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Quantifying the Impact of Atmospheric Deposition on the Biogeochemistry of Fe and Al in the Upper Ocean

A Decade of Collaboration with the US CLIVAR-CO₂ Repeat Hydrography Program

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OVERVIEW

The aerosol deposition of continental material and its partial dissolution in the surface ocean exerts an important control on the distribution of iron and other potentially limiting trace metal (TM) micronutrients in the open ocean. This dust deposition has implications for the regulation of global climate through the coupling of biolimiting TM cycles, marine productivity, and the global carbon cycle. Thus, it is important to determine the locations of dust deposition in the open ocean and to quantify the magnitude and subsequent dissolution of the dust. At present, there are too few dust deposition estimates and solubility measurements in the open ocean to adequately constrain this key source term in global biogeochemical models.

While early sampling efforts were invaluable in highlighting the importance of TMs in regulating nutrient cycling and phytoplankton productivity in vast ocean regions, they lacked the spatial resolution and global coverage required to constrain model simulations and identify features that illuminate the

processes controlling TM distributions. Starting in 2003, the US Climate Variability and Predictability (CLIVAR)-CO₂ Repeat Hydrography Program provided an hour of ship time for dedicated TM sampling at every degree of latitude or longitude along selected cruise tracks. The principal goals for CLIVAR TM sampling were to produce a high-resolution dissolved iron (Fe) and aluminum (Al) data set with global coverage to better understand upper-ocean Fe biogeochemistry, determine patterns of atmospheric dust deposition based on surface dissolved Al levels, and improve our estimates of the fractional solubility of aerosol TMs using a dedicated shipboard aerosol sampling program. This paper describes recent advances in our understanding of dust deposition and the solubility of aerosol material resulting from 10 years of collaborative work under the US CLIVAR-CO₂ Repeat Hydrography Program.

ATMOSPHERIC DEPOSITION: THE OCEAN PERSPECTIVE

To collect samples for TM analysis within the time frame allotted on CLIVAR cruises, a TM clean rosette-based system instrumented with a conductivity-temperature-depth (CTD) sensor and fluorometer that could collect 12 samples within the upper 1,000 m of the water column was developed (Measures et al., 2008a). This system was the prototype of the 24-bottle sampling system that is now being used by the US-GEOTRACES program (Cutter and Bruland, 2012). The decision to sample the upper 1,000 m frequently rather than obtaining full-depth water column profiles less frequently on CLIVAR cruises was motivated by the desire to maintain high-resolution

coverage and the fact that most TM input and cycling occurs within the upper 1,000 m. The first deployment of the system in 2003 during the CLIVAR A16N cruise (Measures et al., 2008b; Barrett et al., 2012) proved that TM sampling can be successfully incorporated into global hydrography programs. Since then, the TM clean rosette system has been deployed more than 600 times along 10 CLIVAR cruise tracks across a wide range of hydrographic and biogeochemical provinces with conditions ranging from tropical to polar (Figure 1). The shipboard Flow Injection Analysis system was optimized to quickly analyze dissolved Fe and Al in order to keep up with the flow of samples produced, check for contamination, and adapt the sampling scheme when unanticipated biogeochemical features were encountered.

Patterns of dust deposition in the open ocean can be estimated by considering the surface ocean as an integrated long-term dust collector (Measures and Brown, 1996). The essence of this approach is that once dust is deposited

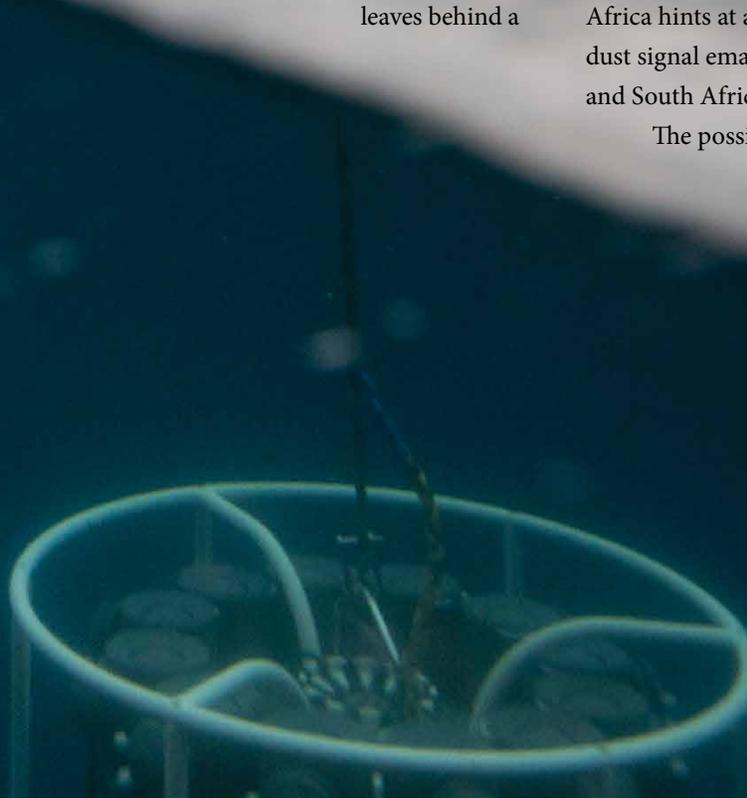
to the ocean surface, the dissolution of lithogenic elements leaves behind a

