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On the Fractional Solubillity of Copper in Marine Aerosols: Toxicity of Aeolian Copper Revisited

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On the fractional solubility of copper in marine aerosols: Toxicity of aeolian copper revisited

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[1] Paytan et al. (2009) argue that the atmospheric deposition of aerosols lead to copper concentrations that are potentially toxic to marine phytoplankton in a large area of tropical and subtropical North Atlantic Ocean. A key assumption in their model is that all marine aerosols (mineral dust and anthropogenic particles) have a high (40%) fractional solubility of copper. Our data show that the fractional solubility of copper for Saharan dust over the Sargasso Sea and Bermuda is significantly lower (1–7%). In contrast, anthropogenic aerosols with non-Saharan sources have significantly higher values (10–100%). Hence, the potential Cu toxicity in the tropical and subtropical North Atlantic should be re-estimated, given the low fractional solubility of Cu in the Saharan dust that dominates aerosol deposition to this region. **Citation:** Sholkovitz, E. R., P. N. Sedwick, and T. M. Church (2010), On the fractional solubility of copper in marine aerosols: Toxicity of aeolian copper revisited, *Geophys. Res. Lett.*, *37*, L20601, doi:10.1029/2010GL044817.

1. Introduction

[2] Because copper (Cu) is a micro-nutrient required for the growth of marine phytoplankton and a potential toxin, its marine biogeochemistry has received considerable attention [*Moffett*, 1995; *Croot et al.*, 2000; *Morel et al.*, 2003; *Maldonado et al.*, 2006]. In seawater, copper speciation is dominated by complexation with organic ligands: biological availability and toxicity for marine phytoplankton depend on the dissolved concentration of 'free' inorganic Cu [*Sunda and Guillard*, 1976; *Anderson and Morel*, 1978; *Moffett et al.*, 1990; *Moffett and Brand*, 1996; *Mann et al.*, 2002]. *Paytan et al.* [2009] have recently argued that the atmospheric deposition of Cu to the sea in aerosols could be toxic to phytoplankton in certain open ocean and coastal regions, including large areas of the tropical and subtropical North Atlantic Ocean. Here we examine a critical parameter in their model estimate of copper toxicity; namely, that the fractional solubility of Cu in aerosols depositing on the sea surface is assumed to be constant at a value of 40%.

2. Samples and Methods

[3] Time-series observations have established that aerosols over the western subtropical North Atlantic Ocean are dominated by soil dust carried from North Africa ('Saharan dust') during the summer and early fall, with a greatly increased proportion of anthropogenic aerosols carried from North America, Asia and Europe during the period from late fall through spring [*Duce and Hoffman*, 1976; *Chen and Duce*, 1983; *Arimoto et al.*, 1995, 2003; *Moody et al.*, 1995; *Huang et al.*, 1999; *Prospero*, 1999]. This seasonal dichotomy facilitates comparisons between different aerosol types in terms of bulk composition and the fractional solubility of aerosol-borne trace elements [*Huang et al.*, 1999; *Sedwick et al.*, 2007; *Sholkovitz et al.*, 2009; *Trapp et al.*, 2010].

[4] Here we consider chemical data from three types of atmospheric samples collected from the Bermuda region of the Sargasso Sea: (1) bulk (>0.5 micron) aerosol samples collected at sea during 2003–2004 (*FeATMISS* cruises); (2) bulk aerosol samples collected at Tudor Hill, Bermuda during 2007–2008 (*FeAST* program); and (3) bulk rainwater samples collected at Tudor Hill during the 2007–2008 *FeAST* program. The Tudor Hill samples were collected atop a 23 m tall walk-up tower during periods of onshore wind. Bulk (~1 week integrated composite) rainwater and aerosol samples were collected and processed using the methods described by *Kim et al.* [1999] and *Sedwick et al.* [2005, 2007] respectively. The bulk aerosol samples were subjected to a 1:3 HF/HNO$_3$ digestion prior to the determination of 'total metals'. Unfiltered rainwater samples were acidified to pH ~1.6 with 2 mL/L of ultra pure hydrochloric acid and then stored for more than 6 months prior to the determination of 'total-dissolvable metals'. Analytical methods are reported by *Sedwick et al.* [2007], except for Cu, which was determined in aerosol digests, leach solutions and rainwater by inductively-coupled plasma mass spectrometry in the medium-resolution mode.

