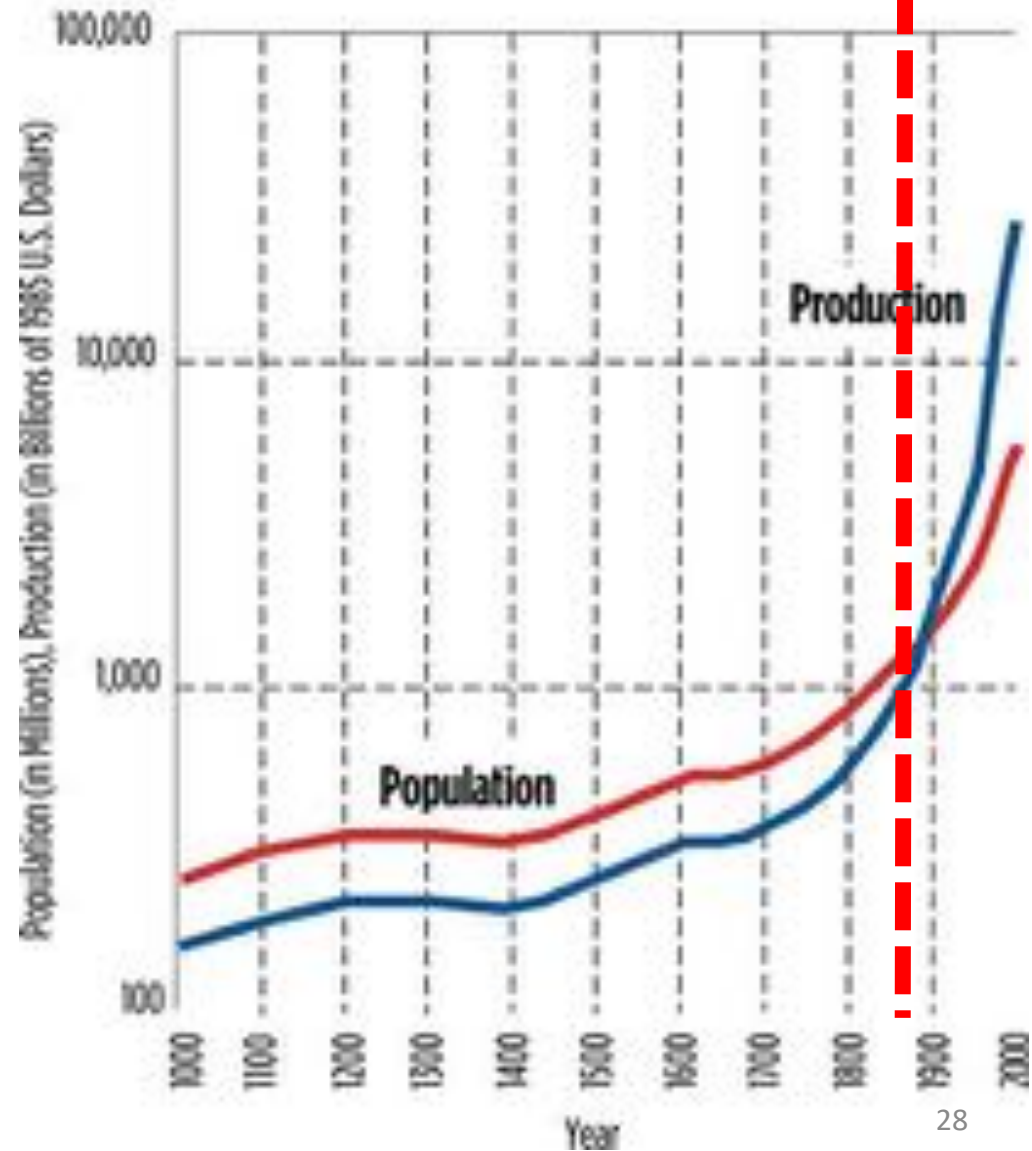
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Some trace metals are
anthropogenic pollutants

