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

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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

### Chemical Elements Essential for Life

<table>
<thead>
<tr>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>Ag</td>
<td>Cd</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td></td>
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</tbody>
</table>

Elements in biochemical function in every living cell of all organisms

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### 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

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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
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.

Rijkenberg et al. 2014 PlosONE
Introduction

Fe

Annual average surface nitrate concentrations
Introduction

Fe

Annual average surface nitrate concentrations

nitrate limited
Introduction

$N_2$ 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](image1)

![Trichodesmium bloom](image2)
Introduction

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!
- 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!
GEOTRACES

- IPY
- performed
- planned
Introduction

GEOTRACES Intermediate Data Product 2014

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

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
Pollution

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

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

Carl H. Lamborg¹, Chad R. Hammerschmidt², Katlin L. Bowman², Gretchen J. Swarr¹, Kathleen M. Munson¹, Daniel C. Ohnemus¹, Phoebe J. Lam¹, Lars-Eric Heimbürger³, Michæl J. A. Rijkenberg⁴ & Mak A. Saito¹

Deep waters:
NADW: North Atlantic Deep Water in the North Atlantic
AABW T-A: Antarctic Bottom Water between Tasmania and Antarctica

Thermocline waters in:
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
Pollution & Hg

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
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
Climate change & Fe

Distribution of dissolved Fe in the Atlantic Ocean

Data: Andrew Bowie, Ken Bruland, Tim Conway, Heinde Baar, Fanny Chever, Seth John, Maerton Klunder, Patrick Lean, Francois Lakan, Rob Midday, Abigail Noble, Micha Rijkenberg, Mak Saito, Geraldine Sarthou, Peter Smedwick, 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
Climate change & Fe

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

particulates > 0.2 µm

solids
Fe₂O₃
Fe(OH)₃
FeOOH

dissolved < 0.2 µm

photoreduction

[FeCO₃] [FeOH⁺] [Fe(II)L]?
[Fe²⁺]

[Fe(III)L]
organic complexes

[Fe³⁺]

[Fe(OH)²⁺]

[Fe(OH)⁺]

~99 % of dissolved Fe is organic complex bound by organic ligand L

Gerringa et al.(2000), Marine Chemistry, 68, 335-346
**Climate change & Fe**

Ocean acidification and warming will affect the chemistry of Fe

<table>
<thead>
<tr>
<th>warming</th>
<th>decreasing pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>inorganic Fe(III) solubility:</td>
<td>↓</td>
</tr>
<tr>
<td>inorganic Fe(II) concentration:</td>
<td>↓</td>
</tr>
<tr>
<td>Fe adsorbed to organic particles:</td>
<td>?</td>
</tr>
<tr>
<td>organically bound Fe:</td>
<td>?</td>
</tr>
</tbody>
</table>

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
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.

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
Biological cycling of Fe

Gruber, 2011, Phil. Trans. R. Soc. A
**Biological cycling of Fe**

DUST Fe flux $2.45 \times 10^{-11} \text{ mol m}^{-2} \text{s}^{-1}$

(flux during major dust event)

vertical diffusive Fe flux above OMZ
$2.19 \pm 2.4 \times 10^{-11} \text{ mol m}^{-2} \text{s}^{-1}$

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

Rijkenberg et al. 2012 GBC
Oxygen minimum zones

Steep gradients in DFe between 100-200 m depth

FIGURE WITH UNPUBLISHED DFe RESULTS REMOVED

Rijkenberg et al. 2014 PlosONE
Climate change & Fe

Upwelling

AFRICA

Dust Fe flux

OPEN OCEAN

DFe fluxes (mol m$^{-2}$s$^{-1}$)

Lateral Fe flux

Upward diffusive Fe flux

Lateral Fe Flux $>\text{Dust Fe flux} > \text{Upward diffusive Fe flux}$

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

Rijkenberg et al. 2012 GBC
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.
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)
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!!

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