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Working group report
WG1- Trace Elements (TEs) in Ecological and Biogeochemical Processes

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Introduction

Many people believe that the era of modern biogeochemistry began with the first large programmes such as GEOSECS. At that time, although we knew of the role of the macro nutrients, few of us thought that trace metals had any kind of role in biogeochemical cycling. There have been exciting changes in our knowledge since that time. We now know that the trace element iron regulates biological processes in a significant proportion of the global ocean. Is this just the tip of the iceberg? Given the large paradigm changes over the last decade it would be foolish not to expect that the next decade will see at least as many exciting new discoveries about the role of trace elements in ecological and biogeochemical processes.

It is now clear that to understand global ocean processes and how they may be affected by climate change it is essential to consider the vital role of trace elements. With this in mind our working group identified 4 key issues, and these are expanded upon below.

1) Interactions between TEs and biota

It is essential to understand how TEs interact with biota at the cellular and molecular level as this determines the function of the trace elements and their cycling. This important role arises because trace metals provide the catalytic centre of the majority of critical enzymes. The key research questions are:

a) **Which trace elements are needed by the biota but may be present at concentrations insufficient for growth?** It is now clear that Fe is limiting in HNLC waters, but we have very limited knowledge of the impact of a wide range of other biologically essential trace elements.

b) **How are these trace elements assimilated at the cellular level? How is uptake influenced by physico-chemical forms of TEs (see below 3c)?** It is important to understand feedback mechanism involved in trace element uptake, e.g. some organisms may produce specific metal binding ligands designed to sequester the metals they require from the surrounding environment. In addition we need to be aware that many metal binding sites in cells may be accessible to more than one metal leading to antagonistic or synergistic effects.

c) **How are TEs recycled? How is this related to the organism concerned?** We have very little understanding of how TEs are recycled once incorporated into biogenic material.

d) **How do TEs influence the species composition and community structure? How will this vary with climate change?** An obvious example is the change that occurs after iron fertilisation, when large pennate diatoms are able to dominate.

e) **Can we extrapolate from this molecular and cellular knowledge to global scales?** This would seem unlikely given the complexity of sources, sinks and cycles influencing TEs. For example, in many situations limiting trace elements will be needed for a complex variety of cellular functions, some of which may be substituted by other materials, e.g. ferrodoxin replaced by flavodoxin.

2) The role of TEs in major global biogeochemical cycles

While a large range of trace elements are undoubtedly essential for biological processes it is not evident they will necessarily influence the major biogeochemical cycles. This will depend in essence on their availability in relation to other controlling factors e.g. macronutrients, temperature, light etc. In other words we need to know under what circumstances TEs are drivers or passengers in biogeochemical cycles? For example**:**

a) **What role do TEs play in controlling the magnitude and stoichiometry of C N P Si export to the deep ocean?** For example under Fe replete condition diatoms may dominate the vertical flux and radically change the C:Si ratio of particles exported to the deep ocean.

b) **What role do they play in the production and cycling of climatically important biogenic gases (e.g. nitrous oxide, methane)?** For example the production of DMS is known to be dependent on species composition.

c) Do trace metals influence nitrogen fixation and denitrification? For example climate induced changes in the supply of iron to the ocean may enhance nitrogen fixation in areas of the ocean that are currently nitrate depleted but replete with phosphate.

d) Does the lack of trace metals for enzyme systems limit the availability of DOP/N/C? Most regions of the ocean have unutilised organically bound N or P. At least one of the enzyme systems (alkaline phosphatase) that can release P from organically bound forms has Zn as its catalytic centre.

How do these processes change with climate?? All of the above processes have potential to be substantially modified by anticipated climate changes.

3) Sources, sinks and transformations of TEs.

The chemical properties of most trace elements are complicated, with variable oxidation states, solubility, hydrolysis and formation of complexes all being possible complicating factors. This makes it essential to develop an understanding of their source and sinks in the oceans and their transformations between different physical and chemical forms. These factors will control the availability of TEs to organisms and their reactivity in abiotic processes.

a) **What will be the impact of global change on the relative importance and variability of sources and sinks of TEs in the ocean? How will these changes be reflected in the oceanic distribution of TEs at all scales?** For example with increased aridity and hence dust transport to the ocean, significant changes in surface water productivity and species composition in currently HNLC regions is anticipated. However the global distribution of iron in the deep ocean may not change greatly if, as many believe, it is limited by the balance between scavenging removal and maintenance by iron binding ligands.

b) **What is the impact on trace element cycles of climate induced changes in the ocean that have been identified?** For example if increasing stratification leads to hypoxia in the deeper ocean, profound changes in the speciation of redox sensitive elements such as Fe will be expected.

