NSF OCE-7986704: Collaborative Research: Quantifying the atmospheric flux of bioactive trace elements to the southwestern Indian Ocean
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As the base of most marine food webs, phytoplankton productivity affects growth and success at all other trophic levels in the oceans. It is believed that the balance among macro and micronutrients along with physical environmental factors controls which phytoplankton grow and their growth rates. The Biological Carbon Pump (BCP, one of the dominant mechanisms for sequestering atmospheric carbon to the deep ocean) is controlled by the interplay between different limiting factors such as the concentrations of available macronutrients (silicon, Si; phosphorus, P; nitrogen, N) and essential micronutrients like manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), and cadmium (Cd). The distributions and cycling of these essential trace elements in the oceans are influenced by a complex combination of chemical, physical, and biological processes (i.e. their "biogeochemistry") and this biogeochemical cycling has direct and indirect impacts on ocean ecosystems, the carbon cycle, and climate change. Understanding the factors that control the sources and distributions of bioactive trace elements is crucial for predicting their effects on the BCP. We also know that trace element micronutrients are delivered to the open ocean by dust deposition and in this way can relieve trace element limitation on phytoplankton growth in many areas. Improved knowledge of the factors that influence aerosol trace element fractional solubility is also necessary for understanding the bioavailability of aerosol-derived trace elements. In addition, atmospheric aerosol deposition supplies other chemical species to the surface ocean (trace elements such as Al and Pb, and water-soluble organic compounds), and they can be used to constrain many important processes in the upper ocean.

We have developed sampling and analytical methods to study the solid-phase characteristics and fractional solubility of trace elements in ambient aerosols (as a function of particle size and source region). We have also developed a method using ^{7}Be (naturally occurring radioisotope, T1/2 = 53.3 d) to quantify the bulk deposition velocities for atmospheric aerosols. This combination allows us to calculate the fluxes (wet plus dry) of bioactive trace elements (total and soluble) to the upper ocean; information that is essential to understand and model the impacts of atmospheric deposition on trace element speciation, bioavailability, and microbial productivity in the upper ocean. These methods, described in detail below, have been successfully applied on research cruises in the subtropical Atlantic, the eastern tropical South Pacific, the central North Pacific, and the Arctic (Kadko et al., 2015; 2019; 2020; Anderson et al., 2016; Shelley et al., 2017; Buck et al., 2019).

This project will measure the atmospheric deposition of bioactive trace elements on a cruise of opportunity, collaborating in a multidisciplinary project dedicated to studying trace element sources, transformations and sinks in the Indian Ocean sector of the Southern Ocean (Fig. 1). Located at the intersection of the Atlantic, Indian, and Southern Oceans, this region of the Southern Ocean is relatively under-studied from a biogeochemical perspective, and to our knowledge, no study in this region has combined atmospheric sampling with multi-element, high-resolution sampling of the entire water column. The cruise track will cross the currents and oceanographic fronts that are major pathways of the general circulation in the region and are critical for energy and chemical species transport. This cruise represents an excellent opportunity to quantify the atmospheric deposition of bioactive trace elements in a region with multiple possible aerosol sources and where aerosol Fe deposition and rainfall rates are predicted to range over 1-2 orders of magnitude. We will collaborate with an international group of scientists to study the impact this has on biogeochemical cycles in this region.

Our specific goals for the research are to answer the following questions:

1. What are the aerosol fluxes (wet and dry) of bio-essential (and other) trace elements to the surface waters of the southwestern Indian Ocean?
2. How do these fluxes affect trace element distributions in the upper ocean and how do they vary with aerosol concentration, aerosol source, and rainfall rate.
3. What is the chemical composition of the aerosols and how does that vary based on source (e.g. mineral dust from southern Africa, emissions from biomass burning, and anthropogenic emissions)?
4. What is the fractional solubility of trace elements in the aerosols and how does the solubility vary as a function of aerosol source and particle size?
5. What is the potential bioavailability of soluble aerosol Fe and other bioactive trace elements?

We will collect bulk and size-fractionated atmospheric aerosols as well as event-based precipitation samples during the cruise. We will measure trace element concentrations and fractional solubility in aerosols, and dissolved and particulate trace element concentrations in rain samples, to evaluate the natural and anthropogenic aerosol deposition on the surface ocean in the region. This cruise will include concurrent sampling of the water column for an extensive suite of biogeochemical tracers and biological process rates by our collaborators (Table 1), allowing us to directly observe the impacts of atmospheric deposition on the upper ocean; an objective that would be difficult to fulfill outside of the comprehensive sampling activities of this cruise. Our efforts will be complemented and extended by sharing aerosol and rainfall subsamples with our collaborators to better characterize atmospheric input and develop/refine chemical-tracer methods to constrain estimates of atmospheric input to the surface ocean (Table 2).

We have been offered, at no cost, two berths on the South West INdian GEOTRACES Section (SWINGS) research cruise in the austral winter 2021 (already funded by the French government). Our collaborators will conduct detailed sampling of particulate and dissolved phases along the cruise track that will allow identification and characterization of the sources and distributions of trace elements (Table 1, Table 2). They will study biological uptake and remineralization mechanisms that modify the speciation and fate of the macro- and micronutrients (including export to the sediment). The project also includes a modeling approach that will couple tracer distributions with simulations of the circulation to quantify trace element transport and transformation. Because this cruise is an approved GEOTRACES section (GS02), it will follow the sampling resolution, rigorous intercalibration, and data sharing/access policies that GEOTRACES requires. This cruise will also be part of the IIOE-21 and SOOS2 programs and may serve as a future GO-SHIP survey section.

