Royal Netherlands Institute for Sea Research

Bio-essential and pollutant trace metals in a changing Atlantic Ocean

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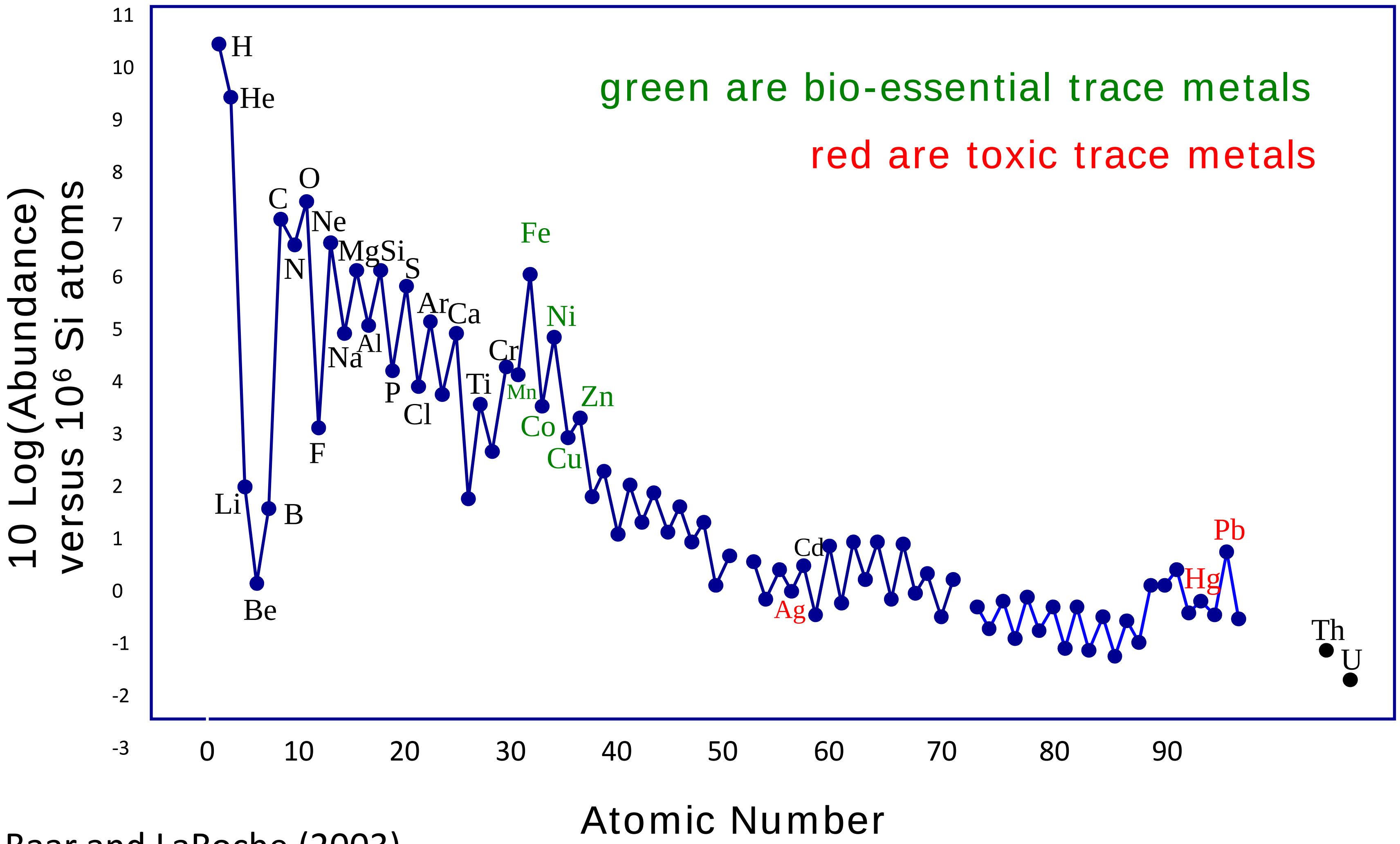
Third International Symposium on the Effects of Climate Change on the world's oceans
Santos City, Brazil, 2015

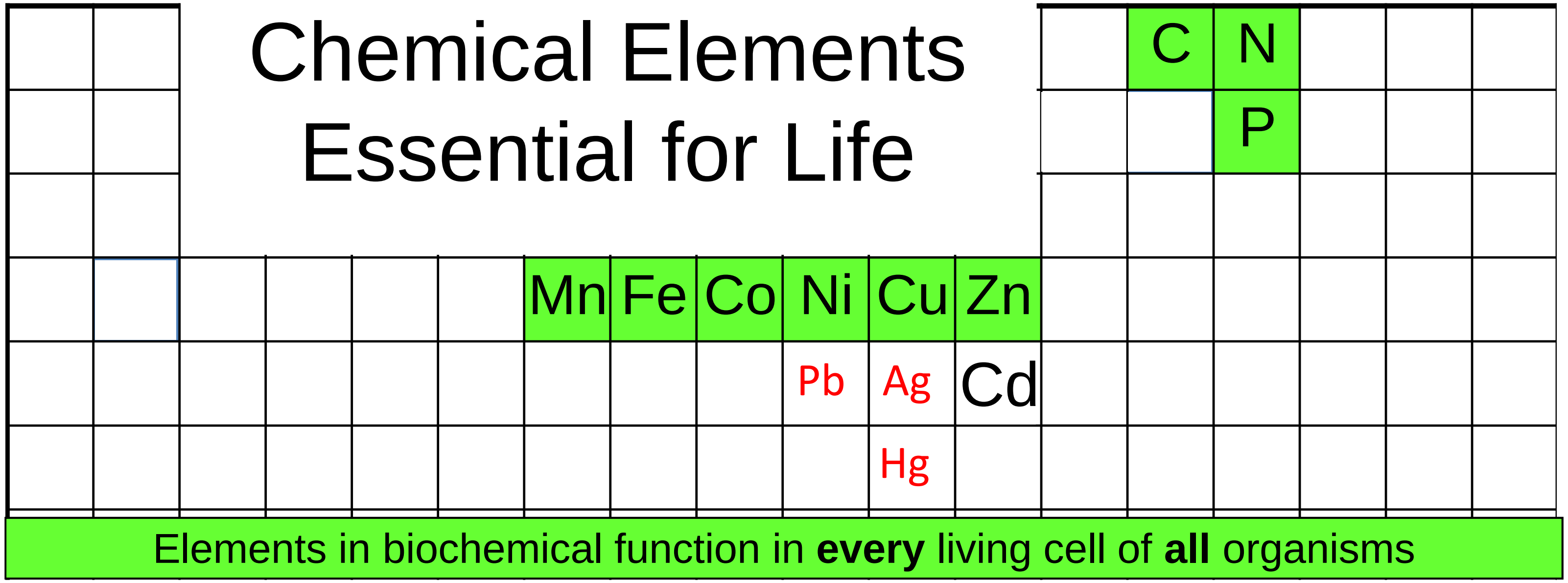
Abundance of chemical elements on our planet

(average crustal abundance on Earth, in the solar system, and in the universe)



de Baar and LaRoche (2003)

Introduction



Bioessential trace elements	
Fe	Iron
Zn	Zinc
Cu	Copper
Mn	Manganese
Co	Cobalt
Ni	Nickel
Cd?	Cadmium

Toxic trace elements	
Pb	Lead
Hg	Mercury
Ag	Silver

after de Baar

Introduction

Pb & Hg

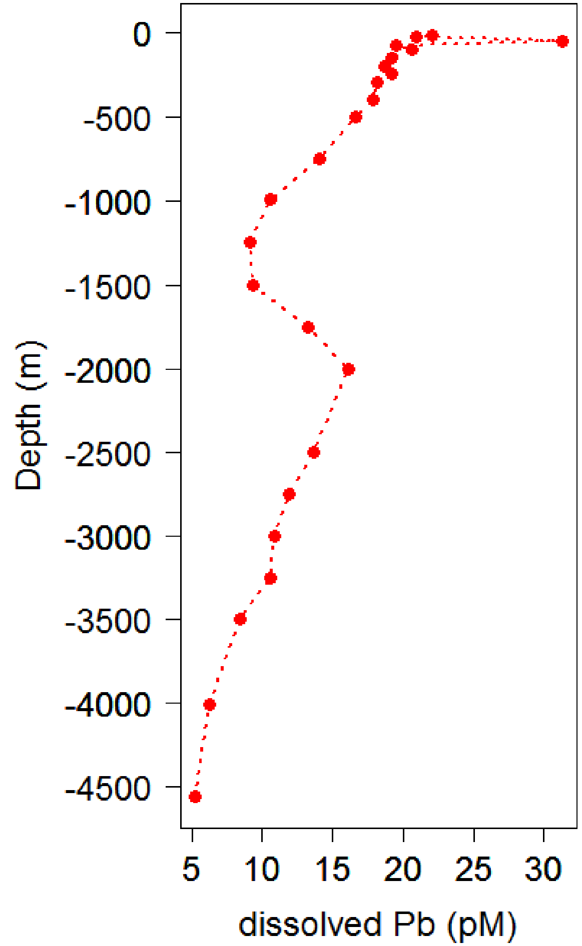
Pb & Hg pollution as anthropogenic impacts on the global environment including the oceans.

