Changing Trace Element Cycles in the 21st Century Ocean

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Human activity is altering the ocean; through climate change, release of pollutants, and direct exploitation of the marine environment. Recent advance in understanding trace element cycles comes at a critical time as society increasingly looks to the ocean as a resource but also recognises the vulnerability of ocean systems to change.

1. Introduction

Oceanic trace element cycles have influenced and responded to global change for billions of years, but today's anthropogenic pressures are leading to new causes of change that are occurring at unprecedented rates. Trace elements can be important nutrients and toxins and are critical for ocean ecosystems, the carbon cycle, and the overall health of the ocean. Quantifying these rapidly changing cycles and predicting the impact these changes will have on ocean systems are therefore important science and policy goals.

Many anthropogenic changes in trace element cycles have been unintentional, including those in response to continuing climate change (e.g. changes in aridity and run-off from land altering dust and river inputs) or related to accidental pollution of the ocean. Other changes are intentional, founded on an implicit misconception that the oceans are so large as to be immune to damage. This perception has led to disposal of trace elements at sea (e.g. intentional release of radionuclides such as ^{129}I and ^{236}U during reprocessing nuclear waste, Christl et al. 2015).

A range of anticipated future human activities will further increase change in trace-element cycles. These activities include exploitation of resources (e.g. offshore hydrocarbons; deep-sea mining); aquaculture (for food or biofuel); and intentional manipulation of the carbon cycle (e.g. by fertilizing the ocean with iron (Fe) or by direct CO_2 storage). Anticipating the response of ocean geochemical cycles to these potential future activities is a critical component in assessing the environmental risks they pose and the nature of unintended consequences.

This article briefly introduces changes in the open-ocean cycling of trace elements known to be occurring and anticipated during the 21st Century.

2. Unintentional changes caused by human activity

Ocean acidification:

Increase in the atmospheric concentration of CO_2 since the industrial revolution has resulted in uptake by the oceans and higher aqueous CO_2. This has led to a decrease in ocean pH and carbonate ion (CO_3^{-2}) concentration, and increased bicarbonate ion (HCO_3^-). If CO_2 emissions continue along current trends, a decrease in the surface ocean pH of ≈0.3-0.5 units and of carbonate ion concentration by 50% by the end of the century is anticipated. These changes will make it harder for marine calcifying organisms to form calcium-carbonate skeletons, with a potential reduction in carbon export because the density of calcium carbonate enables the downward transport of less-dense organic material (Yool et al., 2013). Such reduced export will impact removal of trace elements taken up by life or scavenged onto particles in the surface ocean.

Changes in ocean pH will also have important consequences for the chemical speciation of bioactive trace elements (Shi et al., 2010) with Fe a critical example (Figure 1). This metal occurs at very low concentrations in oceanic waters due to its low solubility, phytoplankton uptake, and scavenging to particles. The dominant inorganic species in seawater is the oxidized form Fe(III), with the reduced form Fe(II) occurring at lower concentration. The concentration of these two species is critical because they are the bioavailable forms used by marine organisms. An important component of trace-element chemistry in seawater is, however, their binding by organic ligands. The concentration of dissolved Fe in seawater is significantly above that expected from solubility due to complexation with such ligands, with the majority of Fe in seawater present in a ligand-bound form.

Reduced seawater pH raises inorganic Fe(III) solubility thereby potentially increasing bioavailability (Morel and Price, 2003). Recent work, however, indicates a competing effect because more Fe(III) becomes ligand-bound at low pH, thereby decreasing bioavailability (Avendano al., 2016). The concentrations and nature of organic Fe-complexing ligands may be the dominant factor in determining Fe speciation and bioavailability in a high CO_2 ocean. Decreasing pH will also affect other trace elements, for instance copper, where the bioavailable cupric ion concentration (which can be toxic) increases with a decrease in pH (Avendano et al, 2016).

Warming and ocean mixing:

Increasing atmospheric CO_2 is causing ocean warming and, because surface water warms more quickly than deeper water, enhancing the density stratification of the ocean. Average sea surface temperature increased by 0.7-0.8°C during the last 100 years and is projected to increase by an additional 0.7-2.7°C by the end of this century (depending on future CO_2 emissions) (Bopp et al. 2013). The decrease in surface density is exacerbated by freshening of waters due to melting of land-ice. This density stratification will increase as warming continues, leading to reduced mixing between deep and surface waters. While shallower mixed layers will likely lead to better light conditions for surface-ocean biology, reduced mixing decreases vertical supply of nutrients to surface waters, which impacts marine primary productivity.