[5] We also estimate the fractional solubility of copper for aerosols collected at the Tudor Hill tower in 2007 and 2008, using a modification of the flow-through deionized-water leaching protocol described by *Buck et al.* [2006]. 250 mL of freshly-produced ultra pure deionized water (pH ~ 5.5) is rapidly passed through an aerosol-laden 0.4 μm polycarbonate filter membrane within several hours of the aerosol sample collection. The filtrate (leachate) was immediately transferred into an acid-cleaned 125 mL low-density polyethylene bottle and acidified to pH ~1.6 with 2 mL/L ultra pure hydrochloric acid. The measured concentration of Cu in this aerosol leachate solution is defined as 'soluble' aerosol Cu, from which a corresponding atmospheric loading of soluble aerosol copper (Cu$_S$, ng m^{-3}) was calculated using the total volume of sampled air. From this we calculate the fractional solubility of aerosol copper (%Cu$_S$), using the total aerosol copper concentration (Cu$_T$) determined for a parallel aerosol sample (see above), as follows: %Cu$_S$ = 100(Cu$_S$/Cu$_T$).

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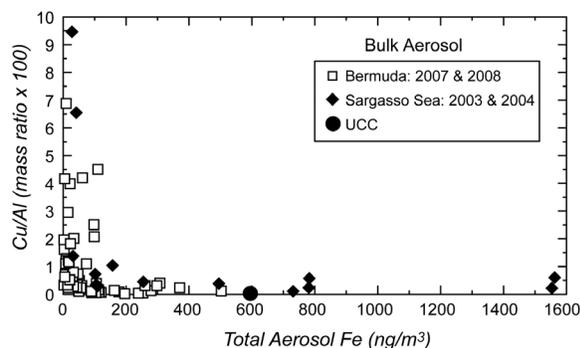
Figure 1. Atmospheric loading of total Cu/Al (mass ratio × 100) versus total Fe from analysis of bulk aerosols collected at the Tudor Hill tower (Bermuda) in 2007–2008 and the adjacent Sargasso Sea in 2003–2004. Also plotted is the Cu/Al mass ratio × 100 (= 0.03) for the upper continental crust (UCC) reported by *Taylor and McLennan* [1985]. Not shown are four data points with high Cu/Al ratios that are off scale with respect to the y-axis; these data reflect aerosol samples with a low load of total iron and a Cu/Al ratio that greatly exceeds that of the UCC. Samples with Fe loading over 400 ng/m^3 are predominately composed of Saharan dust.

[6] Laboratory studies of aerosol dissolution are unlikely to reproduce the conditions experienced by aerosol particles deposited to the surface ocean. Hence, such operationally-defined solubility measurements are expected to yield information on the relative solubility of trace elements in aerosols rather than the true fractional solubility of these elements in the surface ocean [*Sedwick et al.*, 2007; *Baker and Croot*, 2010; *Trapp et al.*, 2010]. Nonetheless, such measurements are thought to provide useful, semi-quantitative information concerning the effective solubility of aerosol trace metals [e.g., *Chuang et al.*, 2005. *Sedwick et al.*, 2005, 2007; *Buck et al.*, 2006, 2010; *Trapp et al.*, 2010]. Moreover, results of a recent study by *Aguilar-Islas et al.* [2010] indicate that "…different types of aerosols produce more variability in aerosol iron solubility estimates than do different leaching protocols". We assume that the same holds true for operationally-defined estimates of aerosol copper solubility, thus allowing the direct comparison of such estimates between different studies, including our estimates and the values used in the model by *Paytan et al.* [2009].

