Molecular-scale interactions impact ocean-scale zinc concentrations

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HOW TO CITE:
Cloete R, Duan J, Myneni S, Roychoudhury A. Molecular-scale interactions impact ocean-scale zinc concentrations. S Afr J Sci. 2025;121(9/10), Art. #20922. https://doi.org/10.17159/sajs.2025/20922

ARTICLE INCLUDES:
☐ Peer review
☐ Supplementary material

KEYWORDS:
zinc, Southern Ocean, biogeochemical cycling, reversible scavenging, synchrotron X-ray absorption spectroscopy

FUNDING:
US National Science Foundation, Princeton University (Scott Vertebrate Funds and Phillips Equipment Fund), Whales and Climate Change Program, South African National Antarctic Programme, South African Department of Science, Technology and Innovation, South African Department of Forestry, Fisheries and the Environment, South African National Research Foundation

PUBLISHED:
29 September 2025

Significance:

This Invited Commentary is based on our recently published paper which highlights how different chemical forms of the element, and micronutrient, zinc (Zn) affect its distribution and relationship with major nutrients (phosphate, silicate) within the Southern Ocean. Using novel X-ray techniques to characterise particle-hosted Zn at the molecular scale, Zn chemistry was shown to change with depth, latitude and season. These observations reveal a new dimension to marine Zn cycling, highlighting an underappreciated importance for inorganic Zn phases. The future balance between organic and inorganic Zn phases, mediated in part by climatic changes, will impact the oceans' biological productivity.

Introduction

Zinc (Zn) is an essential trace element micronutrient for marine microorganisms called phytoplankton, which require Zn to produce enzymes and proteins responsible for a host of cellular processes, notably carbon fixation (photosynthetic conversion of inorganic atmospheric carbon dioxide [CO_2] into organic compounds) and assimilation of major nutrients such as phosphorus.[1] Previous work has shown that low levels of Zn in the surface ocean may hinder phytoplankton growth[2] and that Zn nutritional stress is more widespread than previously thought[3]. As a result, the distribution and availability of Zn in the surface ocean can impact phytoplankton growth with knock-on effects for marine primary productivity and, therefore, the ability of the ocean to absorb excess atmospheric CO_2 and regulate Earth's climate.

Despite Zn being abundant in Earth's crust (70 parts per million), its concentrations in the ocean are in the nano-to-picomolar range (parts per billion – parts per trillion). In seawater, Zn can be classified into two operationally defined pools: zinc dissolved in the water column (dissolved zinc, dZn) and Zn associated with small (micrometre scale) suspended organic or inorganic particles (particulate zinc, pZn). The oceanic concentration of Zn is affected by several factors, including its sources (e.g. atmosphere, rivers, hydrothermal vents) and water column processes (e.g. photosynthesis, respiration, adsorption-desorption termed 'scavenging' and precipitation-dissolution) which partition Zn between dissolved and particulate pools. These local biological and chemical processes are superimposed on different water masses which are defined by distinct physical characteristics such as temperature, salinity and oxygen, and have unique transport pathways. Combined, the individual water masses form the global thermohaline circulation and transport Zn horizontally and vertically, thus playing a major role in setting large-scale Zn distributions.[4]

The majority of studies to date have focused on the dissolved pool, in particular, relationships of dZn with major dissolved nutrients like phosphate (PO_4) and silicate (Si). An interesting feature of these studies pertains to the observed correlation between dZn and Si, but a lack thereof between dZn and PO_4 throughout the global ocean[5], which is at odds with their respective nutrient roles in phytoplankton. Mechanisms behind the so-called 'Zn paradox' are under debate and rely predominantly on modelling approaches testing the sensitivity of the correlation to biogeochemical forcings. This Invited Commentary highlights how our study[6] focused instead on pZn and adopted a new analytical approach to examine changes in pZn chemistry across different geographical locations, water depths and seasons. The observations provided direct, molecular-scale evidence for a mechanism coupling the distributions of dZn and Si and revealed a new dimension to marine Zn cycling.