Important source of Pb: was/is leaded gasoline
Important source of Hg: coal fired power plants

Depth profiles result from processes like:
1) atmospheric input (Pb & Hg)
2) bio-accumulation in the surface (Hg)
3) organic matter remineralization at depth (Hg)
4) scavenging by particles (Pb & Hg)
5) horizontal advection (Pb & Hg)

NADW: North Atlantic Deep Water

FIGURE WITH UNPUBLISHED totalHg RESULTS REMOVED



western South Atlantic Ocean
Pb by Rob Middag
Hg by Carl Lamborg group

Introduction

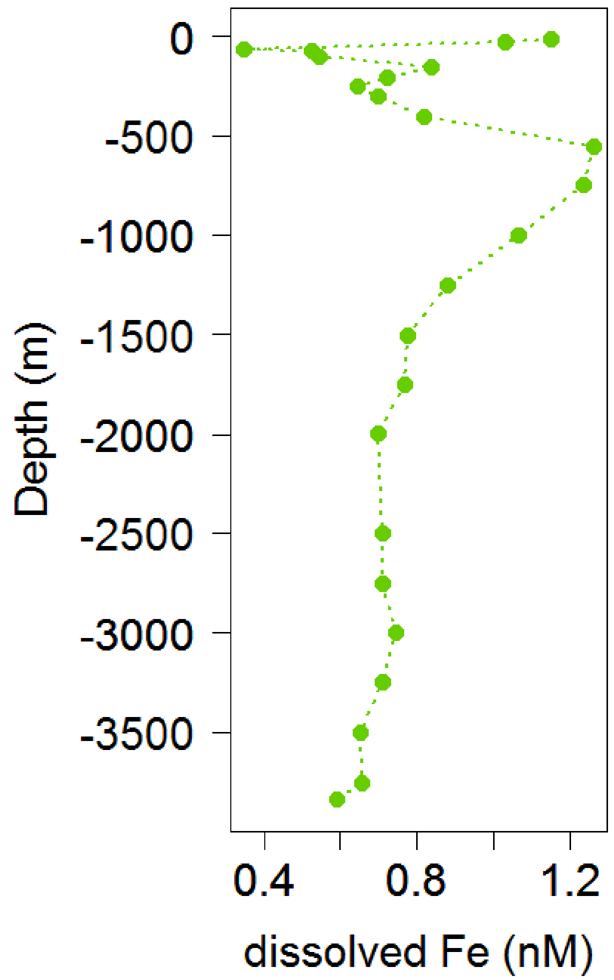
Fe

Fe is bio-essential with functions in many biochemical pathways like e.g. photosynthesis and nitrogen fixation

Fe has a very low solubility which is enhanced due to its complexation to organic Fe-binding ligands.

Fe shows a combined nutrient and scavenged type depth distribution due to:

1) atmospheric input,
2) bio-accumulation in the surface,
3) organic matter remineralization at depth ,
4) Scavenging by particles at depth



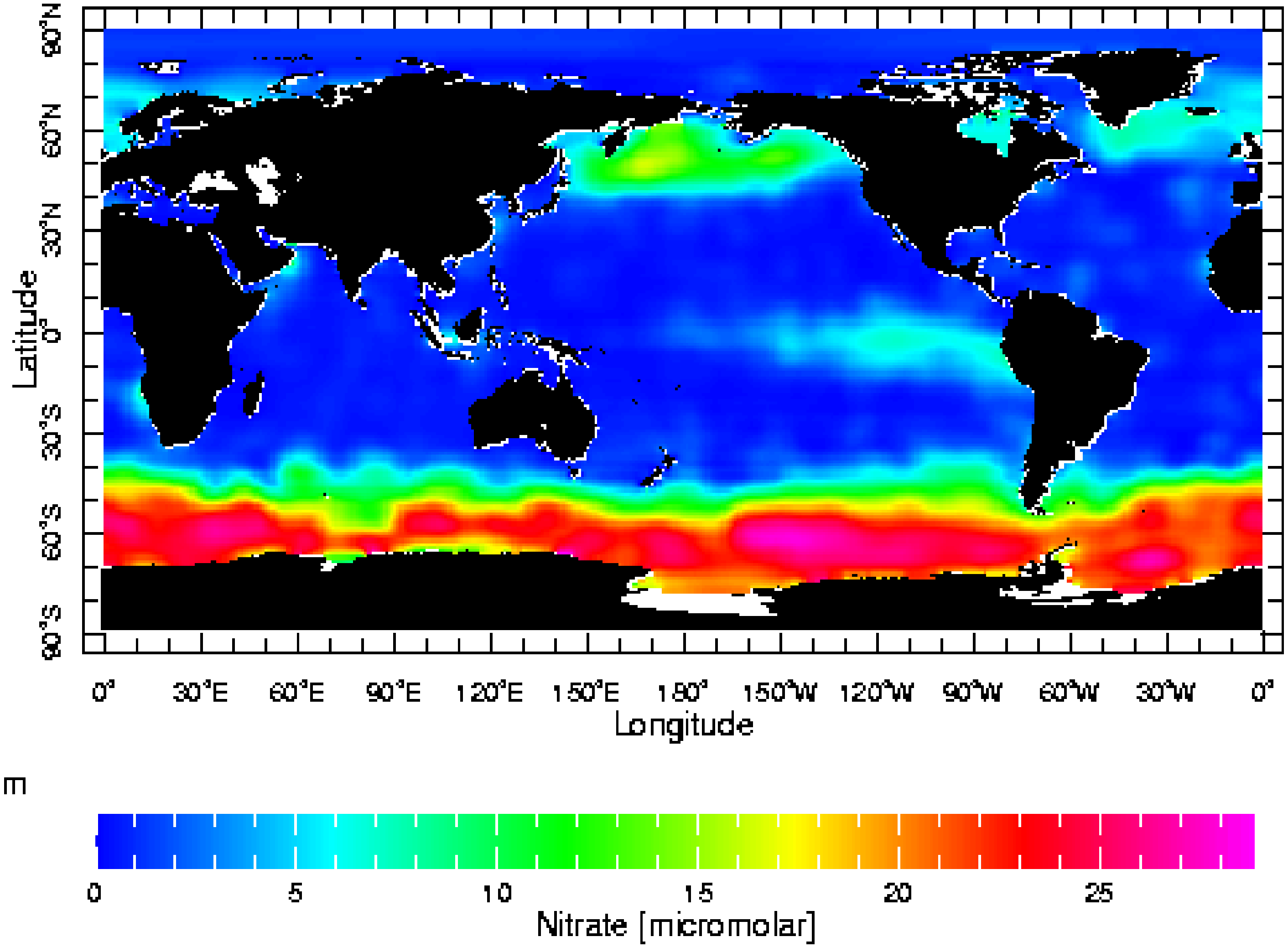
western North Atlantic Ocean

Fe by Patrick Laan

Rijkenberg et al. 2014 PlosONE

Fe

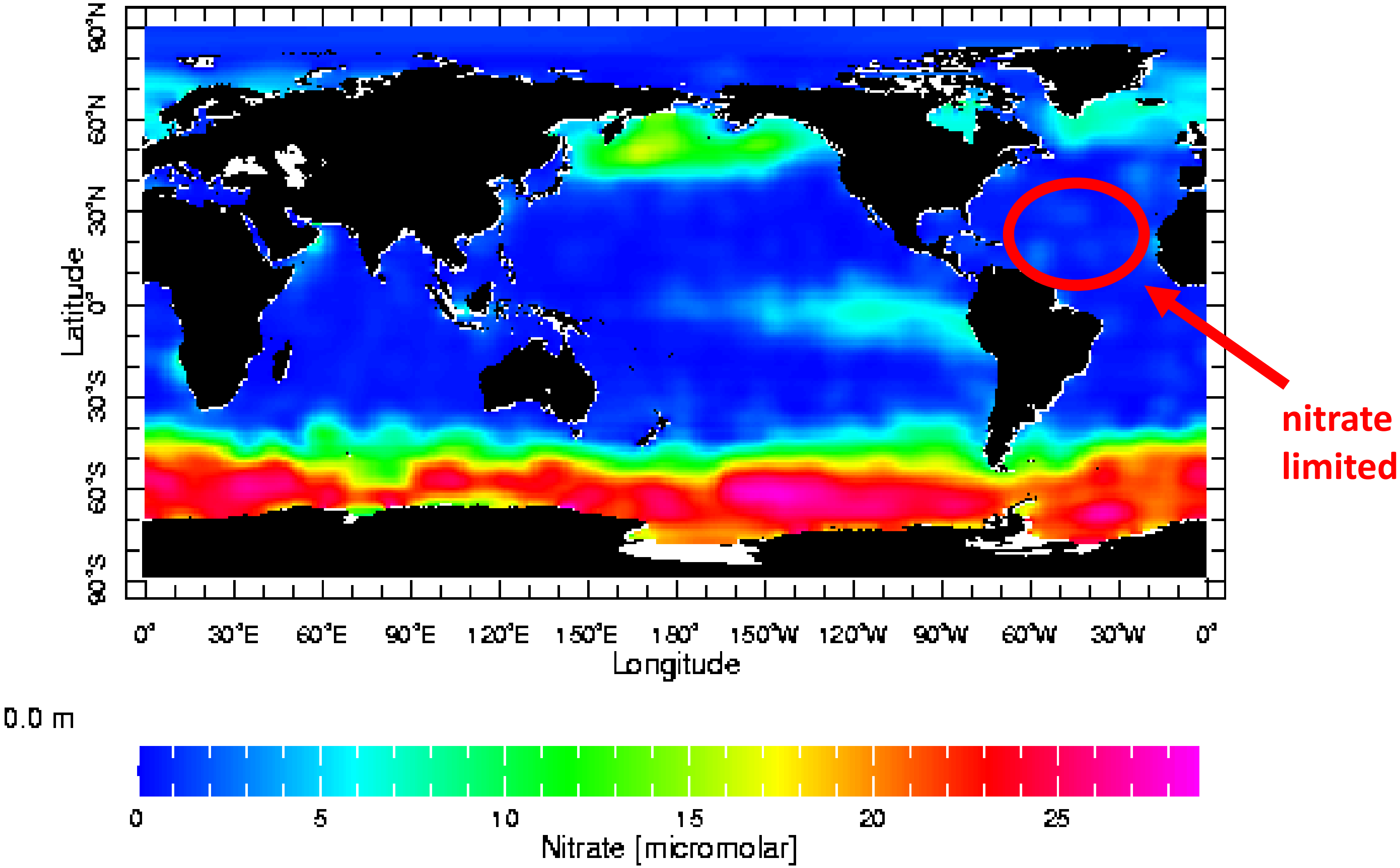
Annual average surface nitrate concentrations



