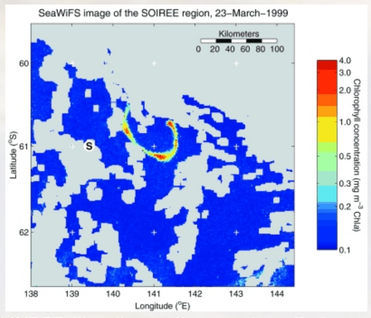
Study of Specific Aspects of the Iron Cycle in Different Marine Environments

Florence Nedelec, Peter J. Statham & Richard Sanders

Southampton Oceanography Centre, School of Ocean and Earth Sciences
University of Southampton
Europen way, Southampton, SO14 3ZH, United Kingdom
Email: fhan@soc.soton.ac.uk

ABSTRACT

The aim of this project is to expand on our knowledge of the biogeochemical cycle of iron in different marine environments. Initially this has involved the development of a highly sensitive flow-injection analyser with chemiluminescence detection to measure picomolar concentrations of Fe in seawater. This work will focus on aspects of the inputs of iron, its redox speciation, the iron present in the colloidal fraction and the photo-reduction processes in surface waters.



SOIREE (Southern Ocean Iron Release Experiment) chlorophyll *a* patch 42 days after the last iron fertilisation [Abraham *et al.* 2001].

RATIONALE

The study of the iron cycle is of great interest as it has been proved through several fertilisation experiments of the ocean such as SOIREE (see Figure on the left) that iron is a limiting nutrient to primary production in high nutrient, low chlorophyll (HNLC) regions [Martin *et al.*, 1994]. As these HNLC areas cover about 40% of the world's ocean, iron limitation can have important implications for global productivity as well as a potential indirect impact on the regulation of CO_2 and dimethyl sulphide in the atmosphere.

Iron is an essential element to all living organisms as it is involved in many metabolism reactions such as photosynthesis for phytoplankton. To explain this limitation, It has recently been suggested that the marine organisms would still have inbuilt requirements for iron from their ancient origins (from the anoxic Archaean Ocean) despite the drastic reduction in its availability during the transition to an oxygenated atmosphere [Whitfield, 2001]. In the present oxidising ocean, dissolved (<0.4 m iron remains at extremely low concentrations (picomolar) in seawater because of its high reactivity and very low solubility in the oxidised form. Measuring dissolved iron in seawater is thus difficult because of the high contamination potential and very low concentration. Therefore clean sampling techniques and a highly sensitive analytical method are required.

As a result of the analytical problems in measuring iron in seawater, the iron cycle has only recently been studied. Several important aspects of its cycle (see Figure below) are still unclear including iron inputs to the ocean, its bio-availability to the biota and its chemistry. Several of these aspects of the iron cycle will be investigated within this project.

CURRENT QUESTIONS ABOUT THE IRON CYCLE & OBJECTIVES

black=current questions about the iron cycle; green=specific aspects studied within this project
blue=how these aspects will be investigated

Question 1: What are the extent of iron inputs to an estuarine system, open-ocean waters and shelf region ?