The Zn paradox

The first seawater Zn measurements were made nearly 50 years ago.[7] Earlier attempts were found to be inaccurate as a result of improper methodology leading to gross overestimation of concentrations. Collecting seawater samples for trace element studies is notoriously difficult due to contamination from research ships and collection equipment. Moreover, the low Zn concentrations are incorporated within a complex seawater matrix, which makes isolating and quantifying Zn analytically challenging, even with modern instruments. However, the past 15 years have seen an order of magnitude increase in observations, driven by methodological and analytical advancements as well as the inception of the GEOTRACES programme[8] – an international collaboration aimed at investigating marine trace element cycles. Data produced under the GEOTRACES framework focused primarily on dZn (the fraction of total Zn that passes through a 0.2 m filter) because dZn is widely accepted to be the fraction of total Zn available to phytoplankton, the main primary producer in the ocean. From these observational data, scientists noticed a peculiar relationship between dZn, Si and PO_4.[5,9] dZn and Si showed a remarkably close, near-linear global correlation (Figure 1a) while dZn and PO_4 were decoupled (Figure 1b). Like Si, dZn is enriched in deep water masses and deficient in intermediate water masses relative to PO_4 (Figure 1c). While dZn and Si show similar spatial distribution patterns, their biogeochemical roles differ significantly. Si is mainly used by diatoms, a group of predominantly polar phytoplankton that require Si to construct their frustules (outer shells). dZn is minimally incorporated into diatom frustules[10] and is instead required across a broader range of phytoplankton species, associated primarily with internal cellular processes and often co-located with particulate phosphorus (pP, the organic form of PO_4 once assimilated by phytoplankton). As cellular materials are expected to decompose (remineralise) more easily than frustules in water columns, Zn and P associated with these organic particles are expected to be concurrently released into seawater at depths where Si in frustules still remains stable. Thus, the coupling of dZn and Si and decoupling of dZn and PO_4 are at odds with their respective physiological roles and biogeochemical behaviour.

Ongoing debate

There is no consensus as to the mechanisms explaining the Zn paradox. However, evidence points toward an importance for the Southern Ocean and its distinct diatom-dominated ecology. The Southern Ocean flows uninterrupted around Antarctica and acts as a central hub for global thermohaline circulation whereby waters moving to and from the Atlantic, Indian and Pacific Oceans mix. Biological and chemical processes occurring in the Southern Ocean water column therefore determine the elemental composition of water masses which subsequently flow northward and control nutrient availability in tropical and subtropical surface waters.[11] Intense, diatom-dominated phytoplankton blooms occur in the high latitude Southern Ocean, spurred on by the large-scale upwelling of nutrient-rich water masses. Surface waters are consequently stripped of dZn and Si, due to biological consumption, to a greater degree than PO_4, overprinting the independent biogeochemical cycles of Zn and Si and transporting a coupled dZn-Si and decoupled dZn-PO_4 signature to other ocean basins.[9] The hypothesis that dZn-Si-PO_4 distributions are controlled by diatoms and Southern Ocean circulation implies that these signatures are not being altered significantly within water masses for hundreds to thousands of years during thermohaline water mass transport. Modelling simulations, however, suggest contrary views, invoking additional water column processes to explain the deep accumulation pattern of dZn. It is suggested that about two thirds of dZn (6–7 nmol/kg) in deep waters outside the Southern Ocean is derived from physical water mass circulation, meaning that one third (3–4 nmol/kg) must have accumulated during water mass transport after leaving the Southern Ocean formation region.[12] According to this scenario, a water column process is required to drive a deeper accumulation of dZn and reconcile the dZn-Si-PO_4 relationships. Reversible scavenging is a potential mechanism whereby dZn is released with PO_4 at shallow depths from decomposing organic matter (e.g. phytoplankton cells), before the dZn is scavenged (adsorbed) onto sinking particles and re-released at depth. Field and modelling investigations show reversible scavenging to be consistent with the concentration profiles of, and isotopic variations in, dZn.[13] Scavenging processes ultimately determine the timescales, and therefore depth, at which dZn is released back into the water column. The hypothesis that reversible scavenging impacts marine Zn cycling confirms the control that geochemical speciation of pZn plays in Zn cycling. However, mechanistic understanding is broadly lacking because of the analytical difficulties associated with assessing detailed chemical forms of marine particulates at molecular scales.