3. Results and Discussion

[7] Figures 1– 3 show the Cu data for our bulk aerosol samples (Figure 1), bulk rain samples (Figure 2), and deionized-water leach solutions of bulk aerosols (Figure 3). Total aerosol iron loading, which is presented on the x-axis of Figures 1 and 3, provides a rough measure of the relative proportions of Saharan dust versus non-Saharan aerosols in the Bermuda region of the Sargasso Sea. As discussed by *Sedwick et al.* [2007] and *Sholkovitz et al.* [2009], the seasonal shift from high to low aerosol iron loadings in this area corresponds to an increase in the proportion of vanadium- and nickel-rich aerosols carried from North America and other non-Saharan sources. That is, high aerosol Fe loadings are typically associated with the transport of mineral dust from North Africa in the summer months, whereas low
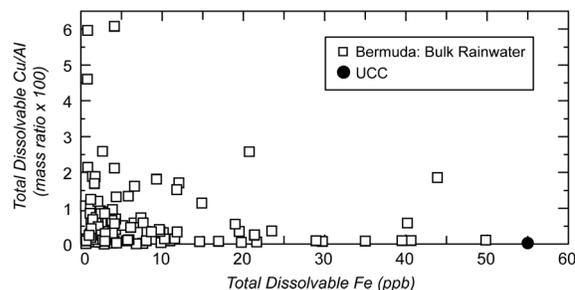
aerosol Fe loadings are typically associated with a greater proportion of anthropogenic aerosols, primarily carried from North America, from late fall through spring.

[8] It is common geochemical practice to normalize the concentrations of trace elements in aerosols to the concentration of Al, in order to distinguish between mineral aerosols with terrigenous (~crustal) source and those with an anthropogenic source. Figures 1–3 reveal roughly hyperbolic relationships between total Cu/Al and total Fe in the bulk aerosols (Figure 1); between total-dissolvable Cu/Al and total-dissolvable Fe in rainwater (Figure 2); and between the fractional solubility of aerosol Cu and total aerosol Fe (Figure 3). There is a significant increase in the Cu/Al mass ratio of bulk aerosols and rainwater from nearly crustal values at high total Fe loadings to values that are well above the crustal ratio at low total Fe loadings. The majority of our aerosol and rainwater samples with crust-like Cu/Al ratios were collected in the summer months, when Saharan dust dominates the bulk aerosol near Bermuda. In contrast, the majority of aerosols with Cu/Al ratios greater than crustal values were collected in the late fall-spring period, when total aerosol Fe loadings are mostly less than 100 ng m^{-3} and non-Saharan aerosols account for a larger proportion of the

Figure 2. Total-dissolvable Cu/Al (mass ratios × 100) versus total-dissolvable Fe in unfiltered bulk rainwater samples collected at the Tudor Hill tower (Bermuda) in 2007–2008. The Cu/Al (mass ratio × 100) value for UCC refers to the bulk composition of the upper continental crust from *Taylor and McLennan* [1985].
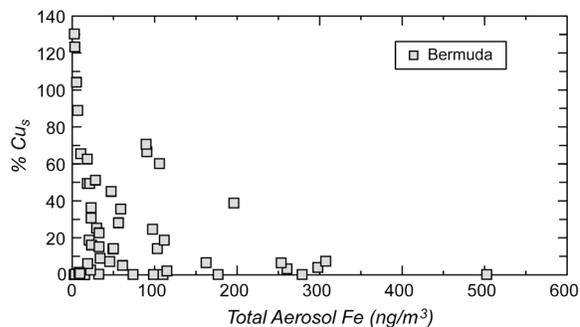

Figure 3. Fractional solubility of aerosol copper in deionized water (%Cu$_S$) versus total aerosol iron loading for bulk aerosol samples collected at the Tudor Hill tower (Bermuda) in 2007–2008. The two samples with %Cu$_S$ values between 120% and 130% reflect the large error involved in calculations using low concentrations of similar magnitudes (here soluble Cu and total aerosol Cu).

bulk aerosol [*Sholkovitz et al.*, 2009]. The orders of magnitude range in Cu/Al ratios at low Fe loadings reflects multiple sources of aerosol Cu, including anthropogenic emissions, soil dust and biomass combustion.