chemical signal that, if it persists for long enough, can be used to reconstruct the amount of dust deposited into that water. Dissolved Al and more recently titanium, which both have no known biological function and are mainly supplied to the surface of the open ocean via dissolution of aerosols, have proven to be adequate tracers of dust deposition integrated over time scales constrained by their residence times (Measures and Vink, 2000; Dammshäuser et al., 2011). It is now well established that dissolved Al in surface waters of the open ocean scales with dust deposition (Measures and Vink, 2000; Han et al., 2008).

Figure 1 shows a contour plot of dissolved Al within the mixed layer of every station of the 10 CLIVAR cruise tracks sampled to date. In the North Atlantic, maxima in dissolved and particulate Al unequivocally reflect the deposition of Saharan dust (Measures et al., 2008b; Barrett et al., 2012). The data also highlight inputs of Asian and Australian dust propagating eastward in the northwestern and southwestern Pacific, respectively (Figure 1). In the Southern Ocean, the section running poleward of South Africa hints at a possible long-range dust signal emanating from Patagonia and South Africa near 45°S and 60°S.

The possibility of Patagonian and southern African dust signals

propagating into the Atlantic and Indian sectors of the Southern Ocean will be clarified once the last CLIVAR TM sampling is completed in the South Atlantic in early 2014. Except for these localized surface Al elevations, it is clear that continental eolian dust is a negligible source of trace elements for most of the Southern Ocean, as illustrated by the extremely low surface Al levels (< 1 nM) sampled there. The meridional section running from the Antarctic margin to the Bay of Bengal in the Indian Ocean shows a sharp discontinuity in surface Al at 30°S, reflecting dust inputs of Australian origin to the north and the generally dust-free regime of the Southern Ocean to the south. The surface waters of the Bay of Bengal are also characterized with some of the highest surface Al values measured on CLIVAR (> 30 nM). However, while the Bay of Bengal does receive dust from the Indo-Gangetic alluvial plains and Southeast Asia during the northeast monsoon (Srinivas and Sarin, 2013), its surface waters are also greatly impacted by the large freshwater influx of the Ganges-Brahmaputra River system. In other words, unlike in the North Atlantic, the elevated surface Al in the Bay of Bengal reflects a combined dust and freshwater signal, which complicates estimates of dust deposition based on surface Al there. We plan to refine estimates of dust deposition to the open ocean using surface Al data from all CLIVAR cruises and an improved version of the Measures and Brown (1996) model, which will



The CLIVAR trace metal rosette prior to recovery in the Southern Ocean.
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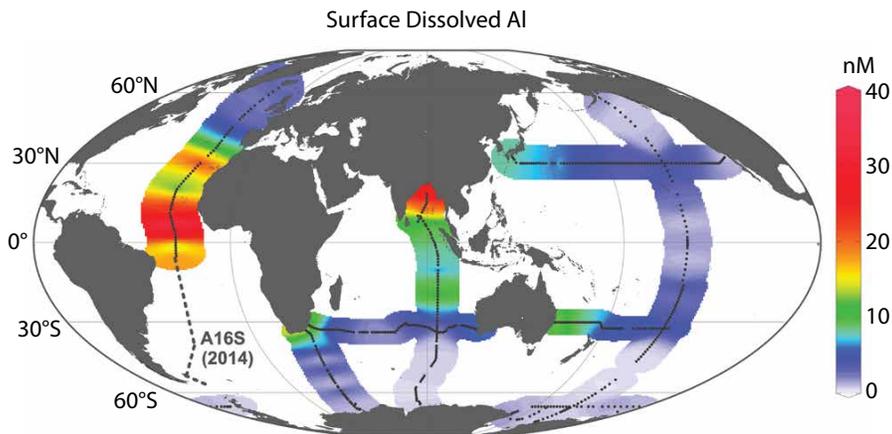


Figure 1. Contoured surface dissolved Al from all stations sampled on CLIVAR cruises with dedicated trace metal (TM) sampling. Black dots represent TM stations. The dashed gray line shows the planned A16S cruise track to be completed in early 2014.

incorporate regionally variable mixed layer depths and Al residence times. These more precise estimates, combined with the aerosol solubility work described below, will better constrain modeled soluble Fe deposition fluxes to the surface of the open ocean.

