Global Biogeochemical Cycles

RESEARCH ARTICLE
10.1029/2022GB007521

Special Section:
The U.S. GEOTRACES Pacific Meridional Transect (GP15)

Key Points:

- Most copper in seawater is present as inert species
- Sunlight appears to transform inert copper into labile forms
- Rivers are an important source of inert copper

Supporting Information:

Supporting Information may be found in the online version of this article.

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Citation:

Moriyasu, R., John, S. G., Bian, X., Yang, S.-C., & Moffett, J. W. (2023). Cu exists predominantly as kinetically inert complexes throughout the interior of the equatorial and North Pacific Ocean. *Global Biogeochemical Cycles*, *37*, e2022GB007521. https://doi.org/10.1029/2022GB007521

Received 9 JUL 2022
Accepted 1 JUL 2023

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Cu Exists Predominantly as Kinetically Inert Complexes Throughout the Interior of the Equatorial and North Pacific Ocean

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Abstract

The chemistry of copper (Cu) in seawater is well known to be dominated by complexation with organic ligands. The prevailing paradigm is that Cu forms strong but labile complexes. Recently, a novel procedure revealed that only a small fraction of dissolved Cu exists as labile complexes. The majority is present as a fraction that is relatively inert on timescales of weeks or more and probably does not participate in coordination exchange reactions, including biologically mediated processes. Samples collected from the 2018 GEOTRACES GP15 cruise show that throughout the interior of the Pacific Ocean, this inert fraction comprises about 90% of the dissolved Cu. Labile Cu accumulates in surface waters, probably arising from photochemical decomposition of the inert fraction. There is also a modest accumulation of labile Cu near deep sea sediments and along the Alaskan shelf and slope. The results have important implications for Cu transport and biological availability. Inert Cu may influence Cu transport throughout the water column and contribute to the linear increase in Cu with depth, a distribution which is hard to explain for a biologically active trace metal. The origins of inert Cu are unknown. It may be produced slowly within the water column on the timescale of meridional overturning circulation. In the Columbia River, between 92% and 98% of the dissolved Cu is in the inert fraction, suggesting a possible terrestrial source of inert Cu to the ocean.

Plain Language Summary

Copper forms strong but labile complexes in natural waters, including seawater. Copper is an essential micronutrient in seawater as well as a toxic species in polluted waters, so the kinetics of its uptake and exchange are important for its geochemistry and its role in biology. Here, we show that throughout the interior of the central North Pacific Ocean, most copper has become transformed into species that are chemically inert. Only harsh treatments such as UV irradiation of prolonged acidification are able to unlock copper from that form. We show that labile forms of copper become important primarily near the surface, probably as a result of photooxidation. Fluvial sources of inert Cu were identified in the study, but it may be formed in situ within the very old waters of the North Pacific. Inert Cu upends our thinking about how copper is scavenged in deep waters.

1. Introduction

Within oceanic regimes, copper (Cu) is considered a micronutrient, as it is used as a cofactor for proteins in many biological processes. Most notably, Cu is used for electron transport by certain marine diatoms (Peers & Price, 2006), denitrification (Granger & Ward, 2003; Ward et al., 2008), ammonia oxidation by archaea (Amin et al., 2013; Jacquot et al., 2014; Walker et al., 2010), and oxidases for high-affinity iron transport in high-nutrient low-chlorophyll regions (Maldonado et al., 2006). However, at elevated concentrations, often from anthropogenic input, Cu can be toxic; it has been found to disrupt manganese and zinc uptake in diatoms (Sunda & Huntsman, 1983), green algae (Sunda & Huntsman, 1998), and cyanobacteria (Mann et al., 2002; Moffett et al., 1997).

The major source of oceanic Cu is fluvial input (Bruland & Lohan, 2003), while the major sink of Cu is scavenging (Boyle et al., 1977). However, natural and anthropogenic aeolian inputs of Cu may also be important. For instance, there are large surface Cu maxima observed in the Indian Ocean, derived from dust inputs from deserts (Saager et al., 1992). In the Pacific Ocean, there are Cu inputs from cities on the Asian continent (Wang et al., 2016).

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In the open ocean, Cu concentrations linearly increase with depth. This linear increase with depth can be explained by benthic inputs from the abyssal plain (Roshan & Wu, 2015). Most of the sedimentary Cu pool is expected to be at the sediment surface since the solubility product of various Cu compounds would be exceeded after a few centimeters (Boyle et al., 1977). Another hypothesis for the linear distribution of dissolved Cu is reversible scavenging by sinking particles (Little et al., 2013; Richon & Tagliabue, 2019). This reversible scavenging model of Cu was originally applied to ^{230}Th by Bacon and Anderson (1982) because ^{230}Th also exhibits a linear depth profile. However, unlike ^{230}Th, which has a source throughout the water column from the α-decay of ^{234}U, Cu does not have a ubiquitous source.

Cu speciation controls the biogeochemistry of Cu in the ocean. Cu bioavailability and toxicity are functions of free cupric ion concentration (Cu^{2+}), rather than total dissolved Cu (Brand et al., 1986; Sunda & Lewis, 1978). Nearly all of the dissolved Cu pool (>99%) is bound by organic ligands (Coale & Bruland, 1988; Moffett & Dupont 2007; Ruacho et al., 2020; van den Berg et al., 1987), and a significant fraction of these ligands are of biogenic origin (Croot et al., 2000; Moffett & Brand, 1996). Cupric ion concentrations as low as 10^{-11} M can be toxic to phytoplankton, and some microorganisms are suspected to produce organic ligands to buffer the concentration of Cu^{2+} to safe levels while having enough to maintain biological activity (Bruland & Lohan, 2003). Cyanobacteria have the lowest resistance to Cu toxicity, resulting in a decrease in reproduction due to ambient cupric ion concentrations as low as 10^{-12} M (Brand et al., 1986). *Synechococcus* sp. was found to produce ligands with conditional stability constants similar to those measured in the water column (Moffett and Brand. 1996).