[9] A key finding here is the relatively low fractional solubility of aerosol Cu (~1–7%) in Saharan dust (Figure 3), which dominates the bulk aerosol during summer months, versus the generally elevated fractional solubility of Cu (~10–100%) in aerosols collected during the non-summer months, when anthropogenic emissions from North America and other sources account for a greater proportion of the bulk aerosol. The %Cu$_S$ and Cu/Al data shown in Figures 1–3 are wholly consistent with our empirical data for the fractional solubility of V and Ni, and for the bulk aerosol V/Al and Ni/Al ratios for the 2003–2004 shipboard aerosol samples [*Sedwick et al.*, 2007; *Sholkovitz et al.*, 2009]. Specifically, aerosols in the Bermuda region displayed relatively low fractional solubility values for V (~5–7%) and Ni (~1–3%), and crust-like V/Al and Ni/Al ratios in summer 2003, when Saharan dust plumes produced high aerosol Fe loadings. In contrast, aerosols collected during spring and early summer 2004, when aerosol Fe loadings were low, displayed elevated fractional solubility values for both V (~40–90%) and Ni (~20–40%), as well as bulk V/Al and Ni/Al ratios greater than crustal values. It is well known that that Ni and V are enriched in oil combustion products, which implies that the fractional solubility of V and Ni are elevated in aerosols associated with anthropogenic fuel combustion, relative to Saharan dust.

[10] Following this reasoning, we suggest that both the fractional solubility of Cu and the bulk Cu/Al ratio are elevated in aerosols carried to the Bermuda region from North America and other non-Saharan sources, relative to typical Saharan dust, for which the fractional solubility of Cu is low (~1–7%) and the bulk Cu/Al ratio is close to the crustal value. At this stage we lack any direct information concerning the genesis of aerosols that contain relatively soluble Cu in non-Saharan air masses; fossil fuel combustion and smelting emissions may be important in this regard.

[11] The study of *Paytan et al.* [2009] is the first attempt to estimate the atmospheric dry deposition flux of Cu to the ocean on a global scale. They note that their model results are expected to provide a conservative estimate of soluble copper deposition, because wet deposition of Cu and emissions from copper smelting operations are not considered. Their aerosol transport and deposition model prescribes that ~63% of the atmospheric dry deposition of Cu to the ocean is in the form of mineral dust from desert soils, ~5% is in the form of natural biogenic particles, and ~32% is in the form of combustion-derived aerosols that are primarily derived from the burning of fossil fuels. From their model simulation of global dry deposition of Cu, *Paytan et al.* [2009] identify regions where aeolian Cu accumulates to concentrations that are potentially toxic to native phytoplankton. The largest region where aeolian Cu is predicted to reach toxic concentrations lies in the tropical and subtropical region of the North Atlantic Ocean, directly under the major transport path of mineral dust from North Africa to Barbados [*Prospero*, 1999]. Other areas where high concentrations of dissolved Cu are predicted due to mineral dust deposition include the Mediterranean and Arabian Seas. *Paytan et al.* [2009] also predict that anthropogenic emissions may lead to toxic dissolved Cu concentrations in the Bay of Bengal and in two areas of coastal Southeast Asia.