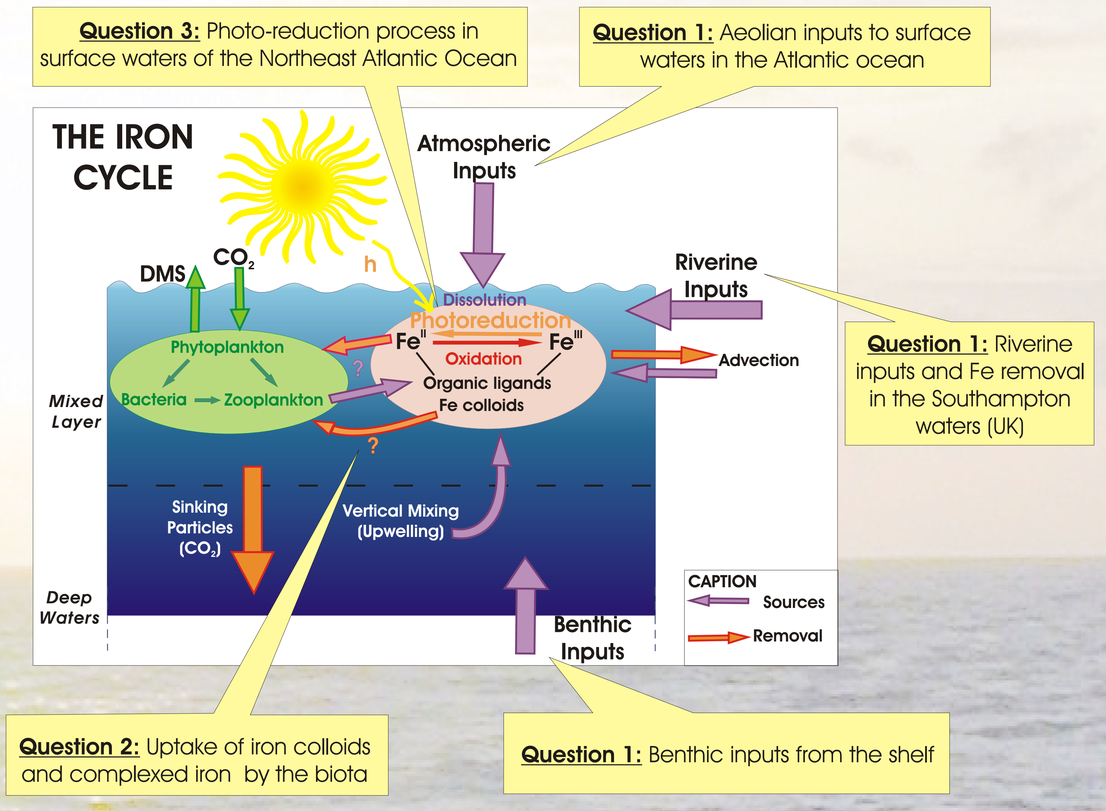
- At this river-ocean interface, iron is mainly supplied by rivers mostly as colloids in the dissolved phase. However very little iron is released to the ocean because of the flocculation of most of these colloids as the salinity increases during the mixing of fresh water with seawater.
  How much of the residual iron which get through the flocculation process are stable enough to actually enter the oceans?
  - Surface water samples from the River Test and Southampton estuary (UK) collected in March 2003
  - Measure of total dissolved Fe (TD-Fe) in relation to salinity gradient
- Open-ocean regions are mainly supplied by aeolian deposition (wet or dry) to surface waters. In the North Atlantic ocean, dust deposition often occurs after a storm event from the Saharan and in the Inter-tropical Convergence Zone tropical rain contains dust and possibly already dissolved Fe(II).
  How much dissolved iron is supplied to the surface waters as dissolved Fe in rainwater?
  - Surface and rainwater samples collected during the Atlantic Meridional Transect (AMT-12) cruise (May-June 2003)
  - Measure of TD-Fe in both surface water and rainwater samples
- Shelf waters are mainly supplied in iron by resuspension from sediments of particulate Fe, which then may be brought to the surface waters by mixing. It is still unclear how dissolved iron is released from these sediments within the water column.
  What is the concentration of dissolved iron in deep waters near the sea floor and how much dissolved Fe actually reaches the surface waters?
  - Samples from the Northeast Atlantic collected during JCR98 (July-August 2003)
  - Determination of TD-Fe in the water column

Question 2: What is the dissolved iron distribution with respect to the biomass ? Is there any uptake of iron colloids ?

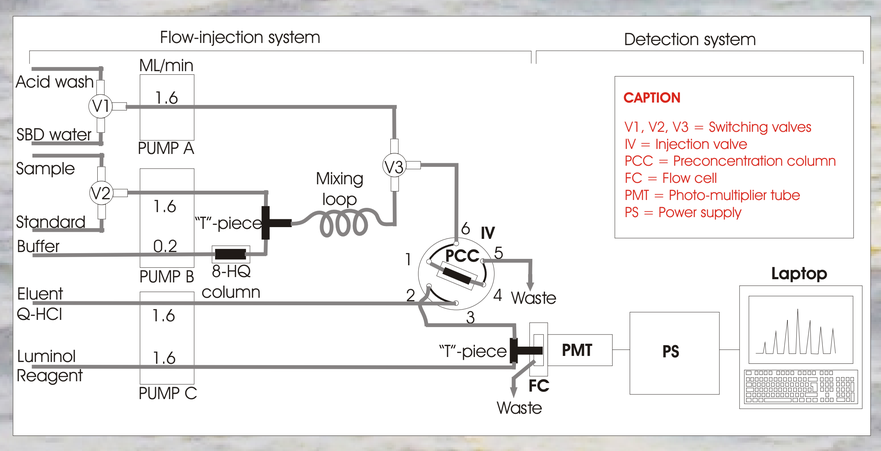
- The uptake of dissolved iron (DFe) by the biota might be expected to occur at the chlorophyll *a* maximum. However a maximum in the DFe concentration at this level has already been observed. It was suggested that this maximum may be due to the release of organic ligands complexing iron in the dissolved phase, in order to stabilise it in solution. An important issue is how organic ligands can stabilise and interact with iron as well as what is their origin and role in the uptake mechanisms developed by the biomass. Colloids (defined here as the fraction between 0.1 and 0.4- m) are also thought to be taken up after dissolution only.
  Is dissolved iron taken up by the biota or is it stabilised at the chlorophyll a maximum ?
  Is there any uptake of colloids by the biomass ?
  - Samples from 300m up to the surface collected during the AMT-12 cruise (May-June 2003)
  - Determination of TD-Fe in the water column in the >0.4- m fraction (defined as DFe) and in the <0.1- m fraction (defined as soluble Fe). The colloidal fraction will be calculated by substracting these two fractions

Question 3: What is the extent of iron release by photo-reduction in surface seawater ?