Cu is also bound by inorganic ligands, primarily carbonate (Byrne & Miller, 1985). This fraction, along with free cupric ions, is assumed to be most rapidly removed by biological uptake and scavenging (Little et al., 2013; Richon & Tagliabue, 2019; Sunda & Huntsman, 1995). The inorganic pool of Cu has been hypothesized to be particle-reactive, while organically complexed Cu remains in the dissolved phase (Davis & Leckie, 1978). Van den Berg and coworkers showed that strong ligands in estuaries stabilize dissolved Cu under high scavenging conditions (Laglera & van den Berg, 2003; van den Berg et al., 1987). Such ligands control the partitioning between the dissolved and particulate phases and act as a buffer for the metal ion in the dissolved phase.

It is generally assumed that while Cu forms stable complexes, coordination reactions between competing ligands are rapid. The concentrations and binding strengths of ligands have been probed by adding synthetic ligands to compete with the naturally occurring ligands. Ligands are typically categorized by the range of their conditional stability constants ($K'^{\text{cond}}_1 = \frac{[CuL_1]}{[Cu^{2+}][L_1]}$). From such competition experiments, a class of ligands has been identified that dominates Cu speciation; these ligands are commonly referred to as L_1 and have a $K_1{}'^{\text{cond}}$ between 10^{13}–10^{16} (Bundy et al., 2013). A category of more abundant but weaker ligands (L_2) on the other hand are organics that are thought to be terrestrial or marine decomposition products (Whitby et al., 2018). The strength of these ligands is operationally defined based on the conditional stability constant of the added chelator. Typically, the strength of the added synthetic ligand is quantified by the partition coefficient (α) which is defined as follows:

$$\alpha_{\text{Cu(AL)}_x} = \frac{[\text{Cu(AL)}_x]}{[\text{Cu}^{2+}]} = \beta_2^{\text{cond}}[\text{AL}]^2 + K'^{\text{cond}}_1[\text{AL}] \tag{1}$$

where $[Cu(AL)_x]$ is the concentration of the complex formed between Cu and the added ligand ([AL]), and $[Cu^{2+}]$ is the concentration of the cupric ions (Campos & van den Berg, 1994). This partition coefficient is equal to the sum of the conditional stability constants of the mono- and bis- complexes. This α is referred to as the analytical window in ligand-exchange studies as it affects the concentrations and binding strengths of the metals and their ligands measured during the analyses.

The major assumption about Cu speciation is that it forms strong but labile complexes so that equilibrium is reached between all ligands, including the added ligand, on the timescale of the experiment. This assumption was first challenged by Kogut and Voelker (2003), who identified an operationally defined “inert” fraction in estuarine waters. Using 1 mM of the Cu chelator, salicylaldoxime, in their experiment (resulting in a log(α) of 8.5 and an equilibration period of 24 and 48 hr), they showed that the lower bound of ligand strength was log $K'_{\text{cond}} = 13$. They argued that while one could nominally assign a binding strength to the ambient ligands, it was more likely that Cu was kinetically inert and that assigning a conditional stability constant was not appropriate. They also hypothesized that inert Cu was in a colloidal fraction.

Moriyasu and Moffett (2022) extended this approach using ligand competition coupled with solvent extraction. This method utilizes a strong ligand (oxine) at high concentration leading to a competitive binding strength