Rise of
industrialization
and the advent of
leaded gasoline

Figure 2

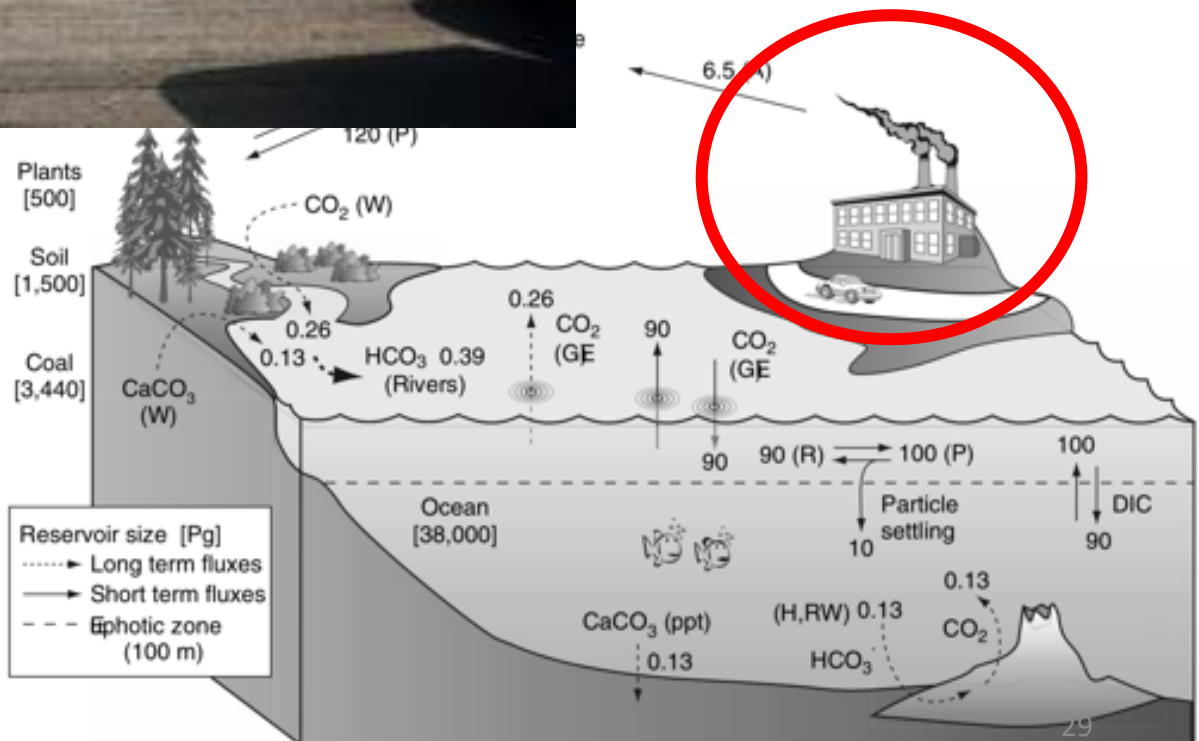
World Population and Production



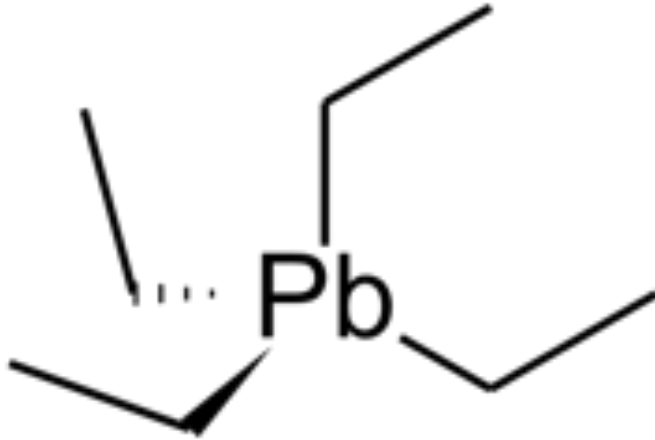


Petrol burning by cars and industry

Fuel burning for industrial activity



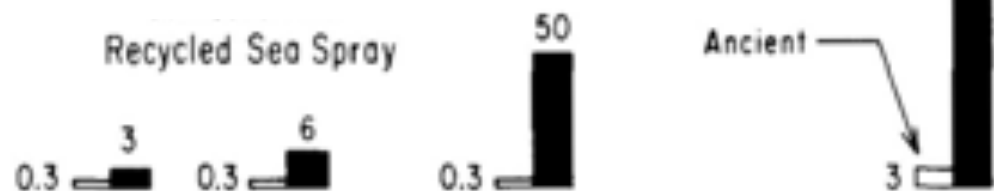
Tetraethyl lead



Pros

- Increases engine efficiency
- Increases vehicle performance

Input of lead into
the surface ocean
(10^{-9} g/cm²)