A novel approach to investigating Zn cycling

Despite advances regarding the dZn cycle, little is known about the concentration and speciation of pZn. The few pZn-focused studies to date are based on quantitative concentration data where bulk pZn is measured by subjecting sample filters to various acid leaches which release the elements from the filter residue.[14] Estimates of the lithogenic (inorganic phases from rocks and mineral precipitation) and biogenic (predominantly organic particles from biological processes) fractions of pZn are typically calculated from crustal (e.g. aluminium to Zn) or cellular (e.g. phosphorus to Zn) ratios of elemental abundance and therefore provide an operationally defined, broad categorisation of pZn speciation. Synchrotron-based X-ray absorption spectroscopic techniques, i.e. techniques involving the absorption of electromagnetic radiation (e.g. X-rays) by matter, can provide information about the chemical speciation (for example, oxidation state and coordination structures with other elements) of elements at nano-to-micrometre scale (10^{-9}–10^{-6} m) and low abundances (on the order of parts per million). In particular, X-ray absorption near-edge structure (XANES) spectroscopy has been used to great effect in mapping chemical species of iron (Fe) in suspended marine particles.[15]

The low-concentration nature of Zn in ocean particles necessitates long collection times of XANES spectra for robust speciation results, limiting the applicability of this technique in terms of the number of particles/samples. Thus, the challenge with spectroscopic techniques such as XANES lies in time and cost trade-offs between its superior capability of providing detailed microscale speciation and structural information of single particles versus the need to examine as many particles as deemed necessary to create a representative picture of a large ocean area. Comparatively, imaging the collected filters by microscale X-ray fluorescence (XRF) can provide an efficient overview of elemental distributions and inter-element associations. Therefore, XRF images are useful guides to target individual particles for XANES analysis. Additionally, the inter-element associations from XRF images can be used to deduce chemical speciation provided with known geochemical associations of elements, overcoming the disadvantages of XANES and allowing a more rapid yet statistically meaningful investigation of elemental chemistry in ocean particles.

Using a two-step XRF-coupled XANES approach, Duan et al.[6] investigated the chemical forms of pZn in the Southern Ocean. In total, close to 4000 particles were analysed from 26 filters representing different locations (Atlantic and Indian sectors of the Southern Ocean), depths (25–3500 m) and seasons (summer and winter). Amongst these, 277 particles were studied in detail using XANES. The XANES analysis was also performed on two sediment cores to assess which pZn species are preserved during vertical transport and deposited on the seafloor. This analytical approach represents the first of its kind performed on Zn-bearing particles from marine settings and provided direct observations to test current hypotheses regarding the conversion of Zn from dissolved to particulate phases and their chemical form.