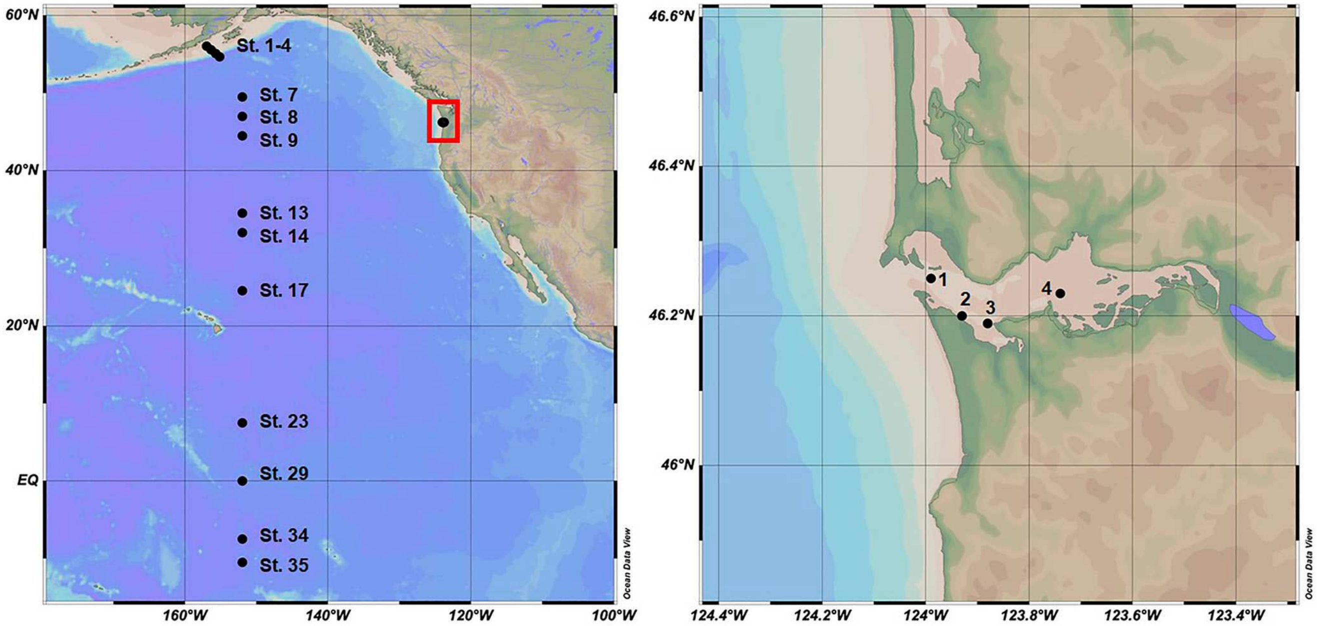

Figure 1. Left: Map of the GP15 transect with markers for stations measured for labile, inert, and total Cu. Right: Stations sampled on the Columbia River.

("detection window") two orders of magnitude greater than that of Kogut and Voelker (2003). Moreover, solvent extraction eliminated the wall loss problems that plague voltammetry, enabling equilibration times of up to several weeks. Here, the method was used to study the distribution of labile and inert Cu along the GEOTRACES GP15 "Pacific Meridional Transect" from the Alaskan Shelf to Papeete, Tahiti. This data set, along with samples preserved from GEOTRACES GA03 (Jacquot & Moffett, 2015), allows us to compare the Cu lability between the Pacific and Atlantic. Additionally, we explore the sources of both labile and inert pools.

2. Sampling

Samples were obtained from the GEOTRACES GP15 cruise aboard the R/V *Roger Revelle* (RR1814 from September 18th–October 21st of 2018, and RR1815 from October 24th–November 23rd of 2018), shown in Figure 1. The *Revelle* was equipped with the GEOTRACES CTD/rosette (Model 32G, Sea-Bird Electronics). This rosette contained 24 Teflon-coated 12 L GO-FLO bottles for trace metal clean sampling (Model 10812 T, General Oceanics) with sensors for dissolved oxygen, conductivity, chlorophyll fluorescence, pressure, beam transmittance, and temperature. These samples were preserved by filtering them through 0.2 μm Acropak-200 Supor capsule filter (Pall Corporation) and freezing them in 1 L Fluorinated Low-Density Polyethylene (Nalgene; FLPE) bottles. Sample bottles were acid-washed prior to RR1814 and RR1815 cruises according to the GEOTRACES cookbook (Cutter et al., 2017).

Surface samples were taken from the Columbia River in Oregon using a peristaltic pump with acid-washed C-flex tubing and a carboy (Figure 1). Samples were filtered with a Binder Free Glass Fiber Grade GF/D + 0.2 μm Supor filter membranes and frozen to preserve speciation. Total Cu measurements for these samples were also made by mass spectrometry. These samples served as end members for fluvial input.

3. Methods and Reagents

3.1. Measurement of Labile Cu

Labile Cu measurements were made using a solvent extraction methodology, described in Moriyasu and Moffett. (2022), and measured using the Thermo Element 2™ Inductively Coupled Plasma—Mass Spectrometer (ICP-MS). In this method, seawater samples are mixed with the organic solvent, methylbenzene (toluene; Sigma Aldrich; CAS #: 108-88-3) at a ratio of 4:5 solvent to seawater. Then, 500 μM of the strong Cu-binding ligand, 8-hydroxyquinoline (oxine; Sigma Aldrich; CAS# 148-24-3; ACS grade), is added. The labile portion of the Cu pool forms a nonpolar bis-complex with oxine, which partitions into the organic solvent layer during 6 hr on a shaker. The toluene is then physically separated from the seawater and evaporated on a hotplate. The labile Cu is then re-dissolved into 1 mL of 5% Optima grade nitric acid solution per replicate (HNO_3; Thermo Fisher; CAS# 7697-37-2) in 15 mL polypropylene Falcon tubes (VWR; Catalog #89049-172). These samples were then measured on the ICP-MS using isotope dilution. All chemistry involving toluene and heating was done in 15 mL Standard Teflon Vials with rounded interiors (Savillex; Catalog #200-015-20) with 33 mm PFA Closures (Savillex: Catalog #600-033-01) and 7 mL Standard Teflon Vials with flat interiors (Savillex: Catalog #200-007-10) with 24 mm PFA Closures (Savillex: Catalog #600-024-01) as typical trace metal clean polypropylene tubes are permeable to toluene and not resistant to heat.

3.2. Measurement of Total Cu

Total Cu measurements for GEOTRACES GP15 were adapted from a method from Rapp et al. (2017). Samples were acidified to a pH of 1.7, and concentrated Optima ™ grade hydrogen peroxide (Fisher; H_2O_2; CAS#: 7722-84-1) was added to treat for organic interference, according to the methods of Baconnais et al. (2019). The sample was then pre-concentrated using the SC-DX seaFAST (Elemental Scientific; M-SFS2-MG-52) automated pre-concentration solid phase extraction columns and measured on the ICP-MS at medium resolution.

3.3. Photodecomposition Experiment

Two GEOTRACES samples from station 8 of GP15 (47.0°N, 152.0°W) were placed within quartz flasks with stoppers, and exposed to natural sunlight at 30°N, 118.3°W from 7–14 February 2022. The depths chosen were 2,100 and 5,000 m. These samples were chosen since they were mid and deep water samples that were unlikely to have been exposed to sunlight prior to collection and contained a high fraction of inert Cu. The weather was projected to be sunny, and it was thought to be an ideal week to conduct an experiment on the destruction of inert Cu (Table 2). After a week, samples went through the solvent-extraction protocol described in Moriyasu and Moffett (2022).