Introduction

Fe

Annual average surface nitrate concentrations



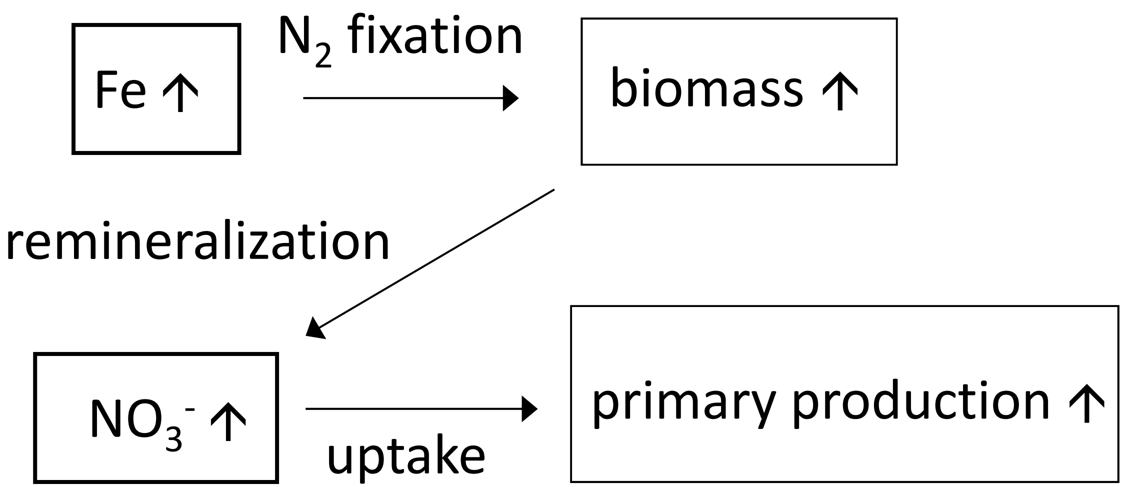
N_2 fixation limited by Fe

Oceanic N_2 fixation

Diazotrophic cyanobacteria fix N_2

N_2 fixation needs about 5 – 10 times more iron than NO_3^- utilisation

In the North Atlantic Ocean N_2 fixation may be limited by Fe (Mills et al. 2004).



Trichodesmium

Trichodesmium bloom

Iron is an important trace metal in the Oceans

1) Iron limits primary production in over 40% of the oceans
2) Iron influences N_2 fixation
3) Iron therefore influences the biogeochemical cycles of:
    a) carbon
    b) nitrogen
    c) but also many other bio-essential elements

There is a need to understand the biogeochemistry of iron now and in the future!

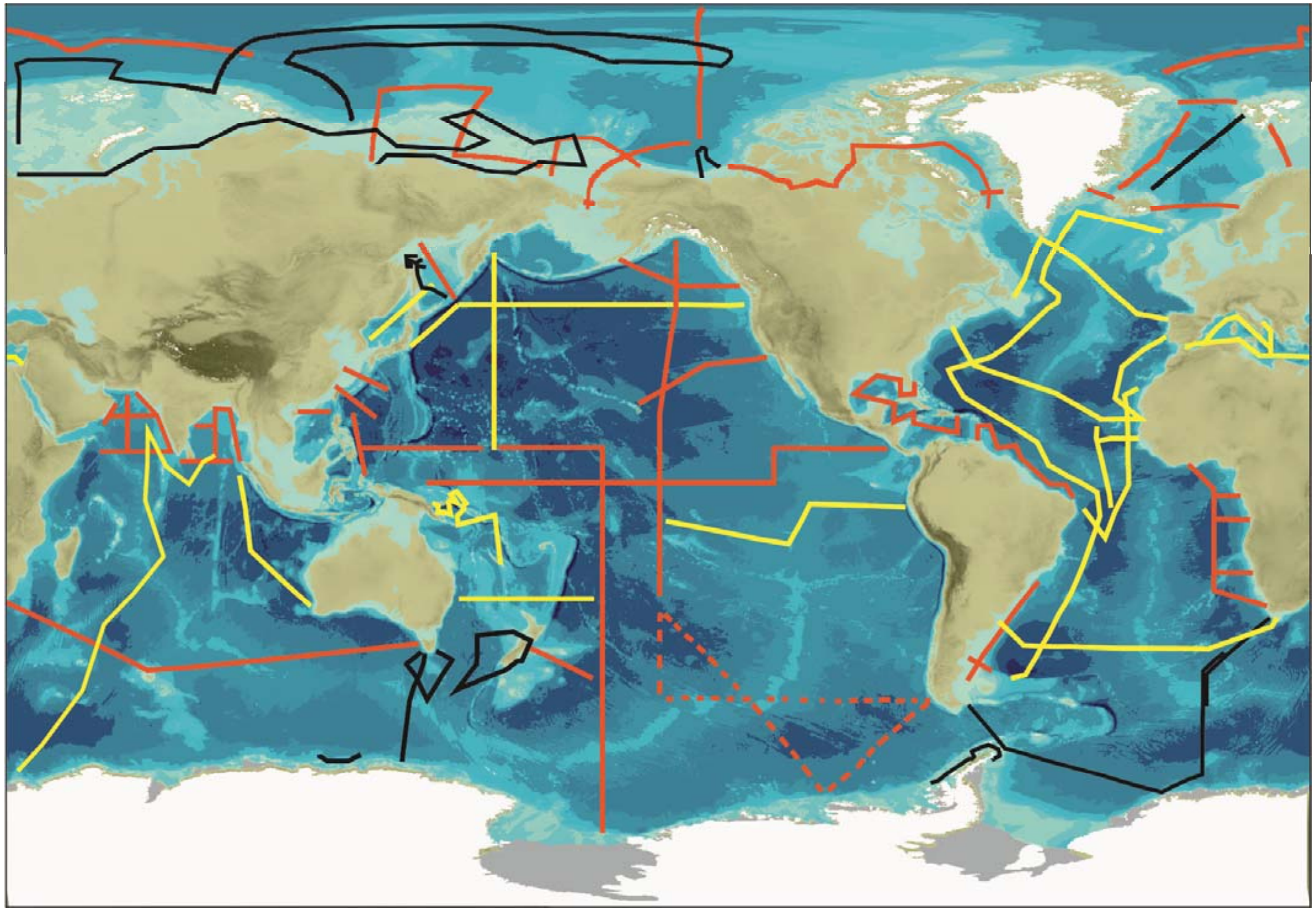
Introduction

GEOTRACES

- International programme
- Scientists from 35 nations
- Examines marine biogeochemical cycles of trace elements and their isotopes
- Will study all major ocean basins over the next decade!

Introduction

GEOTRACES



- IPY
- performed
- planned

GEOTRACES Intermediate Data Product 2014

GEOTRACES Intermediate Data Product released February 2014 at the Ocean Sciences meeting in Honolulu

NATURE | NEWS

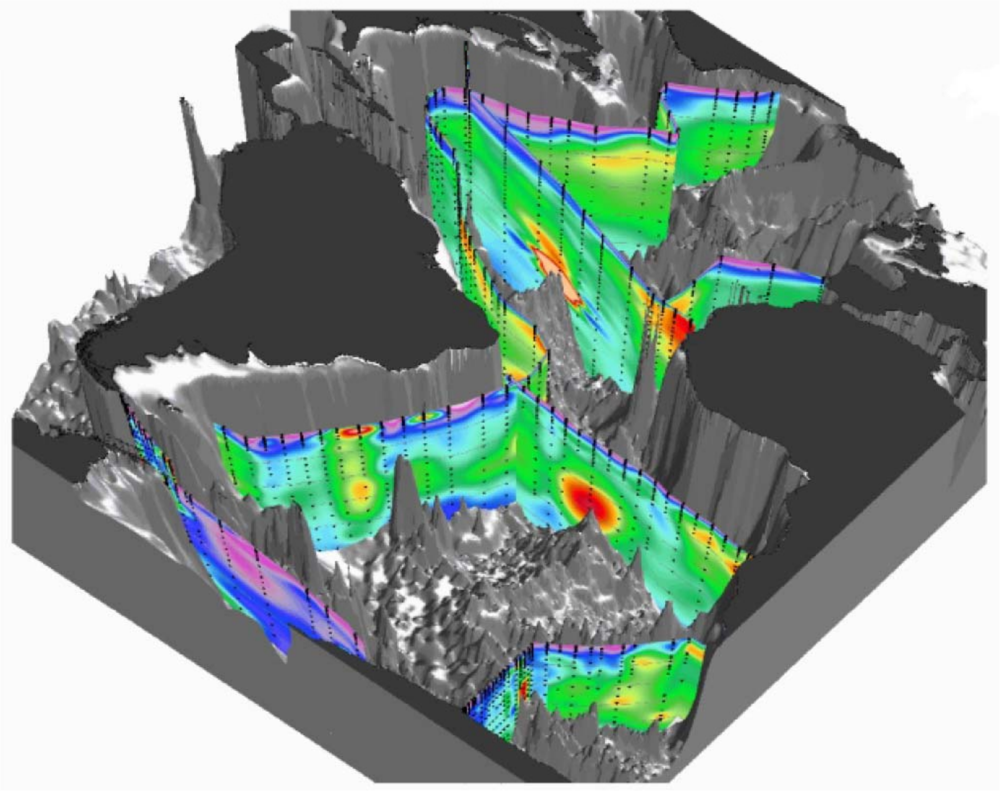
Digital atlas shows oceans' iron levels

Three-dimensional map reveals global sources and sinks for trace metals.