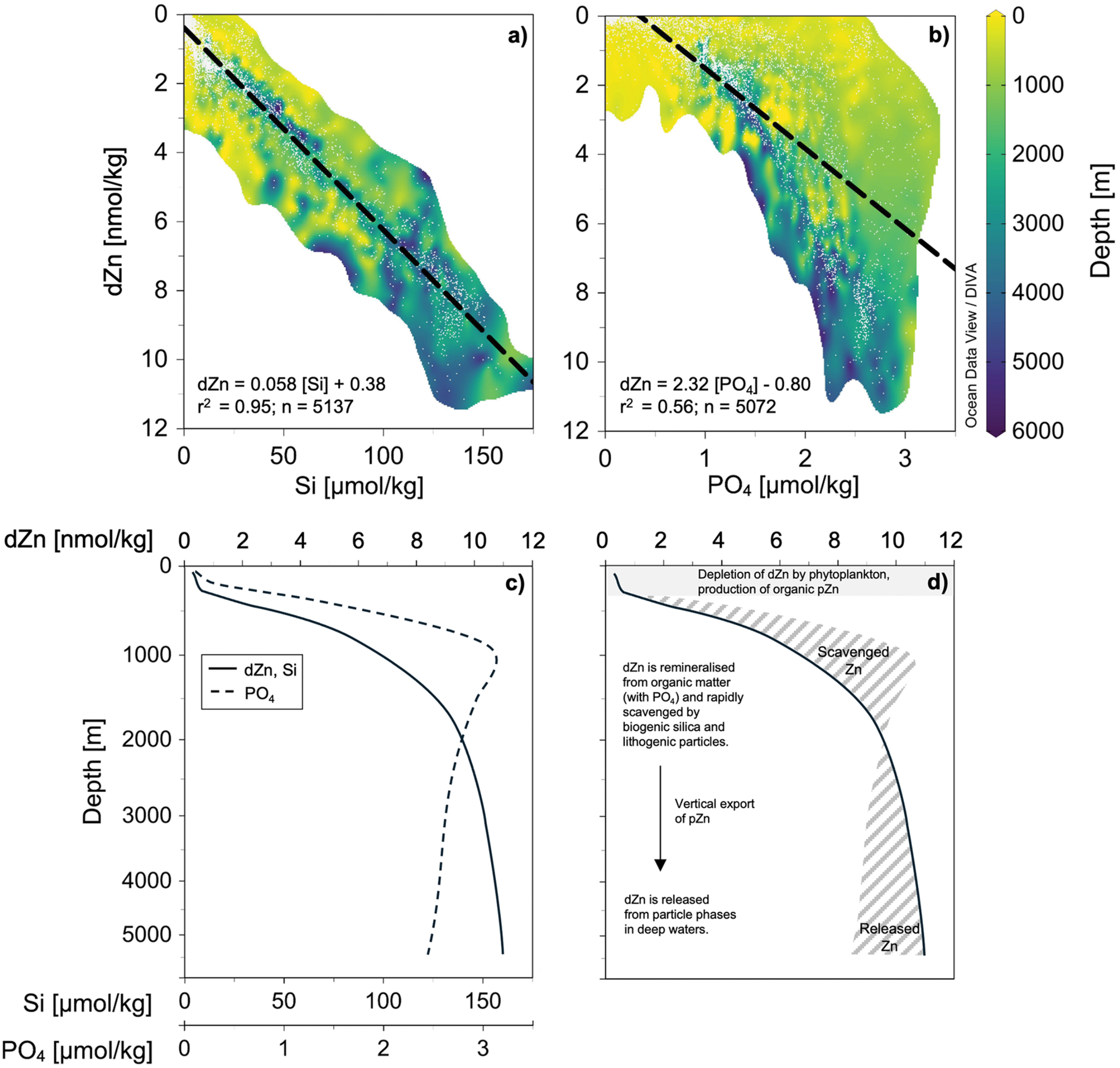
Diverse chemical forms of Zn

Changes in the speciation of pZn with season, location and depth, as described by Duan et al.[6], can be interpreted in the context of water column processes and sources. Depth changes in pZn reflect the relative stability of biogenic and lithogenic phases in the water column. In the surface ocean, phytoplankton assimilate dZn and produce biogenic complexes, including pZn bound to phosphoryl, cysteine, histidine and carboxyl ligands. Biogenic pZn complexes are more abundant in summer and accounted for nearly 75% of particles analysed, reflecting expected higher summer productivity (evidenced by higher concentrations of the photosynthetic pigment chlorophyll-a) and resulting increased demand for Zn by phytoplankton. In contrast, poor winter growing conditions reduce organic matter production, leading to similar proportions of lithogenic and biogenic pZn complexes. Biogenic pZn-Si complexes are found at sites where diatoms dominate the phytoplankton community, and are more abundant in deeper waters than in surface waters, implicating a control of pZn chemistry by biogenic silica in water column processes. The ratio of biogenic to lithogenic pZn phases generally decreases with depth and the only phases that are preserved in ocean floor sediments are biogenic silica and lithogenic complexes (silicates, clays and carbonates). Bacterially mediated remineralisation releases Zn from biogenic particles associated with sinking phytoplankton cells, replenishing the dZn pool in subsurface water masses (Figure 1c). While some of the released dZn can be subsequently adsorbed (scavenged) onto biogenic silica (diatom frustule material), coupling Zn and Si, lithogenic phases also show a strong affinity for dZn scavenging in deep waters. In particular, pZn associated with clays and iron, manganese, and aluminium oxides are abundant in deep waters. The latter are potentially sourced from hydrothermal systems or transported from continentally influenced waters such as the Agulhas Current.[14] The newly acquired data document a mechanistic view of reversible scavenging in the marine Zn cycle, providing evidence for a link behind the coupling of dZn and Si and decoupling of dZn and PO_4 (Figure 1c, d). Revealing the chemical form of important Zn scavengers provides valuable insights into the sensitivity of the marine Zn cycle to global climate change.

Zinc cycling in a changing climate

The newly discovered importance of lithogenic phases in the ocean Zn cycle has implications under changing climatic scenarios. Sources of lithogenic material are supplied to the Southern Ocean via atmospherically transported dust[16], sediment fluxes from sub-Antarctic islands[17] and continental shelves[18] as well as ice sheet[19] and iceberg[20] meltwater entrained with sediment from rock interactions. In today's climate, these sources are often localised or periodic. However, future climate scenarios may perturb the magnitude of these sources with knock-on effects for Zn chemistry and primary production.