4. Results

The GP15 transect, summarized in Figure 2, can largely be divided into groupings of shelf stations and main transect stations. Most of the water column throughout the transect was dominated by inert Cu. At almost all stations, we observed maxima in the % labile Cu within the mixed layer (Figure 2e and Figures S1–S21 in Supporting Information S1). Within the mixed layer, the labile Cu as a percent of total dissolved Cu ranges between 30% and 40% while at most other depths on the transect, this value is typically between 10% or less of the total. While we observed a slight increase in the concentration of labile Cu with increasing depth, the total Cu concentrations also increased, resulting in an overall lower fraction of labile to total Cu (Figure 2e).

4.1. Stations Along the Main Transect

Depth profiles for 10 stations were taken along the cruise transect from 49.5°N, 152.0°W to 10.5°S, 152.0°W (see Figures S1–S14 in Supporting Information S1 for specific station numbers and coordinates). Total Cu increased linearly with depth (Figure 2b), as previously observed, and the labile fraction of Cu (% labile Cu) was high throughout the surface of the entire main transect (Figures 2a and 2e). At most stations, labile Cu was highest in the shallowest samples, decreased rapidly with depth and ranged between 30% and 40% of total Cu. The Cu pool between 1,000 and 4,000 m was made up mostly of the inert fraction.

At depths ≥4,000 m, labile Cu concentrations sharply increased. Additionally, the percent labile Cu is shown to increase to 15%–30% of total Cu compared to less than 10% labile Cu found between 1,000 and 4,000 m. Surprisingly, there was not a corresponding increase in total Cu near the seafloor. Thus, the sharp increase in labile Cu must be associated with a decrease in inert Cu.

A water mass analysis was completed for GP15 (Lawrence et al., 2022). None of the spatial trends in Cu speciation conformed to water mass boundaries identified in that paper. However, the penetration of shallow water

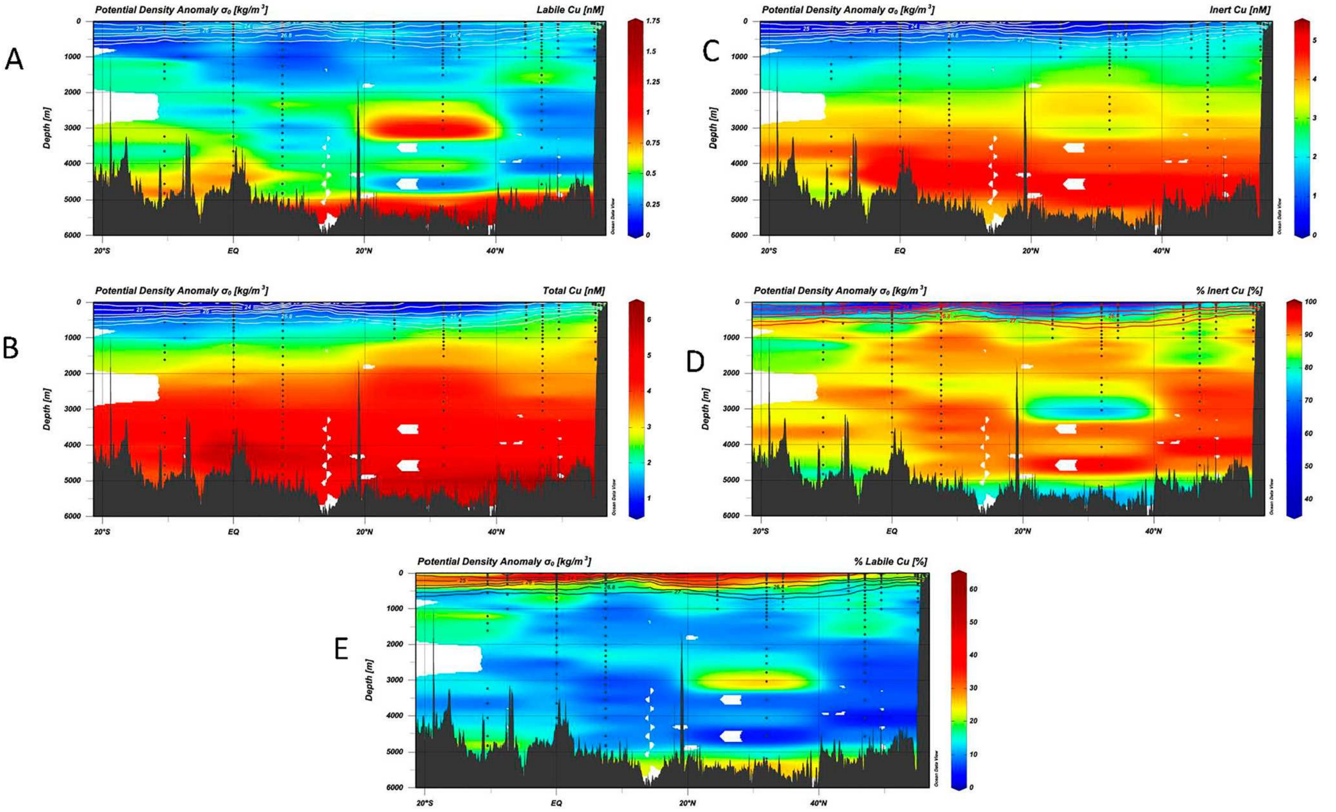

Figure 2. (a–e). The distributions of labile, total, inert, percent inert, and percent labile Cu along the GP15 transect from station 7 to station 35 (49.5°N, 152.0°W to −10.5°N, 152.0°W).

containing elevated fractions of labile Cu throughout the transect was constrained by the $\sigma_\theta = 26.8$ isopycnal. The significance of this observation will be explored in the discussion. There was one measured mid-depth maximum in labile Cu concentration at station 14 (32°N, 152.0°W), centered around a depth of 3,000 m. This may be associated with Pacific Deep Water, but we have no explanation as to why there was no mid-depth maximum at station 8 (47.0°N, 152.0°W). The stations occupied between these two stations only sampled to a depth of 1,200 m.