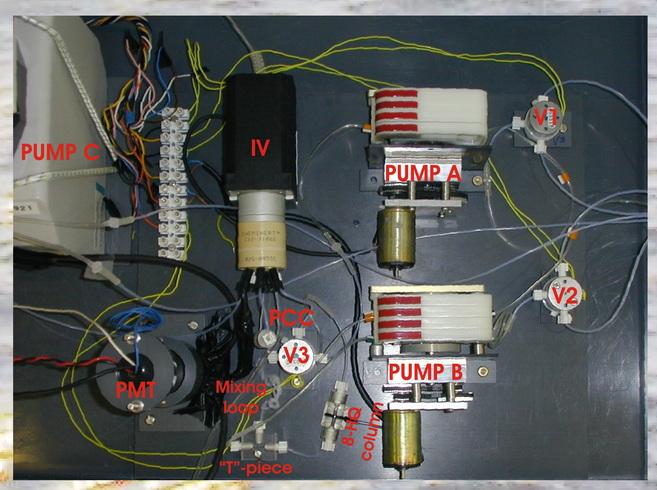
- The photo-reduction process has been observed in surface waters where dissolved Fe(III) is indirectly reduced with sunlight to DFe(II). This reaction is important in that it produces some readily available iron to the biota.
  How much DFe(II) is released from particulate iron that originates from benthic sources and thus available to the biota ?
  - Continuous underway sampling of surface water during the JCR98 cruise (July-August 2003)
  - Measurement of Fe(II) concentration in surface waters and dark/light experiments



ANALYSER FOR IRON AT PICOMOLAR CONCENTRATIONS



- This flow-injection analyser with chemiluminescence detection (FIA-CL) is designed to measure Fe(II) at extremely low concentrations (picomolar) in seawater and is based on the work of Bowie *et al.* (1998).
- The detection system consists of a photo-multiplier tube which detects the photons emitted during the oxidation of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) induced by the oxidation of Fe(II) at high pH ($\sim$10.5) [Rose, 2002].
- The selective pre-concentration of Fe(II) onto the 8-hydroxyquinoline resin allows the removal of the sea-salts, which may precipitate in the manifold at high pH, and potentially interfering trace metals (e.g. Mn(II) and Cu(II)).
- This method only requires a portable and relatively low-cost instrument, a low sample volume (few mL), it is selective to Fe(II), very sensitive (detection limit $\sim$ 40 pM), and allows close to real-time measurements.



ONGOING WORK

- Final stage for the optimisation of the iron analyser
  - Assessment of the precision and accuracy (use of NASS standard) of the analyser
- Analysis of a set of samples including profiles and surface water samples collected during the AMT-12 cruise (May-June 2003)
  - These samples have been filtered and acidified for preservation until analysis
  - The first samples analysed seemed to show values similar to reported TD-Fe concentration with depth, which is consistent with the general nutrient-like distribution of TD-Fe in the water column in open-ocean waters
- Analysis of the estuarine samples collected in the Southampton estuary in March 2003
  - These samples have been filtered and acidified for preservation
- Some photo-reduction experiments may be done on samples from the Southampton estuary in the near future
- Preparation of the iron analyser to allow underway measurement of Fe(II) concentration in surface waters all the way during the JCR98 cruise (July-August 2003)

REFERENCES

Martin, J. H. *et al.*, **1994**. Testing the iron hypothesis in ecosystems of the equatorial Pacific Ocean. *Nature*, **371**, 123-129

Whitfield, M., **2001**. Interactions between Phytoplankton and Trace Metals in the Ocean. *Advances in Marine Biology*, **41**, 1-128

Bowie, A. R. *et al.*, **1998**. Determination of sub-nanomolar levels of iron in seawater using flow-injection with chemiluminescence detection. *Analytica Chimica Acta*, **361**, 189-200

Rose, A. L. *et al.*, **2002**. Chemiluminescence of luminol in the presence of Fe(II) and oxygen: oxidation mechanism and its implication for analytical use. *Analytical Chemistry*, **73**, 5909-5920

AKNOWLEDGMENTS

I would firstly like to thank Dr Peter Statham and Dr Richard Sanders for giving me the opportunity to work on this interesting and important topic as the study of the iron cycle in the oceans and the Southampton Oceanography Centre for providing the means to work on it in such good conditions. This project wouldn't be possible without the essential work of Dr Matt Mowlem and Dr Ralf Prien on this computer controlled system. UKORS people are also thanked for allowing us to work in good conditions in the clean laboratory container over the two cruises planned during this project. I finally thank the European Union for the financial support which allows me to attend this SOLAS summer school.