Atmospheric dust and meltwater, from ice sheets and icebergs in particular, are sources of lithogenic material that are likely to increase,



Data source: GEOTRACES[23] (released under a CC BY 4.0 International Licence)

Figure 1: Nutrient distributions in the ocean. Correlations of (a) dissolved zinc (dZn) and silicate (Si) and (b) dissolved zinc (dZn) and phosphate (PO_4). Colours represent depth (m) in the water column. Data points are indicated by small white dots. Black dashed lines are the linear regressions between nutrient concentrations, and corresponding equations are shown on the top of each panel. Typical ocean water column distributions of (c) dZn, Si and PO_4 and (d) dZn showing schematically the effect of reversible scavenging in coupling dZn and Si and decoupling dZn and PO.

according to the latest consensus from the Intergovernmental Panel on Climate Change (IPCC).[21] Current model predictions indicate decreased precipitation levels in the subtropics, including the Southern Ocean dust emitting regions of South America, southern Africa and Australia. Together with modest surface warming, these regions will likely become drier in the coming decades, thereby raising the potential for dust supply. The polar regions are further predicted to experience stronger warming trends than elsewhere on Earth, consequently increasing freshwater melt fluxes and iceberg calving. The anticipated increase in lithogenic particle supply to the Southern Ocean may provide extra scavenging potential for dZn, enhancing vertical export (moving Zn from the surface to deep ocean) and decreasing the reservoir of bioavailable Zn for resupply to support primary productivity. Although Fe is the primary micronutrient limiting phytoplankton growth in the Southern Ocean[22], a decreased abundance of bioavailable Zn could result in more widespread co-limitation patterns, reducing the future capacity of the Southern Ocean to sequester carbon dioxide through biological processes.

Conclusions and perspectives

The observations of changing pZn chemistry in the Southern Ocean water column provide a new perspective on Zn cycling. Biogenic pZn complexes are prevalent in the surface ocean, consistent with known metabolic roles of Zn in phytoplankton. With depth, pZn is released back to the water column and the regenerated dZn is subsequently scavenged to inorganic complexes involving biogenic silica and lithogenic phases, thereby reducing the dZn pool available for resupply and enhancing deep pZn flux. The water column shifts in Zn chemistry are imprinted on Southern Ocean water masses which are responsible for redistributing Zn and major nutrients globally, and similar water column processes are expected in other oceans beyond the Southern Ocean. In particular, the association of Zn and biogenic silica suggests diatoms modify the deep ocean Zn cycle and provides a mechanistic link to the globally observed correlation of dZn and Si, which was previously at odds.

By focusing on the products (pZn) of chemical ocean processes, as opposed to the reactants (dZn), synchrotron-based approaches offer new tools to investigate nutrient trace elements such as cadmium, copper, nickel and cobalt, which may experience similar chemical changes to those observed for Zn. The molecular mechanisms responsible for the chemical partitioning between dissolved and particulate phases in trace elements thus have wide implications for understanding biological productivity and global carbon cycling and predicting their responses to changing climate conditions.

Acknowledgements

We appreciate the assistance we received from R. Tappero, S. Nicholas, K. Zhao, D. Schlesinger, L. Pincus, E. Stavitski, D. Leshchev and S. J. White during the acquisition of X-ray data. The Zhang and Onstott labs at Princeton University provided access to the clean room and the laminar flow hood for sample preparation. We thank the captains and crew of the SA *Agulhas II* research vessel for their efforts onboard as well as the chief scientists and participants during each voyage. We are grateful to the TracEx team members for their help with sample collection. This research used resources of the National Synchrotron Light Source II (USA), the Advanced Photon Source (USA), Brookhaven National Laboratory (US Department of Energy) and Argonne National Laboratory (US Department of Energy). Portions of this work were performed at GeoSoilEnviroCARS (University of Chicago, IL, USA) at the Advanced Photon Source.

Funding

We acknowledge funding and support from the US National Science Foundation, Princeton University (Scott Vertebrate Funds and Phillips Equipment Fund in the Department of Geosciences and student internships in the High Meadows Environmental Institute), an anonymous charitable donor trust as part of the Whales and Climate Change Program, the South African National Antarctic Programme (SANAP), the South African Department of Science, Technology and Innovation (DSTI), the South African Department of Forestry, Fisheries and the Environment (DFFE) and the South African National Research Foundation (NRF).

Declarations

We have no competing interests to declare. We have no AI or LLM use to declare. All authors read and approved the final manuscript.

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