4.2. Stations Along the Alaskan Shelf

Samples were taken across the Alaskan shelf at stations 1–4 (Figure 3). The deepest sample was at 1595 m from station 3 (55.1°N, 155.7°W). Total Cu (Figure 3b) was elevated at the station closest to shore (station 1), reaching concentrations ≥4 nM near the surface, which were 90% inert. Labile Cu was greater at station 2 than 1 (Figures S1 and S2 in Supporting Information S1), possibly reflecting a source of labile Cu from shelf sediments or suspended particles in the region (Turner et al., 2017). The rest of the shelf stations had similar values for % labile Cu at the surface comparable to the rest of the transect.

4.3. Stations From the North Atlantic GEOTRACES GA03 Transect

Samples from five stations (3, 14, 16, 18, and 22) of the GEOTRACES GA03 transect from our frozen archive were measured for Cu lability. Details regarding sampling and preservation are reported in Jacquot and Moffett (2015). Cu speciation in that work was unaffected by several years of storage at −20°C and we assume that no deterioration occurred in the subsequent 8 years interval. Results are summarized in Figure 4 and full station data are shown in the Figures S15–S19 in Supporting Information S1. While constrained by the modest numbers of samples remaining in the archive, several important observations emerge. The highest values of percent labile Cu are within the mixed layer in both oceans. Percent Labile Cu was higher below the euphotic zone in the Atlantic than in the North Pacific, particularly between 300 and 1,500 m. The labile fraction at all stations of GA03

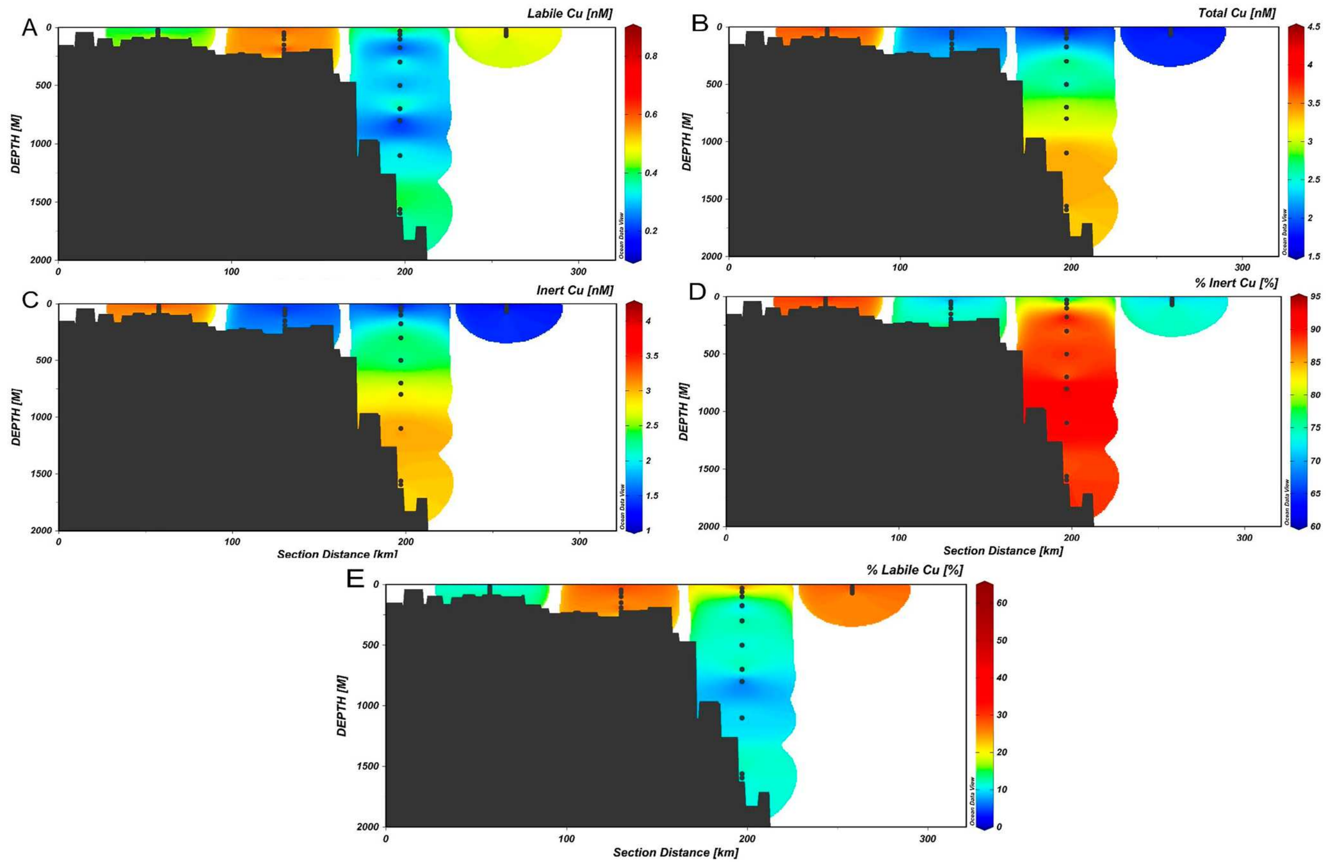

Figure 3. (a–e). Labile, total, inert, percent inert, and percent labile Cu transect profiles for stations 1–4 that were sampled along the Alaskan Shelf.

ranged from 15% to 50% throughout the water column and never fell below 10% even at intermediate depths (2,000–4,000 m), in contrast to all of the stations in the Pacific.