We will apply our methods for quantifying aerosol deposition (wet and dry) of trace elements to the surface waters of the southwestern Indian Ocean sector of the Southern Ocean, an area where aerosol concentrations and rainfall rates are predicted to vary by 1-2 orders of magnitude, but where there has been little prior biogeochemical study. We will establish the range of fractional solubility of key atmospheric components and study the processes that underlie that variability. The magnitude and variability of aerosol solubility are essential parameters for global biogeochemical models that include, for example, the contribution of bioavailable Fe from atmospheric deposition. We will compare our results for aerosol concentrations and flux with a state-of-the-art global dust model (Hamilton et al., 2019).

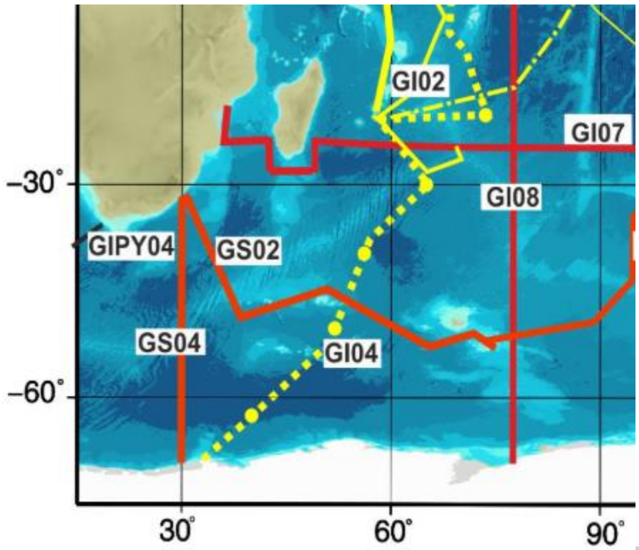

Figure 1:

Top: Part of the GEOTRACES implementation map illustrating the relatively poor coverage of the southwestern Indian Ocean and showing the cruise transect (GS02). (Red cruise tracks: not yet completed; Yellow tracks: partially completed)

Bottom: 3D view of the cruise section with the positions of fronts and currents. The numbers are explained in Table 1.

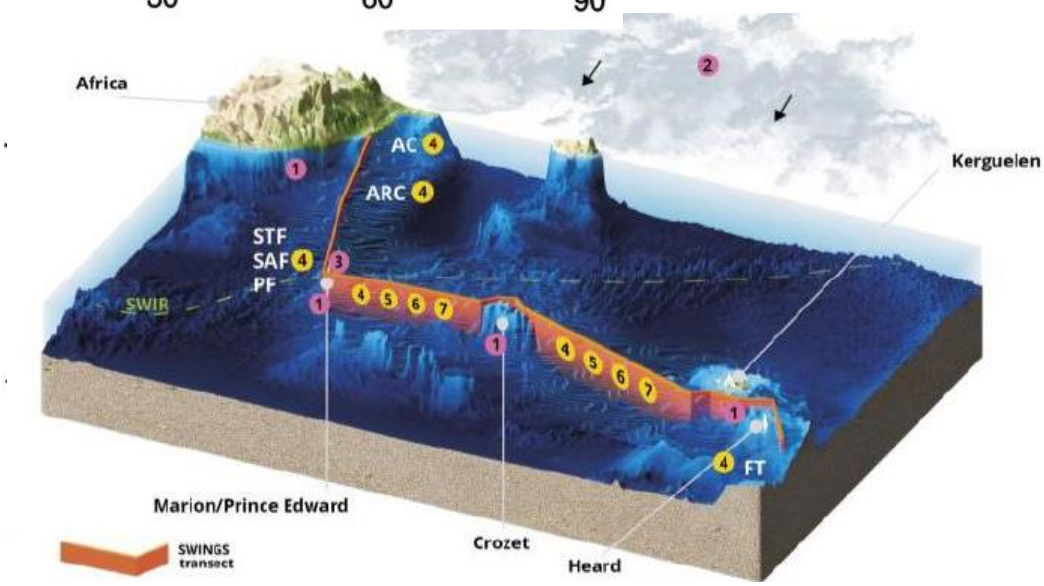

Table 1: Source tracking and process studies (with the corresponding tracers to be analyzed by our collaborators. The colored numbers are keyed to Fig. 1): 1. Land-ocean exchange; 2. atmospheric input; 3. hydrothermal input; 4. circulation and transport; 5. microbial activity; 6. biological uptake; 7. particle-solution exchange.

SOURCE TRACKING	PROCESSES
1 LAND-OCEAN: δFe, δZn, δCd, Ra, ^{227}Ac, εNd, Th, Pa, Pb, REE	4 CIRCULATION: ^{13}C, ^{15}N, Δ^{30}Si, εNd, REE, Ra, ^{227}Ac, Th/Pa, Pb
2 ATMOSPHERIC: Hg, ^{232}Th/^{230}Th, Pb	5 MICROBIAL ACTIVITY: ^{13}C, Th, Pa, Ba_{xs}, Fe&Cu org. speciation
3 HYDROTHERMAL: δFe, δZn, δCd, Ra, ^{227}Ac, εNd, REE, Hg, Pb, δ^7Li, Cr, Sr	6 BIOLOGICAL UPTAKE: δFe, δZn, δCd, Δ^{30}Si
	7 PARTICLE-SOLUTION EXCHANGES: δFe, δZn, δCd, Th/Pa, εNd, Ra, Pb, REE
+ MEASURED IN ALL FRACTIONS, IN DUST, RAIN, WATER COLUMN & SEDIMENTS: Al, Mn, Fe, Ni, Cu, Co, Cd, Ba, REE	