[12] Importantly, the estimate of soluble aeolian Cu deposition by *Paytan et al.* [2009] is directly dependent on the assumption that all aerosol-borne Cu, irrespective of source and type, has the same fractional solubility of 40%. This assumption is clearly at odds with our empirical data from the Sargasso Sea, which indicate a much lower fractional solubility (~1–7%) for Cu in Saharan dust, but a higher fractional solubility (10–100%) for Cu in non-Saharan aerosols (Figure 3). In support of their fractional solubility value of 40%, *Paytan et al.* [2009] cite the study of *Chester et al.* [1993] who use seawater leaching to estimate the fractional solubility of Cu in aerosols; their 'crust-rich' aerosols refer to natural mineral dust from the west coast of Africa and the Red Sea; 'urban-rich' aerosols were collected from Liverpool (U.K.) and Corsica; and their 'mixed' aerosols refer to unspecified mixtures of natural and anthropogenic aerosols from the Arabian Sea and Cape Verde. The two sets of crust-rich aerosol yield mean fractional solubility values of 1% and 2% for Cu, with a range of <1–4%. The two sets of urban-rich aerosol yield mean fractional solubility values of 30% and 34%, with a range of 20–54%. The two sets of mixed source aerosol yield intermediate fractional solubility for Cu, with mean values of 13% and 29% and a range of 9–33%. Hence, the aerosol Cu solubility estimates of *Chester et al.* [1993] agree remarkably well with our Bermuda aerosol data, which suggest a low fractional solubility of Cu in mineral dust from North Africa, and significantly higher solubility values for anthropogenic aerosols.

[13] *Hsu et al.* [2005] report mean fractional solubility values of 26% and 42% for Cu in aerosols collected at two sites near the coast of Taiwan. *Desboeufs et al.* [2005] report fractional solubility values of 36% and 27% for Cu in fly ash from heavy fuel oil and coal, respectively, and a solubility value of 75% for Cu in urban particulates. They also report solubility values 'below detection' for Cu in Arizona soil dust and 28% for Cu in Cape Verde loess, the latter sample having a uniquely high fractional solubility among published values for Cu in mineral dust. Although the potential contributions from multiple sources of non-soil-dust aerosols renders it difficult to assign a uniform value to %Cu$_s$ in combustion emissions, the high values that we have estimated for non-Saharan aerosols and other estimates reported above are in rough accord with the 40% fractional solubility used by *Paytan et al.* (2009). Thus, given *Paytan et al.*'s [2009] model predicts that ~32% of the total dry deposition of Cu enters the ocean as combustion emissions, their estimate of the total aeolian flux of soluble Cu to the global ocean may not be grossly in error; that is, their overly high estimate of %Cu$_s$ for soil dust may be offset by a relatively high fractional solubility (>40%) of Cu in combustion aerosols. However, the assumption of constant %Cu$_s$ will clearly introduce error in the predicted distribution of soluble Cu deposition on a regional basis.

4. Conclusion

[14] Based on our empirical data from Bermuda in the Sargasso Sea and a reassessment of data published in the literature, we conclude that the fractional solubility of copper in mineral aerosols from North Africa ranges from 1 to 7%. The model-based conclusions of *Paytan et al.* [2009] assume that the fractional solubility of aerosol copper in the surface ocean is constant at 40%, irrespective of the type and source

of the copper-bearing aerosols. Our data suggest that model-results for Cu toxicity need to more accurately consider the large range in the fractional solubility of aerosol-Cu being deposited in the coastal and open ocean. In particular, potential Cu toxicity in the tropical and subtropical region of the North Atlantic should be re-estimated, given the apparently low fractional solubility of Cu in the Saharan dust that dominates aerosol deposition to this region. On the other hand, we estimate moderate to high values (10–100%) for the fractional solubility of copper in anthropogenic aerosols sampled in the Bermuda region that are consistent with the 40% solubility value assumed by *Paytan et al.* [2009]. Hence, aeolian inputs to the ocean might result in dissolved Cu concentrations that are toxic to marine phytoplankton, but we would argue that this situation is likely to be observed only in areas that are strongly impacted by human emissions, rather than open ocean regions where aerosol Cu deposition is dominated by desert dust.

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