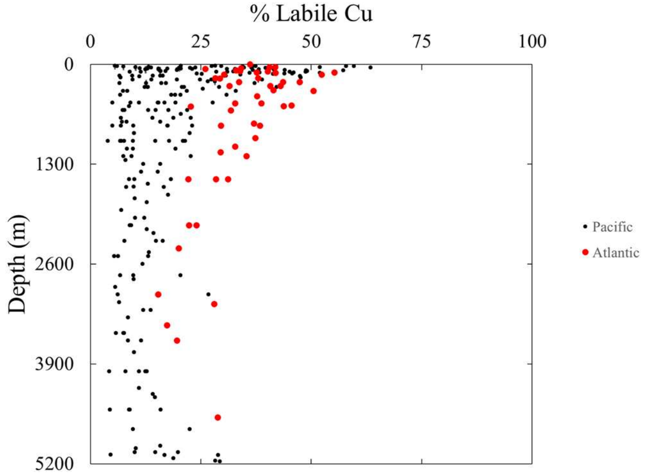

Figure 4. Percent labile Cu (% Labile Cu) by depth of the Pacific (GP15) versus the Atlantic (GA03).

4.4. Stations From the Columbia River

Four samples were taken from the Columbia River outflow on the coast of Oregon on the 28th of September 2021 (46.15°N, 123.59°W to 46.13°N, 123.44°W). These samples were reported in this study to assess the potential for fluvial sources of inert Cu. The Columbia River was chosen since it is one of the largest riverine sources in the Northeast Pacific Ocean. The salinities at all four locations were all less than 1 PSU. Cu species for these samples are reported in Table 1. The fraction of labile Cu in all of these samples was ≤8% of the total, with the highest labile Cu being found at the location closest to the Pacific (46.25°N, 123.99°W).

4.5. Photochemical Decomposition of Inert Cu

Moriyasu and Moffett (2022) showed that inert Cu becomes solvent extractable after 2 hr of exposure under a UV-lamp. From these results and the observed surface maxima of labile Cu, it is plausible that the compounds comprising inert Cu undergo photo-decomposition. This hypothesis was tested by leaving two GEOTRACES samples from station 8 (47.0°N,

Table 1

Samples Taken Along the Columbia River and Respective Cu Species Concentrations

Sample #[a]	Lat. (°N)	Long. (°W)	Labile Cu (nM)	Total Cu (nM)	Inert Cu (nM)	% labile[b]	% inert[c]
1	46.25	123.99	0.49 ± 0.05	6.40 ± 0.01	5.92 ± 0.05	7.60 ± 0.7	92.4 ± 0.8
2	46.20	123.93	0.27 ± 0.04	6.90 ± 0.01	6.62 ± 0.04	0 ± 0.6	96.0 ± 0.6
3	46.19	123.88	0.39 ± 0.01	6.57 ± 0.01	6.18 ± 0.01	5.9 ± 0.1	94.0 ± 0.3
4	46.23	123.74	0.20 ± 0.03	8.02 ± 0.01	7.83 ± 0.04	2.47 ± 0.4	97.5 ± 0.5

Note. All samples were taken from the surface using a peristaltic pump. Errors were estimated by standard deviation within 2 confidence intervals.

[a] Sample # is independent of GEOTRACES sample numbering. Please refer to Figure 1 for locations. [b] % Labile refers to the concentration of labile Cu as a percent of total Cu concentration. [c] % Inert refers to the concentration of inert Cu as a percent of total Cu concentration.

152.0°W) in quartz flasks and exposing them to sunlight. Flasks were immersed in a bath where the water temperature was approximately 22°C. Results of this experiment are reported in Table 2.

After 1 week of exposure to UV radiation from sunlight, ≥95%, of inert Cu becomes labile by our method (Table 2). This supports the theory that photo-decomposition of Cu binding compounds in near-surface waters is one potential source of labile Cu. The results are consistent with previous studies showing that Cu complexes undergo photodecomposition in sunlight (Laglera and van den Berg, 2006; Moffett et al., 1990; Sato et al., 2021). Most likely the light-induced reaction involves a mechanism such as a photochemical ligand to metal charge transfer reaction that results in the formation of Cu(I) (which re-oxidizes) and the irreversible oxidation of the ligand, which destroys or diminishes its binding strength (Moffett et al., 1990).

5. Discussion

5.1. Processes Influencing the Distribution of Dissolved Cu Between Inert and Labile Forms

The distribution of inert Cu and labile Cu on the GP15 transect leads us to propose a control of their partitioning by several processes summarized in Figure 5. Inert Cu dominates the inventory of dissolved Cu throughout most of the water column. Only in stratified surface waters does the concentration of labile Cu reach comparable values. This feature is attributed to photochemical decomposition of inert Cu, resulting in a redistribution of Cu amongst labile complexes. Labile Cu is available for biological uptake and adsorption onto sinking particles, resulting in vertical transport. Remineralization and reversible scavenging result in low steady state concentrations of labile Cu throughout the water column. Subduction of surface waters enriched in labile Cu, such as North Atlantic Deep Water (NADW), may also contribute to the labile pool in deeper waters, but we will argue below that this is probably secondary compared with reversible scavenging.