Jessica Morrison

25 February 2014

http://www.geotraces.org/dp/idp2014



Data: Ken Bruland, Tim Conway, Hein de Baar, Fanny Chever, Seth John, Maarten Klunder, Patrick Laan, Francois Lacan, Rob Middag, Abigail Noble, Micha Rijkenberg, Mak Saito, Geraldine Sarthou, Jingfeng Wu
Graphics: Reiner Schlitzer

Pb & Hg pollution

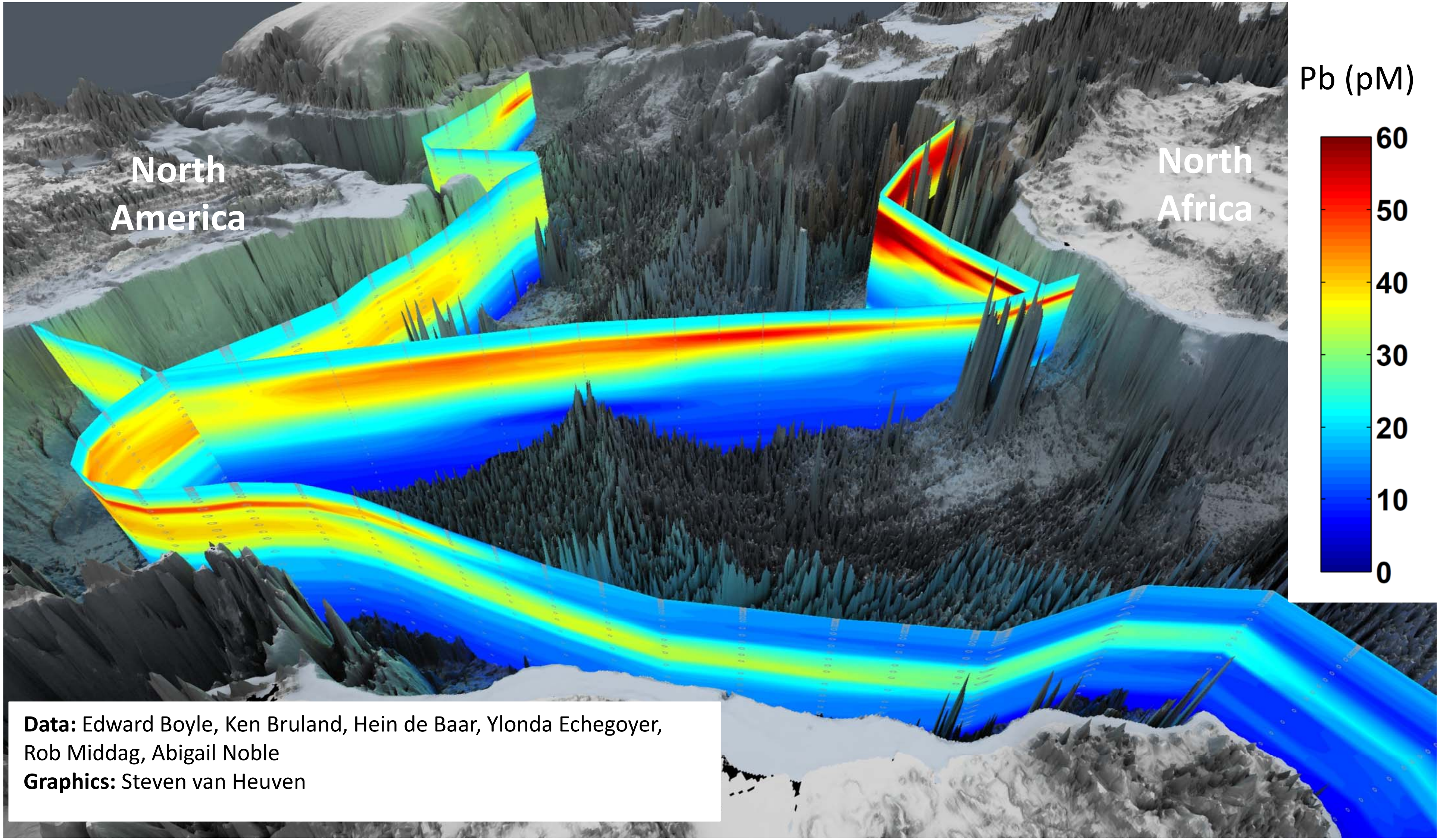
1) The open ocean receives most of its Pb and Hg pollution via atmospheric transport

2) Rapid economic growth results in increasing transport and deposition of Pb and Hg into the ocean

3) Deep water formation transports these surface pollutants to the deep sea where it will enter the global conveyor belt

Pollution & Pb

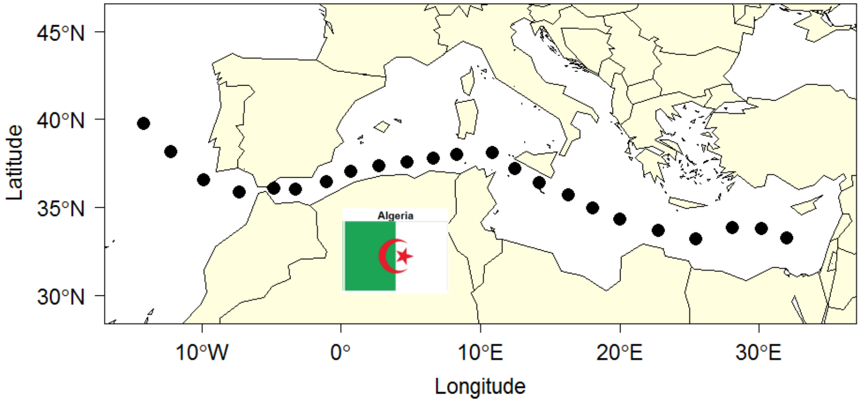
Distribution of dissolved Pb in the Atlantic Ocean



Data: Edward Boyle, Ken Bruland, Hein de Baar, Ylonda Echegoyer, Rob Middag, Abigail Noble
Graphics: Steven van Heuven

Pollution & Pb

Distribution of dissolved Pb in the Mediterranean Sea



Algeria aims to phase out leaded gasoline in 2015

FIGURE WITH
UNPUBLISHED Pb
RESULTS REMOVED

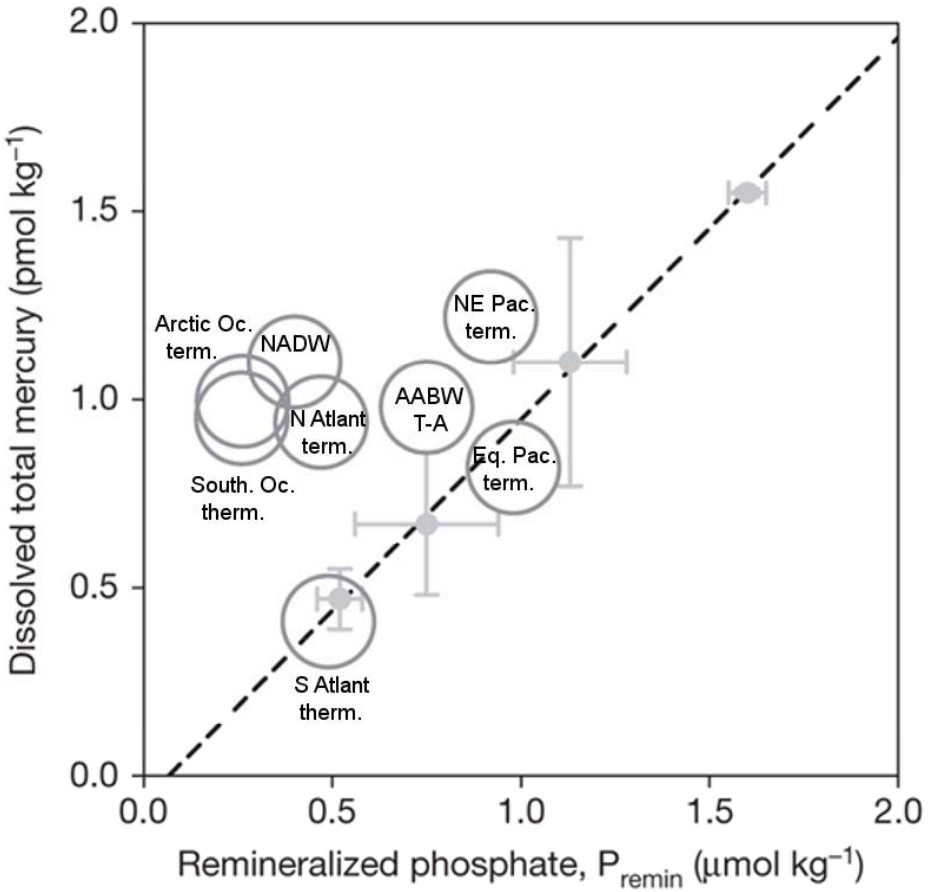
Pollution & Hg

LETTER

doi:10.1038/nature13563

A global ocean inventory of anthropogenic mercury based on water column measurements

Carl H. Lamborg[1], Chad R. Hammerschmidt[2], Katlin L. Bowman[2], Gretchen J. Swarr[1], Kathleen M. Munson[1], Daniel C. Ohnemus[1], Phoebe J. Lam[1], Lars-Eric Heimbürger[3], Micha J. A. Rijkenberg[4] & Mak A. Saito[1]



<u>Deep waters :</u>

NADW : North Atlantic Deep Water in the North Atlantic

AABW T-A: Antarctic Bottom Water between Tasmania and Antarctica

<u>Thermocline waters in:</u>

NE Pac. : North East Pacific Ocean

Eq. Pac. : Equatorial Pacific Ocean

S Atlant. : South Atlantic Ocean

N Atlant. : North Atlantic Ocean

South Oc. : Southern Ocean between Tasmania and Antarctica

Arctic Oc. : Arctic Ocean

Dissolved total Hg in the world oceans

Results from this study showed that:

1) the ocean contains about 60,000 to 80,000 tons of pollution mercury

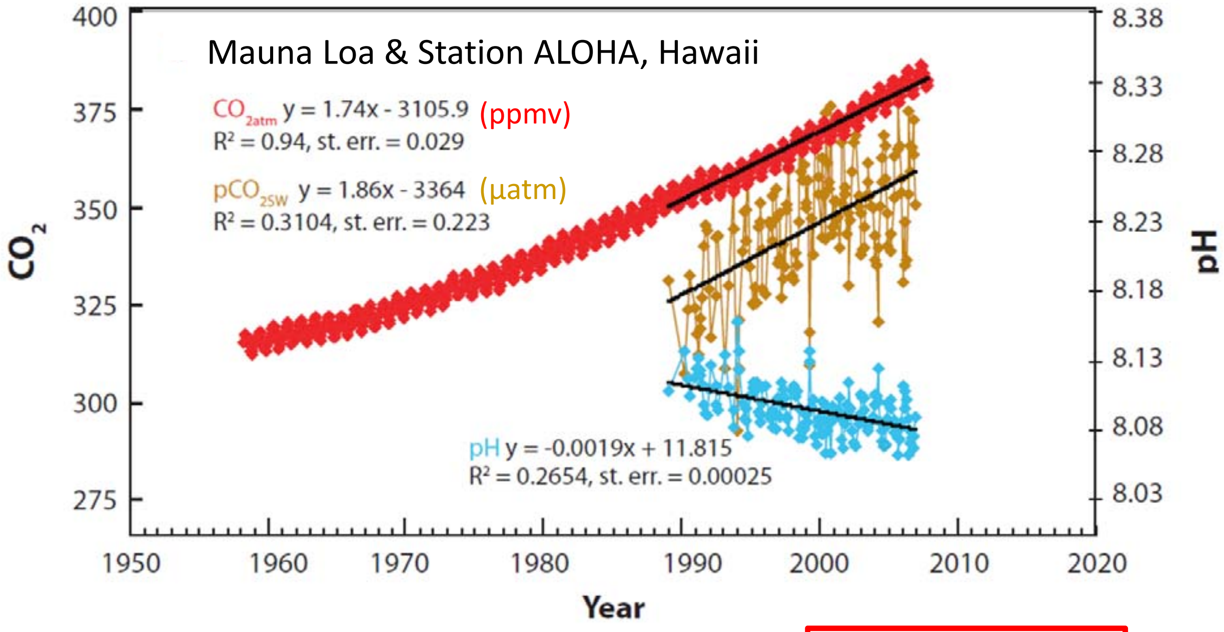
2) ocean waters shallower than about 100 m have tripled in mercury concentration since the Industrial Revolution