AEROSOL SAMPLING: DEPOSITION RATES AND FRACTIONAL SOLUBILITIES

Long-term measurements of aerosols (and, by inference, total atmospheric deposition rates) have been predominantly collected at (or on) island-based sampling stations in the Northern Hemisphere. Thus, current estimates of deposition to the surface ocean, most

notably in the Southern Hemisphere, are primarily based on extrapolations of valuable historical data (e.g., Duce et al., 1991) that were not coordinated with sampling of the surface ocean. Atmospheric samples have been collected on all 10 CLIVAR cruises since 2003, providing a snapshot of deposition rates to the open ocean (Buck et al., 2010, 2013). However, given the episodic nature of dust deposition events, estimating total atmospheric deposition to the open ocean using a 24-hour shipboard aerosol sampling period is fraught with large uncertainties. Shipboard collections measure atmospheric aerosol concentrations near the sea surface, and dry deposition rates are estimated by

applying an assumed deposition velocity (e.g., $1,000 \text{ m day}^{-1}$) to the suspended aerosol load. In addition, measurement of wet deposition rates is entirely dependent on encountering precipitation events while at sea. For all these reasons, total deposition rate estimates based on shipboard aerosol sampling suffer from large uncertainties. Shipboard aerosol sampling on CLIVAR is thus mainly devoted to the determination of the solubility of Fe and other dust-laden elements of biogeochemical interest.

Baker and Croot (2010) reviewed the many factors influencing aerosol iron fractional solubility, and Sholkovitz et al. (2012) compiled a global data set of values from the literature. These valuable works highlight the variety of methods used to assess aerosol solubility. Relatively few studies, however, have measured aerosol solubility in filtered surface seawater and compared the results to aerosol solubility in ultrapure deionized (DI) water. The former could be expected to most closely approximate the dissolution of aerosol particles in the surface ocean while the latter mimics aerosol dissolution in precipitation (Buck et al., 2010). An advantage to the DI water leaching treatment is that the leach solutions can be easily and directly analyzed for most of the GEOTRACES “key parameter” trace elements and isotopes (TEIs) using HR-ICP-MS (High Resolution Inductively Coupled Plasma Mass Spectrometry; SCOR Working Group, 2006). Trace element analyses are more difficult in a seawater matrix. Replicate aerosol samples collected on North Atlantic (A16N) and Pacific (P02 and P16) CLIVAR sections were extracted with a rapid flow-through procedure using either filtered surface seawater or ultrapure deionized water (Buck et al., 2006). Comparison of the

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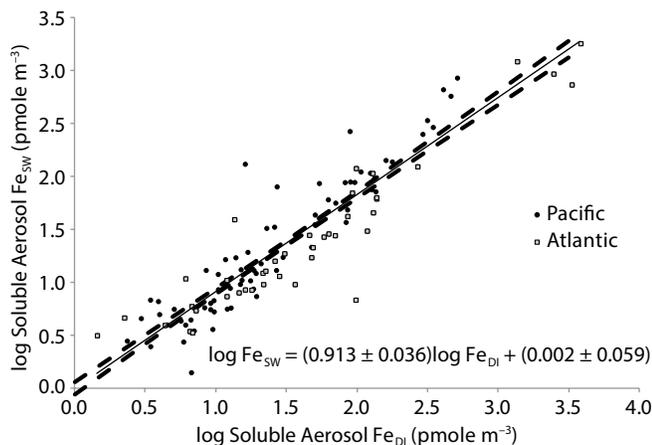


Figure 2. Log transformed deionized (DI) water and seawater (SW)-soluble Fe data plotted with a linear least-squares regression trend line and 68% confidence limits. Aerosol Fe fractional solubility was $15\% \pm 8\%$ (DI water) and $9\% \pm 5\%$ (SW) in the Atlantic and $10\% \pm 5\%$ (DI water) and $8\% \pm 9\%$ (SW) in the Pacific. Figure from Buck et al. (2013)

paired log-transformed data shows a strong linear relationship, $\log Fe_{SW} = (0.829 \pm 0.050) \log Fe_{DI} + (0.041 \pm 0.091)$; $R^2 = 0.93$, which can be used to predict the concentration of soluble aerosol Fe, and therefore fractional solubility, in seawater from the simpler DI water measurement (Figure 2). Analysis of CLIVAR aerosol samples from other regions is ongoing and will investigate this relationship further.

Once the A16S cruise is completed in the South Atlantic in January 2014, we will be able to assemble a global view of trace elements in the main thermocline that can be used to constrain oceanic Fe models and improve our understanding of the fractional solubility of aerosol TMs. These data will be valuable in future process studies and in time-series endeavors.

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