The impact on trace element cycles caused by warming, stratification and productivity changes is uncertain (Hutchins and Boyd, 2016). Warming will increase the rate of oxidation of soluble Fe(II), with subsequent removal into insoluble Fe oxyhydroxides reducing bioavailable iron (Figure 1). But warmer waters would also impact phytoplankton Fe recycling by speeding biological processes. Enhanced ocean stratification would probably induce a reduction in the vertical supply of all nutrients to the surface ocean (Bopp et al; 2013), but macronutrients such as N and P may be more affected than Fe, because of increase in aeolian Fe input caused by increased aridity and human activity on land (Tegen et al. 2004).

De-oxygenation:

Warming of the oceans is reducing oxygen solubility, while increased stratification impedes downward mixing of oxygen. These processes reduce oceanic oxygen concentrations and cause a spread and intensification of oxygen minimum zones (OMZs) (Schmidtko et al., 2017). Ocean-floor sediments are an important source of many redox-sensitive trace elements to deep waters (e.g., Fe, Mn), with particular importance on continental shelves and in OMZs. The metal flux from such sediments is enhanced under low bottom-water oxygen levels so decreasing ocean oxygen has a significant impact on their cycles. A fraction of the metal released is transferred to the open ocean where these fluxes impact primary production. Lower oxygen concentration increases these fluxes due to slower oxidation of Fe(II) to insoluble forms. Consequently a strong correlation between dissolved Fe and oxygen has been observed in OMZs and an enhanced future Fe supply to surface waters is anticipated as OMZs expand and intensify (Figure 1).

Metals also play an important role in the cycle of the nutrient, nitrate. Nitrate is converted back to N_2 in OMZs with that loss balanced by N_2 fixation by diazotrophs which explicitly require Fe. Future intensification of OMZs will increase Fe supply and therefore N_2 fixation, but might not compensate for enhanced nitrate loss as OMZs expand (Landolfi et al, 2013).

3. Contamination of the ocean

Pollutant metals:

The distribution of most metals in the ocean has been influenced by human activity. Lead and mercury pollution have been a particular concern due to their toxicity and known anthropogenic release (Hatje et al.; this volume). Many other metal cycles are known to be significantly perturbed in estuarine and coastal environments, and concerns have led to legislation in some cases (e.g. banning of tri-butyl-tin as a ship antifouling agent). Research into broader environmental risks is needed as such contamination spreads into the open ocean, and as further pollutants are identified. As an example, silver is released by coal burning and from the increasing use of Ag nanoparticles in consumer goods for their anti-bacterial properties. Increasing concentrations of this toxic metal are seen in coastal seawater (Lodeiro et al., 2017) and potentially the open ocean. Shipping is also leading to new sources of pollution due to increasing traffic (particularly at high latitudes as sea-ice reduces), and the use of scrubbers on stack fumes which can result in oceanic discharge of V, Cu and Zn (Turner et al 2017).

Plastic pollution as a vector in metal cycles:

The presence of plastic litter in the marine environment is a global concern recognized by UNEP; 5-13 million tons are estimated to reach the ocean each year. Plastics contain metals, including high concentrations Cd and Zn (Munier and Mendell, 2018). These may leach into seawater, or are taken up directly by marine organisms following ingestion. Plastic debris adsorbs metals, notably Cu and Pb, with polyvinyl chloride a particularly efficient adsorbant (Munier and Mendell, 2018). The typical entry points of plastics to the ocean are rivers and, because of high riverine metal concentrations, plastic particles form a new vector for metal transfer to marine systems, with implications for cycling of bioactive and toxic species.

Oil and gas production and decommissioning:

Offshore hydrocarbon extraction involves input of metals to the ocean from infrastructure (platforms, pipelines), drilling tailings, and from leakage of hydrocarbons (noticably during failures such as Deepwater Horizon). Extraction extends to ever-deeper waters (presently 2,900 m), increasing the impact of contaminants on the open ocean. Additional impact is also expected from decommissioning offshore infrastructure. A 1991 plan to dispose of Shell’s Brent Spar platform by sinking in deep-water proved particularly controversial (Dickson and McCulloch, 1996), partially because of concerns about metal contamination. Present decommissioning protocols typically involve removal of above-water infrastructure for disposal on land. Deeper infrastructure, which is left on the seafloor, will become a component of trace element cycling. This source will increase if the high costs of decommissioning leads to re-consideration of deep-water disposal.