3) the ocean as a whole has shown an increase of roughly 10% over pre-industrial mercury levels

Lamborg et al. 2015 Nature

Climate change

Rising CO_2



$$CO_{2(atmos)} \rightleftarrows CO_{2(aq)} + H_2O \rightleftarrows H_2CO_3 \rightleftarrows \boxed{H^+ + HCO_3^-} \rightleftarrows 2H^+ + CO_3^{2-}$$

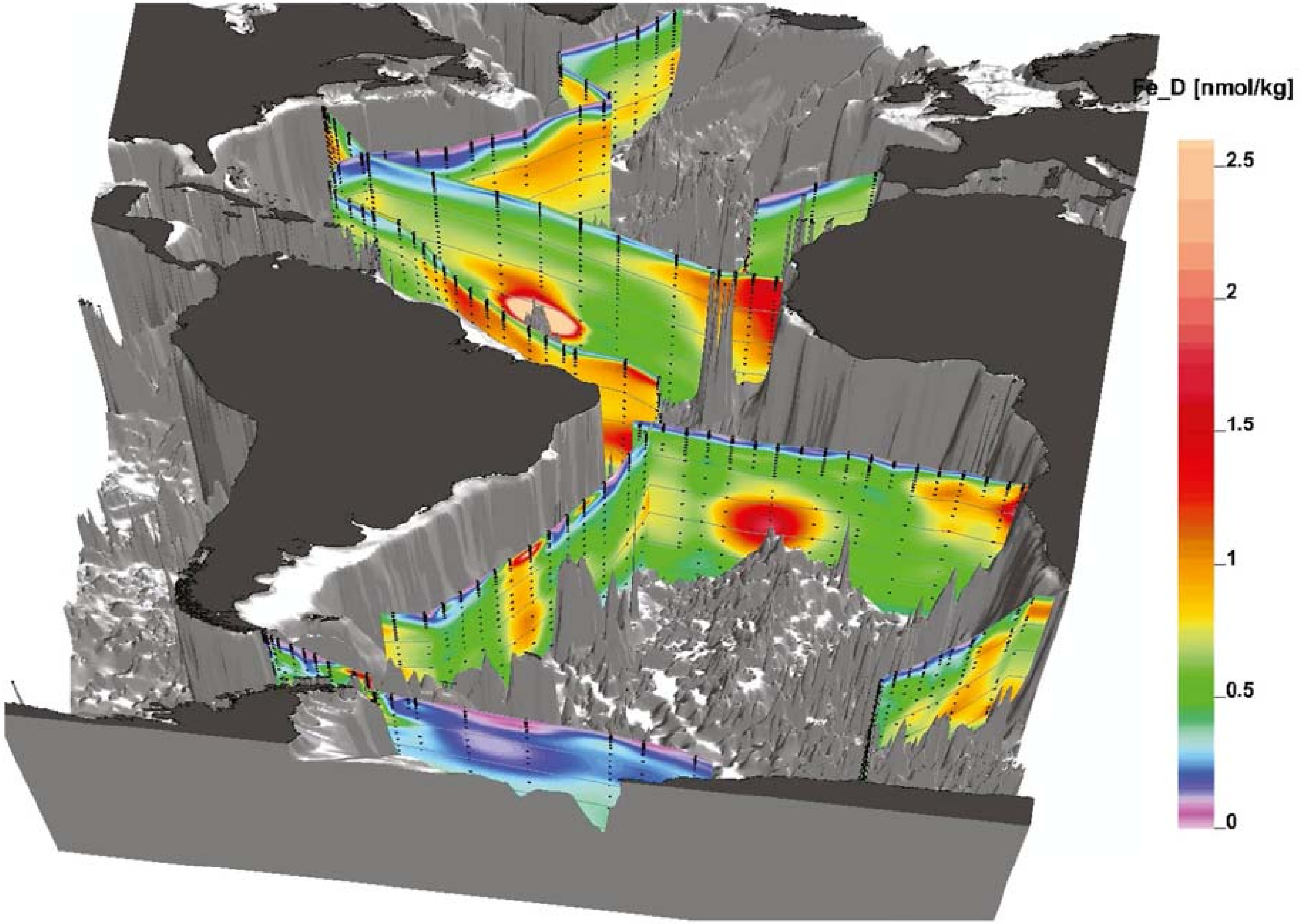
Rising CO_2 levels will result in:

1) a decrease in pH termed ocean acidification (surface pH of ~ 7.7 by 2100)
2) warming of the oceans (2°C increase in the surface by 2100)
3) resulting in decreasing oxygen concentrations
3) changes in atmospheric and hydrographic processes

Figure adapted from Doney et al. 2009 Annu. Rev. Mar. Sci.

Climate change & Fe

Distribution of dissolved Fe in the Atlantic Ocean



Data: Andrew Bowie, Ken Bruland, Tim Conway, Hein de Baar, Fanny Chever, Seth John, Maarten Klunder, Patrick Laan, Francois Lacan, Rob Middag, Abigail Noble, Micha Rijkenberg, Mak Saito, Geraldine Sarthou, Peter Sedwick, Jingfeng Wu Graphics: Reiner Schlitzer

Climate change & Fe

Distribution of dissolved Fe in the Atlantic Ocean

The movie shown here can be found via the below web address:

http://www.egeotraces.org/scenes/Atlantic_Fe_D_CONC_BOTTLE.html

Median depth profile of DFe of the entire western Atlantic Ocean

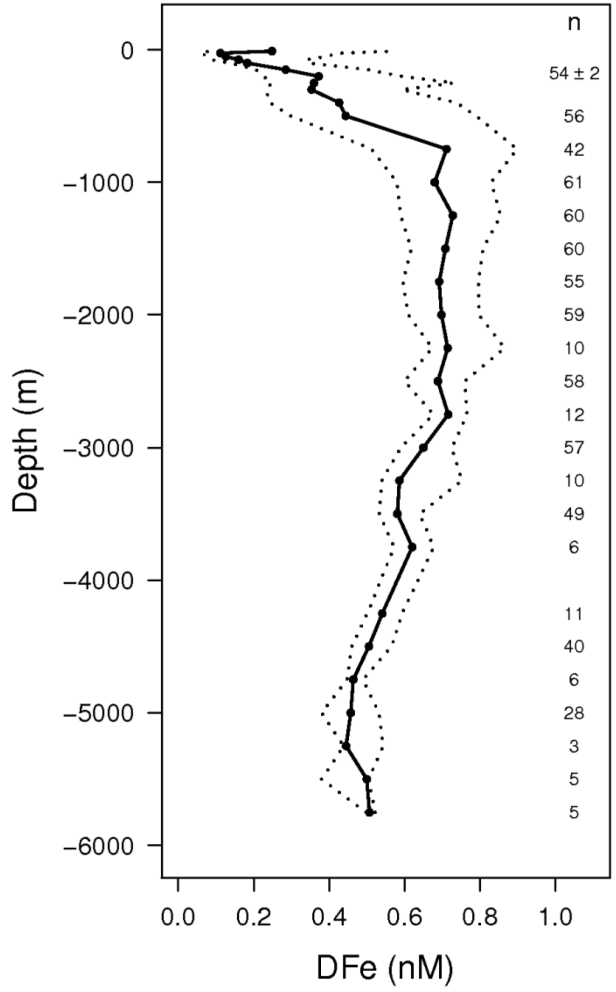
Hybrid-type depth profile

West Atlantic Ocean

Biological uptake

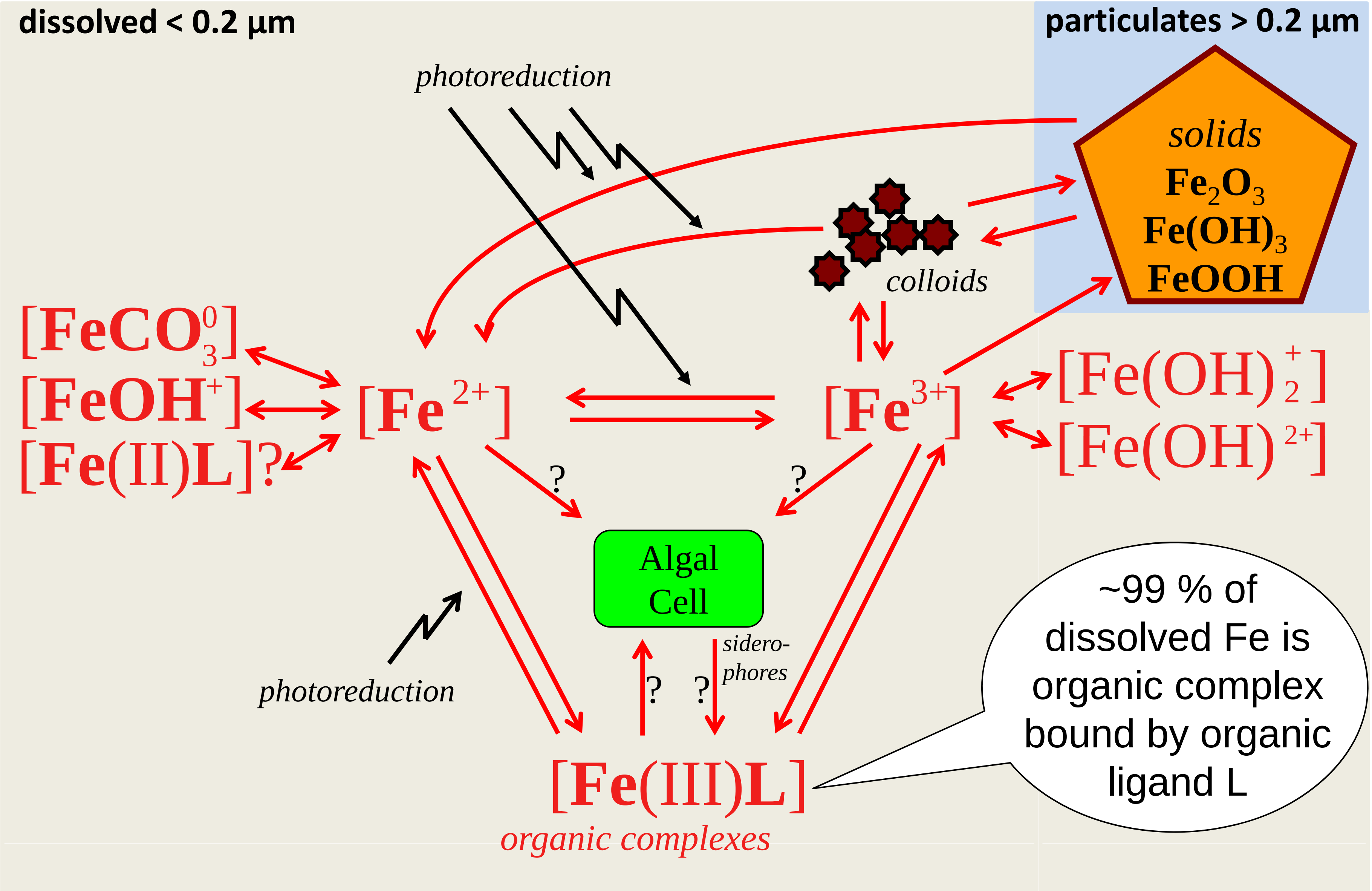
Remineralisation > Scavenging

Scavenging > Remineralisation



Rijkenberg et al. 2014 PlosONE

Climate change & Fe



Gerringa et al.(2000), *Marine Chemistry*, 68, 335-346

Climate change & Fe

Ocean acidification and warming will affect the chemistry of Fe

	warming	**decreasing pH**
inorganic Fe(III) solubility:	↓	↑
inorganic Fe(II) concentration:	↓	↑
Fe adsorbed to organic particles:	?	↓
organically bound Fe :	?	?

Hoffmann et al. 2012; Millero et al. 2009; Shaked et al. 2008; Breithbarth et al. 2010; Shi et al. 2010: Gledhill et al. in press

Climate change & Fe

Biological cycling of Fe

An oversimplified view:

Seawater pCO_2 and ocean warming increase phytoplankton growth because:

1) CO_2 is the main substrate for photosynthesis
2) metabolic rates increase with increasing temperature

However, mesocosm studies showed that:

1) peak biomass was lower at elevated temperature
2) The community shifted to smaller cell sizes

Furthermore, phytoplankton Fe requirements and uptake may change.

Hutchins et al. 2009: Passow and Carlson, 2012

Climate change & Fe

Atmospheric and oceanographic processes

Ocean warming results in:

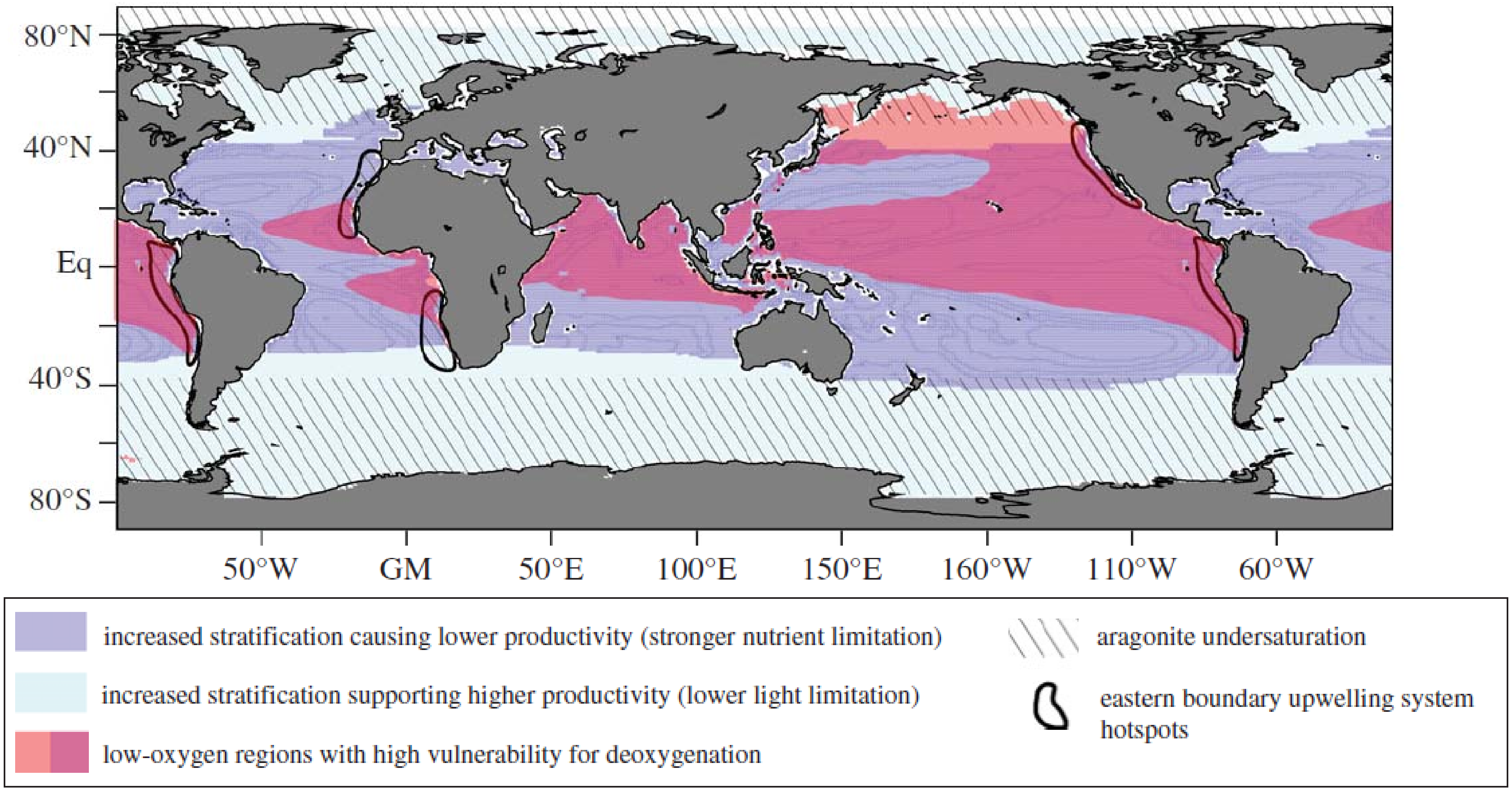
1) enhanced stratification
2) a decrease in oxygen concentration

Climate warming results in:

1) changes in upwelling favorable winds
2) dust transport
3) changes in precipitation

Climate change & Fe

Biological cycling of Fe

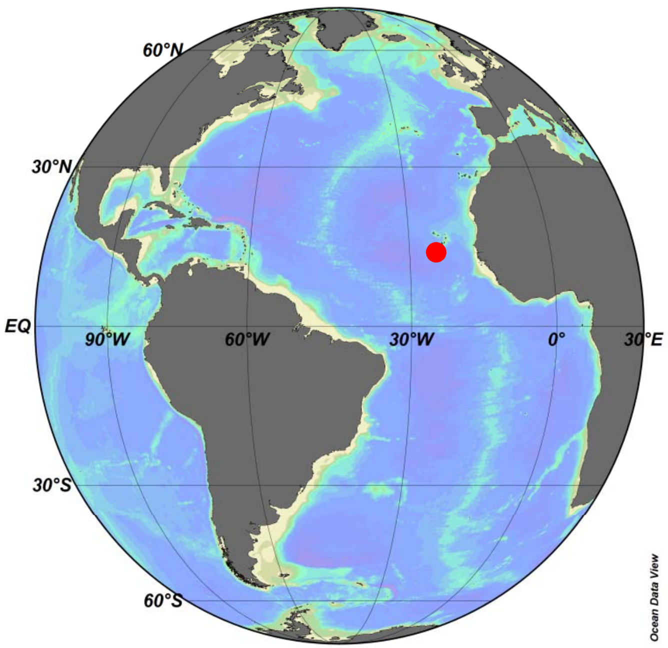


Gruber, 2011, Phil. Trans. R. Soc. A

Climate change & Fe

Biological cycling of Fe

DUST Fe flux 2.45 10^{-11} mol m^{-2} s^{-1}
(flux during major dust event)



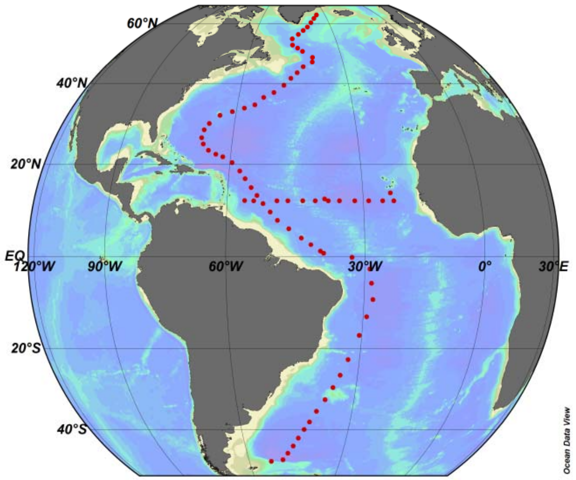
vertical diffusive Fe flux above OMZ
2.19 +/- 2.4 10^{-11} mol m^{-2} s^{-1}