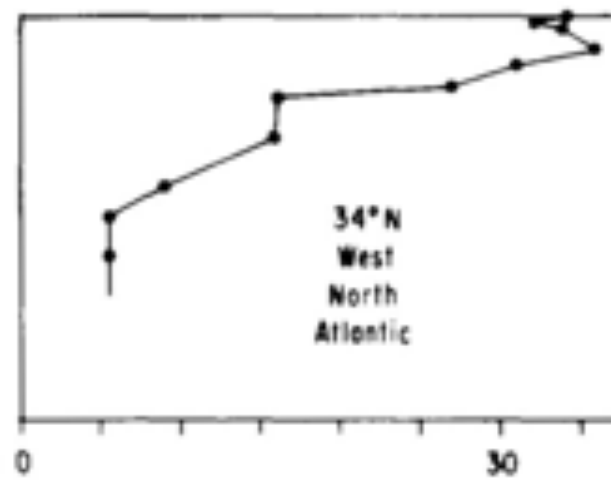
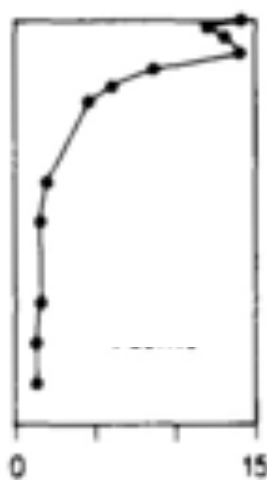
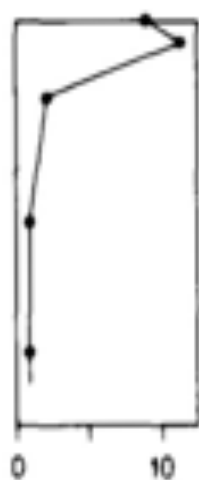
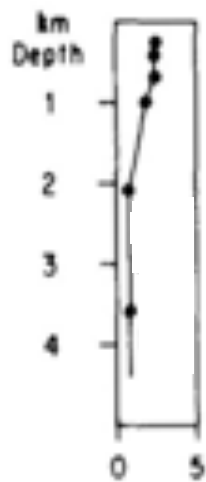