c) **Why are most bio-active metals organically complexed in the ocean? What is the impact of metal-ligand feed-backs on residence time and fate of TEs?** Our current understanding is that the chemical speciation of most bio-active trace metals in the ocean is dominated by the formation of complexes with organic ligands. We do not understand how the majority of these ligands have arisen, and whether they have a specific ecological purpose or are a consequence of biogenic and abiotic processes in the ocean. In addition we know very little of the chemical nature of many of these metal binding materials and how selective they are for individual metal ions.

d) **What is the importance of colloids in TE cycles?** Colloids are important for a variety of reasons. They have very large surface to volume ratios and therefore a large number of sites for adsorption of TEs. Colloids also act as the bridge, through coagulation, between species in solution and large sinking particles. Therefore they will figure prominently in the biogeochemical cycling of surface-active elements. The classic example is Th (as Th-234), which is currently used as a proxy for carbon export. However, scavenging is also thought to be important for the deep water cycling of some bio-active elements such as Fe and Co.

4) Proxies

a) The study of TEs has the potential to provide an improved mechanistic understanding of global biogeochemical cycles, and of the proxies and tracers that are used to study these processes. This potential arises because many TEs interact strongly with biota both actively (e.g. Fe) and passively (e.g.Th). However, many existing proxies and tracers have not been rigorously assessed in terms of how they reflect in the sediments the processes occurring in the water column.

b) **We also encourage the development of new TE based proxies, e.g. TE isotopic ratios, for past export production, relative nutrient utilisation, to distinguish bio-mediated and abiotic processes, circulation, and sedimentary oxidation**. The development of new proxies (e.g. stable isotopic ratios of metals) must proceed hand-in-hand with an understanding of the function and fate of these TEs at the cellular and molecular level.

Strategies and Approaches

1) **The global database for some TEs and ancillary data is inadequate to understand or effectively model their cycles, and needs to be expanded.** For example, we know very little about the concentration and lifetime of the ligands proposed to maintain Fe in solution in deep waters, or the distribution of organic forms of N and P in the ocean. (Linkage to e.g. GEOSECS II).

2) **To ensure accuracy and global comparability of data, rigorous inter-calibrations and quality control measures (e.g. use of reference materials) should be applied.** We need to learn the lessons obtained during earlier large-scale programmes. Inter and intra-national group activities are essential to ensure consistent sampling and handling. It is particularly important that different research groups, especially from different countries, have the opportunity to participate in joint activities both in the laboratory and at sea to ensure comparable protocols are developed and used.

3) **Fundamental laboratory studies on cellular and molecular scale processes are needed to develop our understanding of how TEs interact with biota.** Instrumental method development will be an essential enabling activity, as has been demonstrated to be the case in the past.

4) **Focussed process studies are needed at different scales, to provide an opportunity to test hypotheses derived from both fundamental laboratory studies and modelling.** Typical scales envisaged are**:** natural systems (e.g. ocean island effects Kerguelen, Crozet), mesoscale manipulations (following IRONEX approach for other elements), microcosms, shipboard manipulations. For studying both long time-scale and episodic events, long time series are needed. Are there important gaps, in terms of the processes and regions important to the OCEANS programme, that are not covered by existing time series e.g. the Southern Ocean.

5) **The development and use of molecular biological techniques relevant to TE processes offer exciting new opportunities.** An example is functional genomic techniques that can be used as a diagnostic of Fe vs P limitation.

6) **To provide the time and space scale coverage needed to understand TE cycles, autonomous platforms and sensors must be developed.** It is not possible to achieve the information requirements (especially to achieve the database required- see 1 above) with existing technology.

7) **A critical feature of the OCEANS programme to ensure its success is the maintenance of close interaction of TE investigators with modellers, biologists and physicists.** This will ensure that new ideas are effectively incorporated and integrated into science strategy and action.

Key study Areas:

It is important to choose regions for study where specific processes are predominant, or may be indicators of climate change, and where there are strong concentration gradients e.g.:
The shelf-ocean interface, oxygen minima, HNLC zones of contrasting nutrient limitation (e.g HNLC, N depleted), within dust input zones.

Impediments:

1. An important identified potential problem is that access to key ocean regimes may be limited through geo-political constraints.

2. There is growing concern about the decreasing recruitment of young people into the fundamental sciences and the application of their knowledge and training to the future research needs of programs such as OCEANS. This is a result of a variety of factors including, failing to ensure that education policies produce a good match between the science skill base and the requirements of international environmental agreements, and the declining status of science as a profession.

Outreach and education:

OCEANS should utilize and build on existing mechanisms for outreach and education that have proved to be effective in earlier national and international programs, such as JGOFS, and WOCE.