Labile Cu has the highest fraction in two distinct places: the surface and benthic layers. Both sources of labile Cu, benthic and surface, are ubiquitous throughout the transect and are likely associated with local processes. The mixed layer maxima of percent labile Cu found in the Atlantic and Pacific Oceans are not associated with

Table 2

Decomposition of Inert Cu by Natural UV Radiation

G#[a]	Depth (m)	$[Cu]_{labile}$ (nM)[b]	Post UV-ox. Cu (nM)[c]	$[Cu]_{Total}$ (nM)[d]	% labile	% inert	% recovered[e]
12919	5050	1.24 ± 0.04	6.03 ± 0.02	6.23 ± 0.01	10.3 ± 0.3	80.1 ± 0.3	96.8
12971	2100	0.32 ± 0.02	3.12 ± 0.02	3.280 ± 0.01	9.0 ± 0.4	91.0 ± 0.2	95.1

Note. Samples were left at 34.0°N, 118.3°W for the span of 1 week in February of 2022. Both samples were taken from Station 8 of GP15 (47.0°N, 152.0°W). Errors are represented by standard deviations with 2 confidence intervals.

[a] Refers to GEOTRACES Sample ID number. [b] Initial labile Cu fraction before exposure to sunlight. [c] Labile Cu after exposure to sunlight on the roof of the Ahmanson Center for Biology, University of Southern California (34.0°N, 118.3°W) from 4 to 17 February 2022. [d] $[Cu]_{Total}$ obtained the following protocol by Rapp et al. (2017) and Baconnais et al. (2019). [e] A % Recovered when comparing Cu measured post-UV oxidation of ligands and total measured.

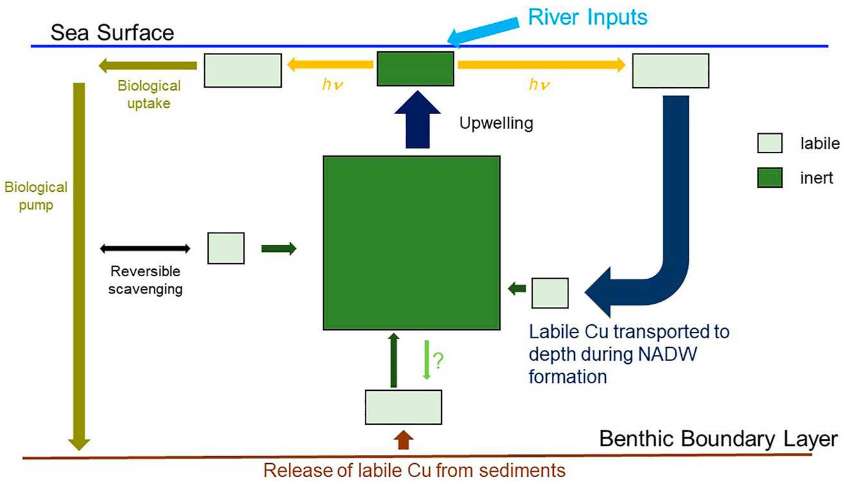

Figure 5. Summary of major processes controlling the transformation of copper between labile and inert forms. Photochemical (hν) conversion of inert to labile Cu in surface waters; Removal of labile Cu from surface waters associated with biological uptake and the biological pump, and subduction such as North Atlantic Deep Water (NADW) Formation (NADW). Reversible scavenging maintains a small steady state concentration of labile Cu throughout the deep water column. Dark green arrows represent the conversion of labile Cu to inert Cu within the ocean interior by processes that are slow but faster than the timescale of general ocean circulation - based on differences in Pacific and Atlantic deep waters. Rivers supply inert Cu to surface waters, while abyssal sediments supply labile Cu to the benthic boundary layer. There may be a process converting inert Cu to labile Cu near the seafloor, indicated by the question mark.

an increase in total dissolved Cu. Most likely, these maxima arise from the internal conversion of inert to labile Cu via photochemical processes. The accumulation of labile Cu is most pronounced in the permanently stratified sub-tropical stations. Surface maxima in labile Cu were less well defined at stations north of 40°N (Figure 2). This trend suggests that the turnover time of inert Cu to labile Cu by photodecomposition is probably slower than the timescales of seasonal mixing, which injects inert Cu into surface waters during winter at high latitudes. While photodecomposition reaction rates might be rapid near the surface, they may decrease rapidly with depth due to light attenuation, leading to overall turnover rates that might extend beyond seasonal timescales. However, it is also possible that there is simply higher biological demand for labile Cu in the more productive higher latitude stations.

The simplest explanation for the increase in labile Cu near the seafloor is release from the oxidation of organic matter at the sediment water interface, as reported elsewhere (Boyle et al. (1977); Klinkhammer (1980)). However, since total dissolved Cu is unchanged, this would have to be offset by an accelerated removal process for inert Cu. That scenario—preferential scavenging of inert versus labile Cu—is at odds with our central paradigm of inert Cu stabilizing Cu in the water column. An alternative explanation is that there is some process localized very near the seafloor that is accelerating the exchange between labile and inert Cu. This process might explain why labile Cu decreases so quickly with distance from the seafloor. Whilst we can readily explain the surface feature through simple photochemical experiments, we have no obvious explanation for the appearance of labile Cu near the seafloor.