20°S
Central
South Pacific

15°N
Central
North Pacific

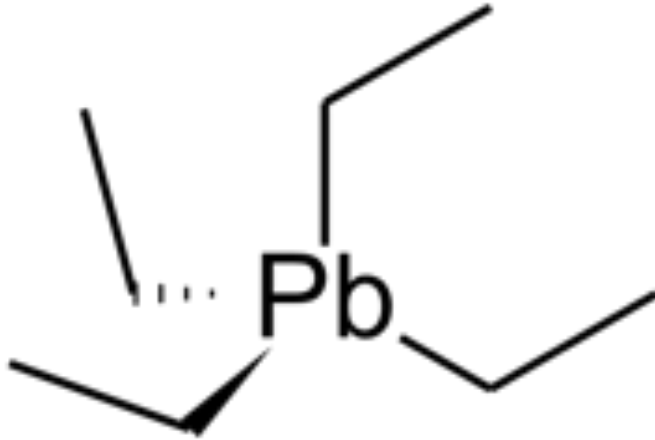
33°N
Central
North Pacific

34°N
West North
Atlantic



Seawater Lead Concentrations 10^{-9} g/kg

Tetraethyl lead



Pros

- Increases engine efficiency
- Increases vehicle performance

Cons

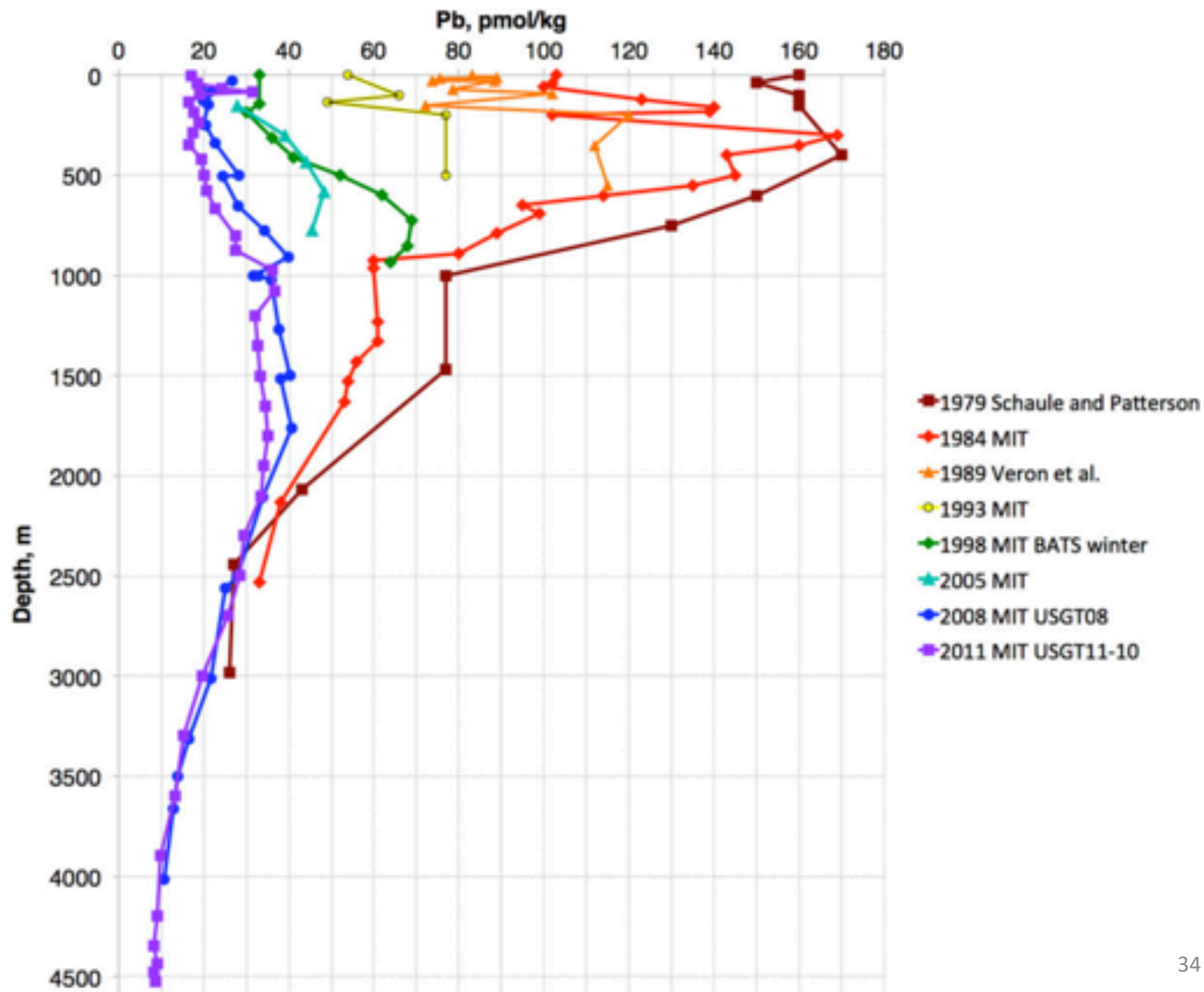
- Found to be highly toxic to many forms of life (including humans)
 - Brain swelling
 - Pulmonary edema
 - Hallucinations
 - Coma
 - Death



Bans/phase-outs of leaded gasoline



Pb profiles near Bermuda, Western North Atlantic, 1979-2011



For the US population, during and after the leaded gasoline bans, the average blood lead level dropped from 16 $\mu\text{g}/\text{dL}$ in 1976 to only 3 $\mu\text{g}/\text{dL}$ in 1991.

Pirkle, Brody, et. al. (1994) National Bureau of Economic Research

Metal level measurements are important to track the degree of anthropogenic pollutants reaching the environment

Other common heavy metal pollutants:

- Mercury
- Arsenic
- Chromium
- Cadmium

Vertical Profiles of Elements in the North Pacific Ocean

(compiled by Y. Nozaki, 2001)