4. Changes caused by intentional perturbation of the ocean environment

Fe fertilisation for CO_2 uptake:

The addition of Fe to alleviate nutrient limitation and fertilise biological productivity was suggested in the early 1990s as a way to enhance biological productivity and mitigate increasing atmospheric CO_2 and climate change (Martin, 1990). The principle is that increased phytoplankton productivity increases the flux of organic carbon to the deep ocean. Despite more than a dozen artificial iron fertilization experiments (Figure 2) the efficiency of such a method in removing carbon is still debated (Williamson et al. 2012).

Using ocean carbon models, the maximum effect from a long-lasting global Fe fertilisation has been estimated at 15-33 ppm of atmospheric CO_2 decrease (Aumont and Bopp, 2006), a relatively small effect compared to the ≈130 ppm increase since the industrial revolution. Fe fertilisation also carries potential risks, including perturbation of food webs and increased emissions of other greenhouse gases. In 2008 the Convention on Biological Diversity called for a ban on major ocean fertilization projects, and fertilization not solely related to research is banned in international waters by the London Protocol.

Alkalinity addition for CO_2 uptake:

The large capacity of the ocean to hold carbon arises from its high alkalinity and consequent high concentrations of bicarbonate and carbonate ions. Increasing alkalinity further by addition of cations such as Ca^{2+} or Mg^{2+} is expected to lead to removal of CO_2 from the atmosphere into seawater and conversion to bicarbonate ion (Renforth and Henderson 2017). Such alkalinity addition might be achieved by adding material (e.g. CaO) directly to the oceans, or by dissolution of silicate rocks on land and riverine transport to the oceans. Theoretically, such alkalinity addition could lead to take up of large amounts of CO_2 from the atmosphere and would oppose ocean acidification, although it remains untested outside the laboratory. The alkalinity for this process would come from geological minerals which contain impurities, including trace elements which act as nutrients (e.g. Fe) or are toxic (e.g. Cr). The impact of addition of such impurities on marine systems has not been addressed, but would be a critical aspect of environmental risk assessment before any pursuit of alkalinity addition for climate mitigation.

CO_2 storage at or below the seafloor:

Limiting future warming will require storage of hundreds of billions of tons of CO_2 captured during energy production and/or removed from the atmosphere. Proposed marine reservoirs for such storage include sub-surface geological structures, deep-ocean seafloor sediments (House et al 2006), and the deep water-column. Any leakage from storage in geological formations beneath shelf and slopes waters would impact the pH of bottom waters, but is expected to be minimal. More impact to the ocean would result from storage of CO_2 in seafloor sediments. Below ≈3000 m, CO_2 is denser than seawater so is gravitationally stable, but injection would perturb sediment conditions and subsequent high CO_2 levels would lower sediment pH, resulting in greater solubility of metals toxic to marine species such as Cu, As, and Hg (Rodríguez-Romero et al. 2014). Storage of CO_2 in the water column would have still greater impact on chemical cycles by capping sediments with lakes of dense liquid CO_2 (IPCC 2005). Such storage has been assessed in the lab and with beaker-scale ocean experiments, but no large-scale demonstration is planned. Research into the impact on metal cycling would be required as part of a broad impact assessment before and during any such demonstration.

Deep-sea mining:

Increases in demand for some metals (e.g. Co, Ni, Te) is driven by new technologies (e.g. batteries) and green-energy production (e.g. solar cells) (Royal Society 2017). These metals can be found at high grade in seafloor deposits. Recovery is now being pursued with successful demonstration of mining offshore Japan in 2017, licenses granted for mining offshore Papua New Guinea, and licenses granted for exploration (but not yet exploitation) in international waters. Deposits are polymetallic sulphides associated with high-temperature hydrothermalism, slow-growing ferromanganese crusts, or polymetallic nodules on the deep seafloor. Mining of any of these would have substantial implications for the trace-metal chemistry of the deep-ocean. These impacts would occur at the site of mining and beyond due to solubilisation and scavenging in resulting sediment plumes. Intentional seafloor disturbance trials were carried out during the 1990s and demonstrated the nature of ecosystem perturbation. But these trials preceded modern knowledge of deep-ocean metal cycling so the impact on these cycles is unknown. Commercial recovery of polymetallic nodules would occur over a broad area of ocean sediment, with long-term implications for this slow-turn-over ecosystem. Sediments disturbed in 1989 still show perturbed chemistry 26 years later (Paul et al. 2018). Commercial mining in the deep-ocean is likely to be pursued in the coming decade, so a full assessment of the amplitude and spatial scale of changes in metal cycling will be critical in considering the environmental impact.