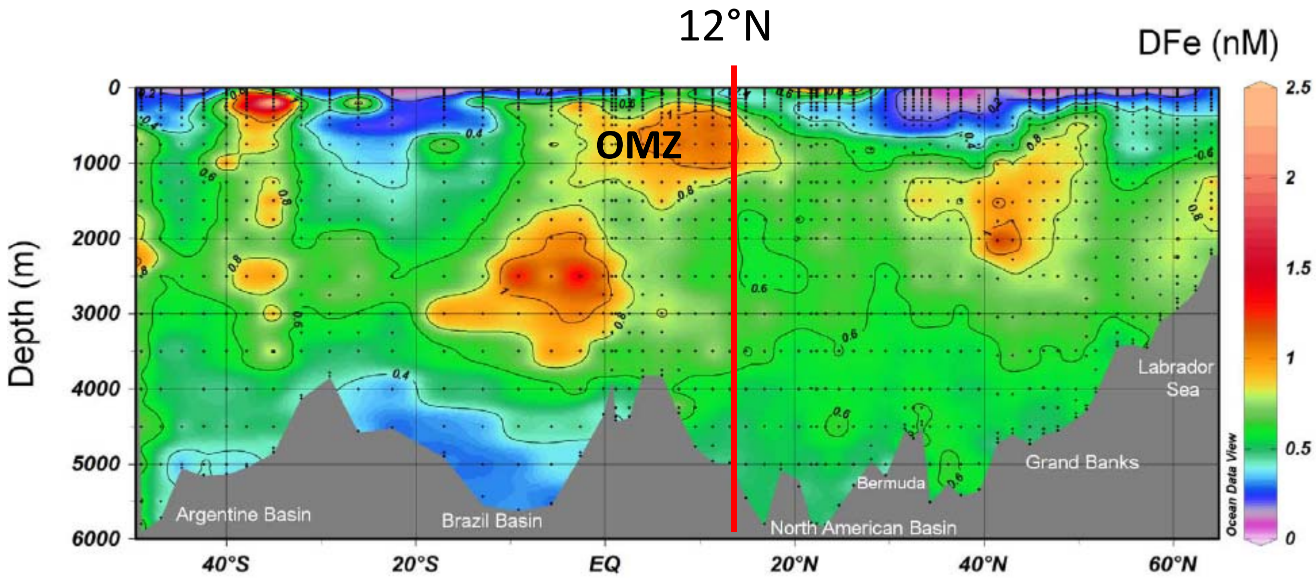
vertical diffusive Fe flux above OMZ = aerosol Fe flux during a major dust event

Rijkenberg et al. 2012 GBC

Climate change & Fe

Oxygen minimum zones





OMZ

OMZ

Steep gradients in DFe between 100-200 m depth

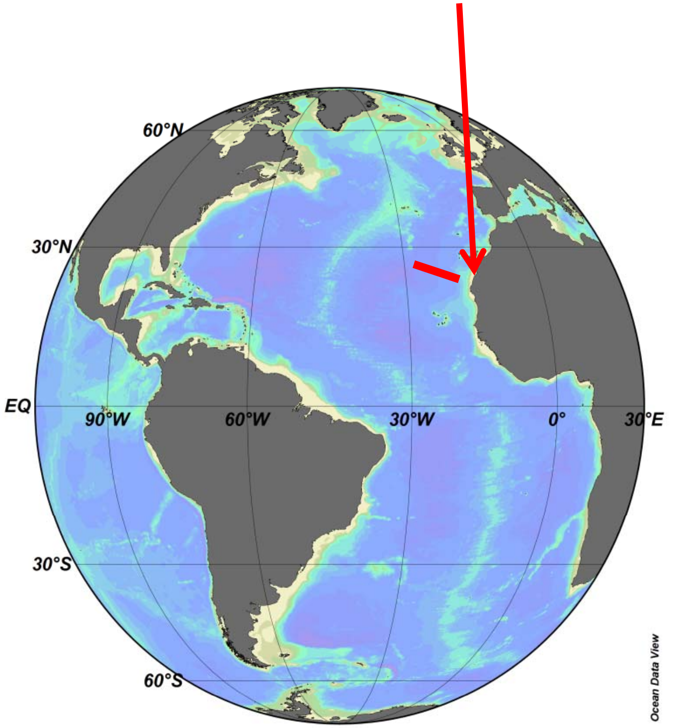
FIGURE WITH UNPUBLISHED DFe RESULTS REMOVED

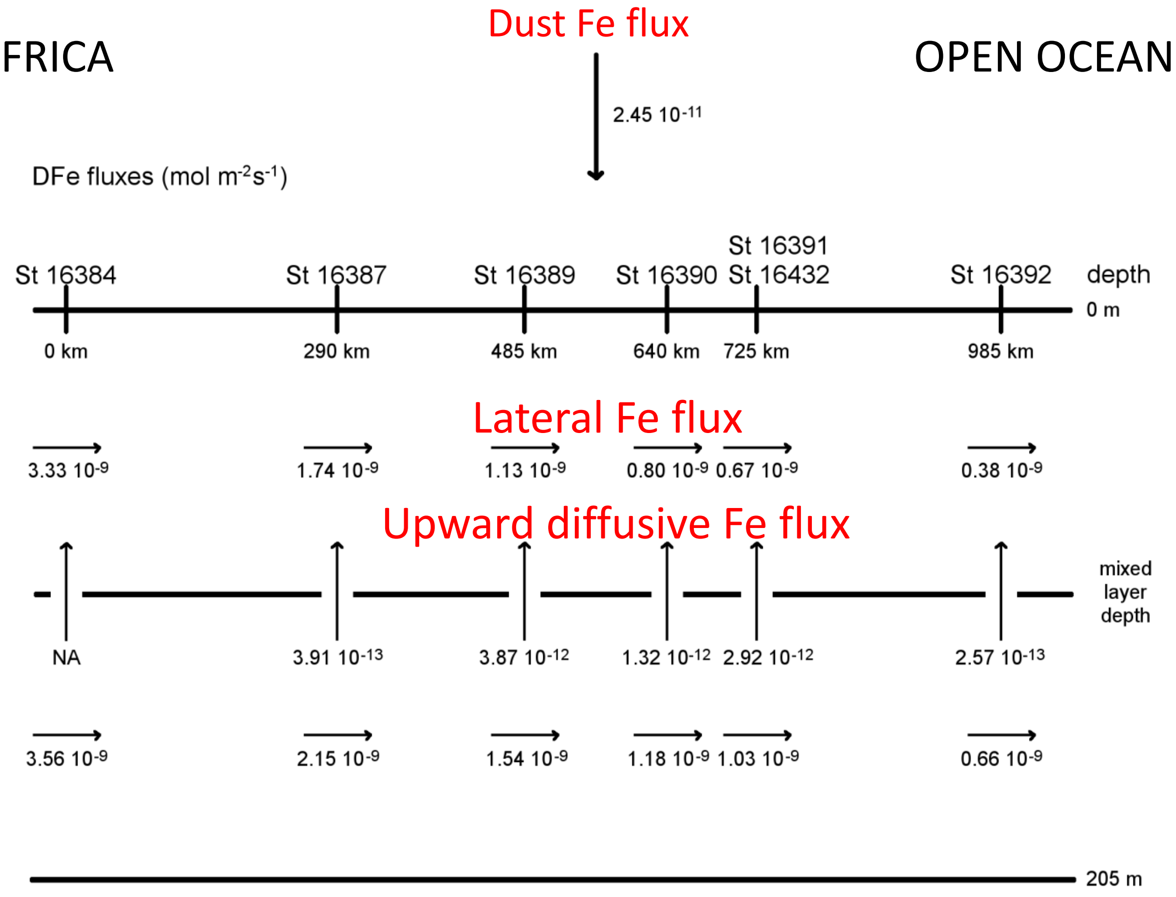
Rijkenberg et al. 2014 PlosONE

Climate change & Fe

Upwelling

Upwelling area





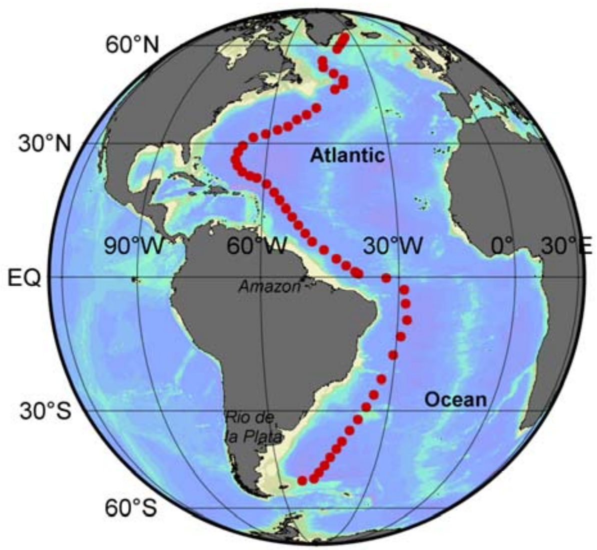
Lateral Fe Flux > Dust Fe flux > Upward diffusive Fe flux

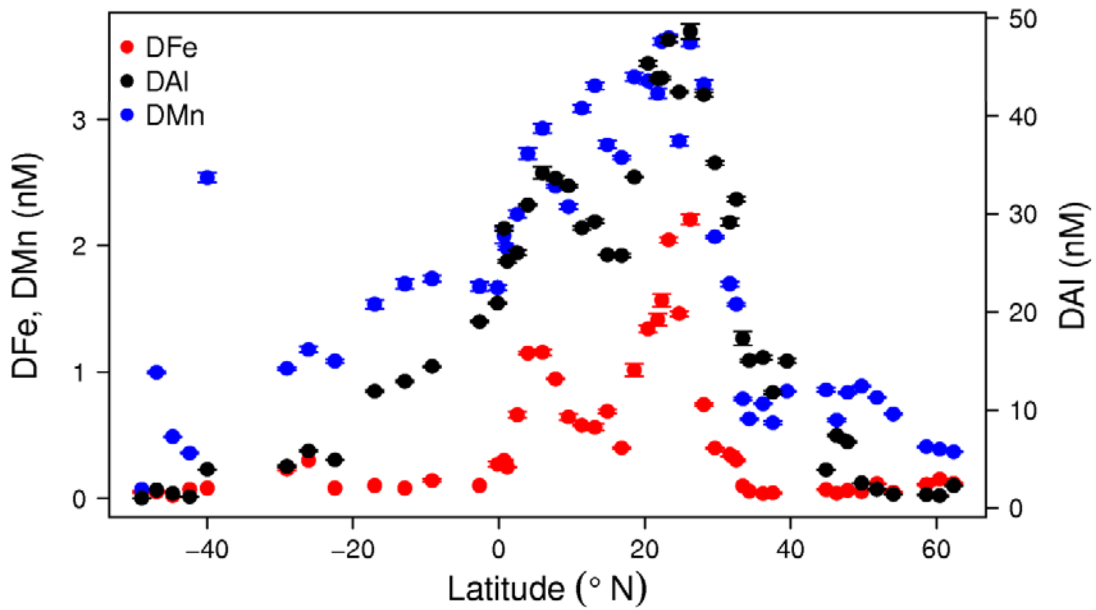
10^{-9} 10^{-11} 10^{-12}

Rijkenberg et al. 2012 GBC

Climate change & Fe

Aerosol Fe in the Atlantic Ocean





Rijkenberg et al. 2014, PlosONE

Saharan dust input is the main source of DFe to the North Atlantic Ocean.

Fishwick et al. 2014 showed no effect of seawater temperature, pH, and oxygen concentration on the dissolution of Fe from dust.

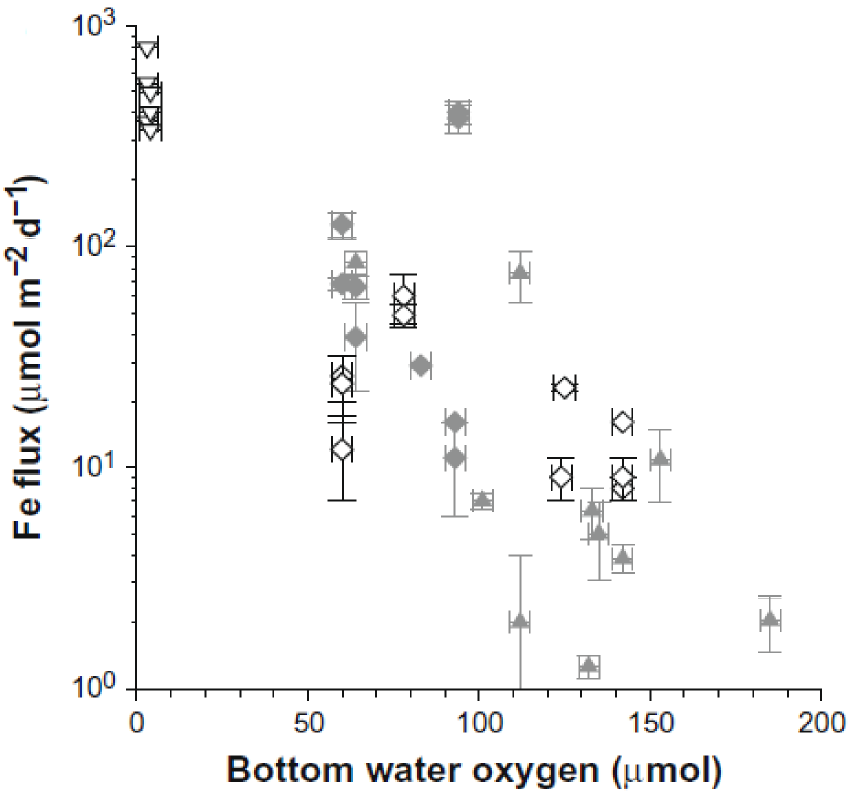
Barrett et al. 2015 found that changes in precipitation increased inventories of Al and Fe under the Saharan dust plume in 2013 compared to 2003 suggesting an increase in dust input.

Climate change & Fe

Release of Fe from sediments

Release form sediments is an important source of Fe and has been observed throughout the Atlantic.

More Fe is released at lower bottom seawater oxygen concentrations.

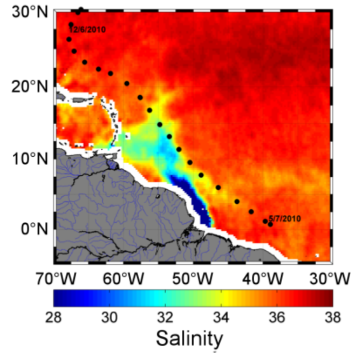


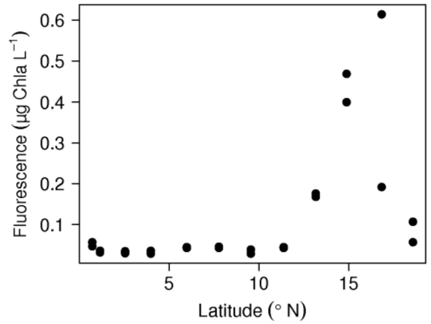
Oregon-California continental shelf (Severmann et al. 2010, GCA)

Climate change & Fe

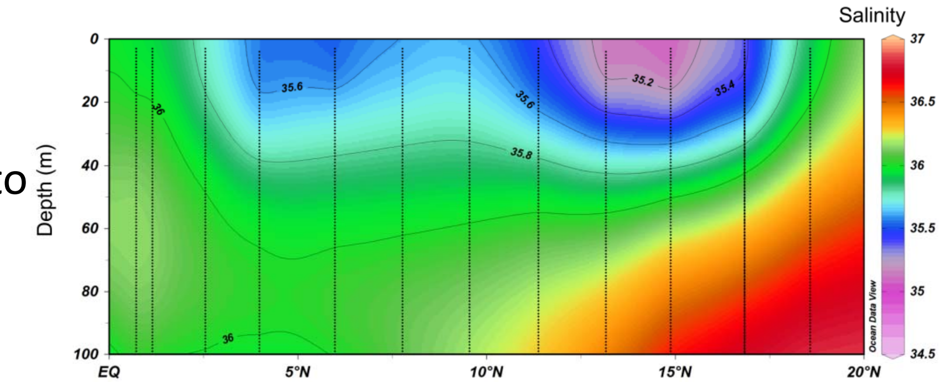
Input of Fe with river run-off

River run-off of Fe important for coastal areas but also to the open ocean.



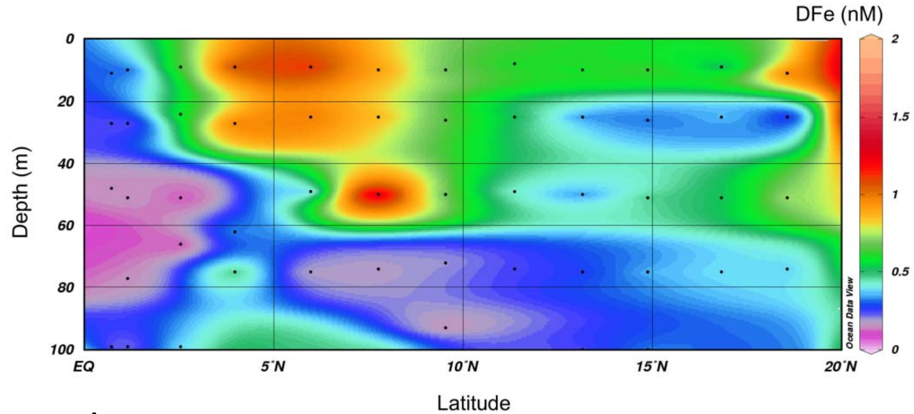


Globally precipitation is predicted to increase. A decrease is predicted in the subtropics (Meehl et al. 2007).



But other factors may influence Fe transport to the open ocean, like changes:

1) in terrestrial sources, e.g. erosion
2) the Fe chemistry, like:
    * complexation to organic matter
    * colloid chemistry
    * redox processes



Hoffmann et al. 2012 MEPS; Rijkenberg et al. 2014 PlosONE

Conclusions

1) The anthropogenic impact of pollutant trace metals can be distinguished and regulation could reduce their impact

2) Only now with GEOTARCES do we start to understand the importance of sources and factors that determine the distribution of Fe in the oceans

3) We need to understand the chemistry of Fe in seawater especially in relation to organic complexation

4) We need to understand and quantify the processes that affect the input of Fe from external sources and the transport and recycling of Fe within the oceans

5) Only then will it be useful to try to predict the changes in the biogeochemical cycle of Fe in the future oceans

Overall, lots of work to do!!

Acknowledgements: Hein de Baar, Crew & Captain John Ellen, Bert Puijman and Pieter Kuijt of **RV Pelagia**, Crew & Captain Bill Richardson **RRS James Cook**, Martin Laan, Lorenz Boom, Jan van Ooijen, Patrick Schmidt, Michiel RvdLoeff, Sven Kretschmer, Viena Puigcorbe, Merce Bermejo, Thomas Reinthaler, Taichi Yokokawa, Daniele de Corte, Santiago Gonzalez, Sander Asjes, Karel Bakker, Marie Boye, Oliver Lechtenfeld, Kerstin Olbrich, Eva Sintes, Leon Wuis, Kristin Bergauer, Maaike Claus, Feifei Deng, Jonathan Derot, Jose Marcus Godoy, Lennart Groot, Alison Hartman, Elizabeth Jones, Adam Klimiuk, Itziar Lekunberri, Sven Ober, Stephanie Owens, Leo Pena, Jan-Dirk de Visser, Evaline van Weerlee, Dominik Weiss, Nikki Clargo, Gabriel Dulaquais, Sharon Ossebaar, Audrey van Mastrigt, Sophie Vergouwen, Jack Underwood, Jason Scott, Gareth Knight, Jez Evans, Jane Thompson, Mark Westcott, Colin Day, Marietta Anthoulas, Marcel Bakker, Pim Boute, Ruud Groenewegen, Joaquin Pampin, John Rolison, Aymen Saadi, Nicolas Sanchez, Hans Slagter, Morten Andersen, Kemal Can Bizsel, Johann Bown, Lars-Eric Heimburger, Franks van Maarseveen, Sharyn Ossebaar, Matt Patey, Jeroen Sonke, Barry
Boerse ... , Ejin
George ... urgaft,
Hendri ... hilling,
Maarte ... Arend
Nieboer, NIOZ MTEC department, NWO, ZKO, and many others......

S3 Changing ocean chemistry: From trace elements and isotopes to radiochemistry and organic chemicals of environmental concern.