5. Future Science

Climate change and environmental contamination are continuing, and will be augmented by new human activities impacting ocean chemistry. Monitoring of trace-metal cycles, and novel approaches to assess their interaction with ecosystems, will be required as the ocean responds to these stressors.

Marine geochemists are well placed to address this challenge. The recent revolution in understanding trace-metal cycles has been enabled by new technologies (e.g. clean sampling, analytical instrumentation, computer modelling). Technological advances continue. Chemical sensors for metals are now applied in the coastal environment (Geißler et al., 2017) and will soon reach detection levels at which open-ocean deployment on autonomous platforms such as floats or ocean gliders becomes possible. These will enable trace-metals to be mapped at unprecedented temporal and spatial scale. New mass-spectrometric approaches are now allowing first characterisation of the chemistry of the ligands involved in binding metals at the picomolar concentrations found in seawater (Boiteau et al. 2016), placing new constraints on their role in metal cycles.

Other exciting advances come from combined study of ocean metal cycles with genomics and proteomics. Genetic sequencing approaches are allowing assessment of the links between ocean trace-metal chemistry and microbial diversity, structure and functioning (Sohm et al. 2016). Fundamental new knowledge of the linkages between metal chemistry and ocean biology that will arise from such research will help scientists assess the impact of global change on the whole ocean-climate system, and will inform policy decisions about society’s future interaction with the ocean.

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Figures:

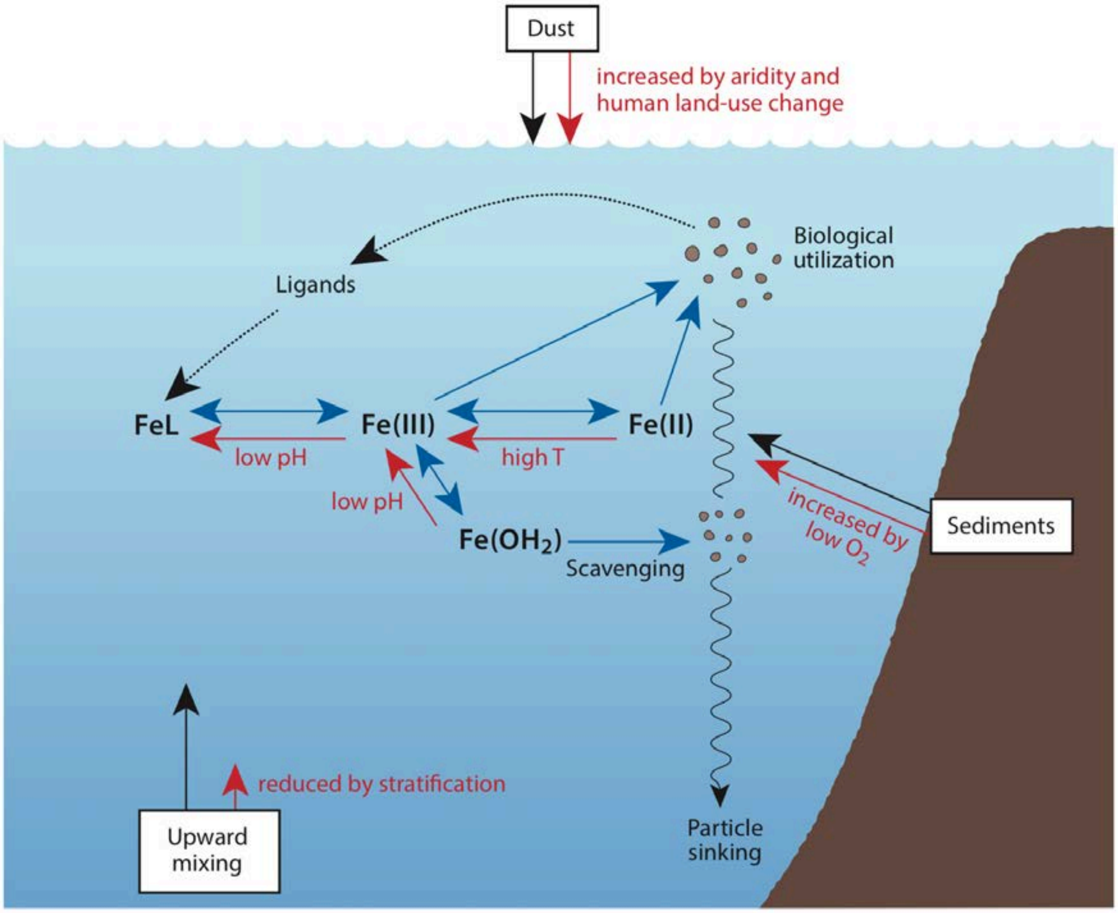

Figure 1: Processes controlling the biological availability of iron in the surface ocean. Black boxes and arrows show the three major inputs of Fe. Blue arrows indicate transfer of Fe between chemical species, including the dominant ligand bound form (FeL), and low-concentration bioavailable forms - Fe(III) and Fe(II). Red arrows show how inputs and speciation are influenced by various changes of the 21st Century. The significance of these changes for ocean productivity varies significantly by location.

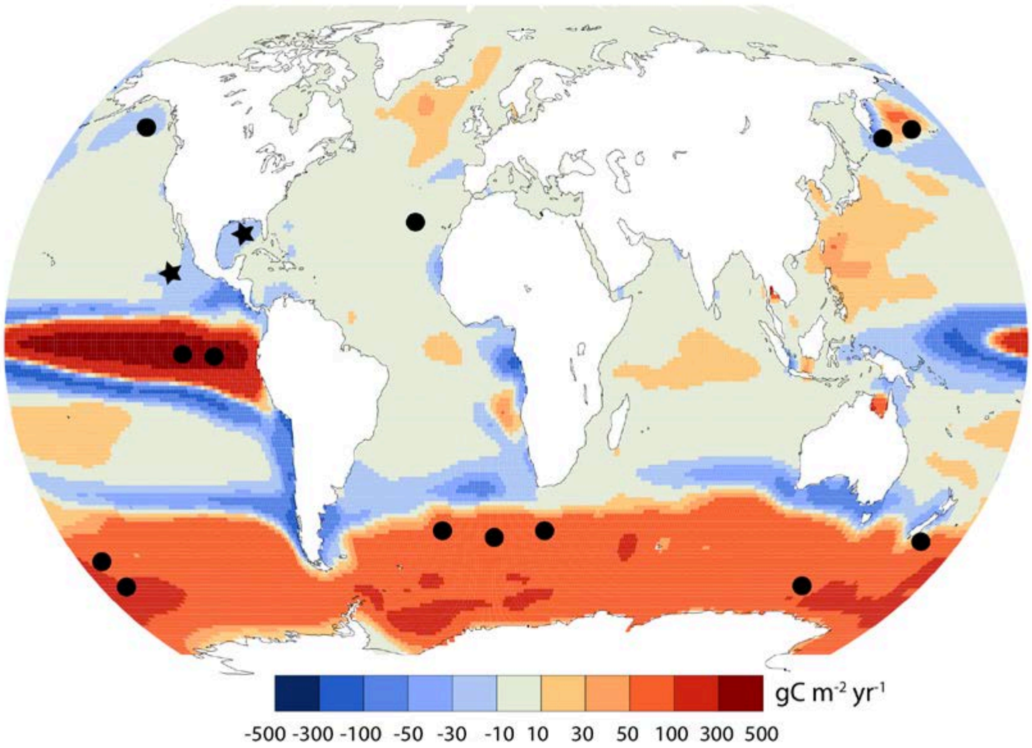

Figure 2: A model of the increase in annual primary productivity expected from prolonged global Fe fertilization (Aumont and Bopp 2006) as might be pursued to remove CO_2 from the atmosphere. Large increases are expected in regions where Fe is presently the limiting nutrient, such as the Southern Ocean and Equatorial Pacific, whereas primary productivity decreases in regions that are limited by other nutrients such as nitrate and phosphate. Overall modelled global productivity increases by ≈50%. The accuracy of such models remains unclear because the C/Fe ratio of resulting biomass, and the effectiveness of downward transport of C, remain uncertain and are regionally variable. Sites of past Fe-fertilisation experiments for research (dots) and commercially (stars) are shown (Williamson et al. 2012).