5.2. Timescales of Non-Light-Dependent-Inert Cu Turnover

Our data show that there is no exchange between inert Cu and oxine on timescales of up to 3 weeks. However, our experiments were conducted with an exceedingly high concentration of a strong, low molecular weight synthetic chelator, which accelerates dissociation by attacking the metal complex. A good analogy is the accelerated removal of Zn^{2+} from proteins using dipicolinic acid, which accelerates metal removal by several orders of magnitude (Hunt et al., 1977). Simple unassisted dissociation of Cu is probably orders of magnitude lower.

It is reasonable to assume that the rate limiting step in the conversion of inert to labile Cu is not dissociation or coordination exchange but decomposition of organic matter binding Cu. In this case, turnover rates in the absence of light might be more comparable to refractory dissolved organic matter, leading to estimates of inert Cu lifetimes of centuries or longer. Interestingly, photochemical oxidation is thought to be a major sink for dissolved organic matter as well (Mopper et al., 2015).

The conversion of labile Cu into inert Cu within the ocean is presumably a slow process. The data from the transect shows that the $\sigma_\theta = 26.8$ isopycnal is an important boundary between the upper water column, where the %labile Cu is high and variable, and the deep water where values are lower (mostly 10% or less) and uniform. The $\sigma_\theta = 26.8$ isopycnal is the shallowest density that does not outcrop anywhere in the basin and defines an abrupt drop-off in tritium-helium-3 and chlorofluorocarbon tracers of ventilation (Fine et al., 2017; Jenkins, 2023 Figure S21 in Supporting Information S1). The tritium ages at this isopycnal are around 50 years—the upper range of that tracer. This suggests that the conversion of labile to inert Cu may occur on multi-decadal timescales. While there are some data shallower than 26.8 where %labile Cu is low, they may be influenced by the subduction of high latitude surface waters near the continental margin, where surface labile Cu is low.

If we assume that the rate of exchange between the labile and inert pools below the $\sigma_\theta = 26.8$ isopycnal is slow—perhaps comparable to the residence time of Cu, then labile Cu can be treated as a scavenged-type element such as aluminum, with surface sources (through photochemistry and aeolian deposition) and scavenging throughout the water column (Bruland & Lohan, 2003). Labile Cu should have a short residence time, similar to other scavenged elements, such as aluminum, which has a residence time of around 200 years (Orians & Bruland, 1985).

So far, we have assumed that inert Cu is only removed from the water column by conversion to a labile form and uptake onto sinking particles. An alternative removal process is the aggregation of colloids, so it is worth exploring whether inert Cu is colloidal. Kogut and Voelker (2003) made this case about the inert fraction they studied. Station 35 was a repeat occupation of GEOTRACES GP16 Station 36. On that cruise, colloidal Cu was measured. Roshan and Wu (2015) reported that about 39% of Cu was colloidal and 61% was dissolved throughout most of the water column below the euphotic zone. Since greater than 90% of the total dissolved Cu was inert, it must be comprised of both dissolved and colloidal fractions. Therefore, a secondary mechanism of Cu removal by aggregation of colloidal inert Cu is possible.

5.3. River Input and the Terrestrial Source of Inert Cu

Dissolved Cu in the Columbia River is overwhelmingly in the inert form. If this observation is typical of rivers, it suggests that the dominant fluvial source of Cu is in the inert fraction This observation is consistent with observations of high concentrations of inert Cu in coastal waters where salinity ranged from 12 to 28 PSU(Kogut & Voelker, 2003).

A fluvial source of inert Cu raises the intriguing possibility that a major source of inert Cu observed on the GP15 transect is terrestrial. Several reports from estuaries concluded that the majority of the Cu-binding compounds were terrestrially derived humic substances (Kogut & Voelker, 2001; Muller & Batchelli, 2013). Humic acids have lower binding constants than L_1-type ligands (Whitby et al., 2018) and are unlikely to account for inert Cu. But it is possible that other terrestrially derived organic matter that does not meet the operationally defined criteria of humic substances may be important in the formation of inert Cu.

The Columbia River is responsible for the input of approximately 2×10^{11} m^3 of water, and with it 4.9×10^{10} mol of organic carbon into the Pacific annually (Dahm et al., 1981). As such, the Columbia has a major impact on the waters in the Northeast Pacific, a large component of the GP15 transect. Previous studies have attributed riverine input to be the main source of Cu in the ocean (Bruland & Lohan, 2003). Fluvial inputs into the Sea of Okhotsk in the western margin might have similar chemistry. The influence of the Sea of Okhotsk extends far into the central basin and could influence our results.

There is an ongoing debate about the magnitude of fluvial sources of Cu worldwide, given its impact on the estimates of Cu residence times. Two models of the biogeochemical cycling of Cu (Little et al., 2014; Richon & Tagliabue, 2019) attribute rivers as the primary source. The mass balance by Little et al. (2014) attributes a Cu flux of approximately 0.6–0.8 Gmol/year while the Richon and Tagliabue (2019) attribute 6.7 Gmol/year. These discrepancies highlight how poorly Cu fluvial sources are understood in terms of both chemistry and fluxes. This difference in fluvial fluxes of Cu caused an order of magnitude difference in residence time between the two models. Historically, the paradigm has been that Cu has a long residence time of around 5,000 years (Boyle et al., 1977) since dissolved Cu concentrations increased linearly with salinity, which would agree with the model of Little et al. (2014). The large fluvial flux estimates by Richon and Tagliabue (2019) results in a residence time of only 400–500 years. They assumed that Cu fluxes could be normalized to Fe fluxes, which in a previous model had been normalized to dissolved inorganic carbon in rivers derived from various databases, leading to

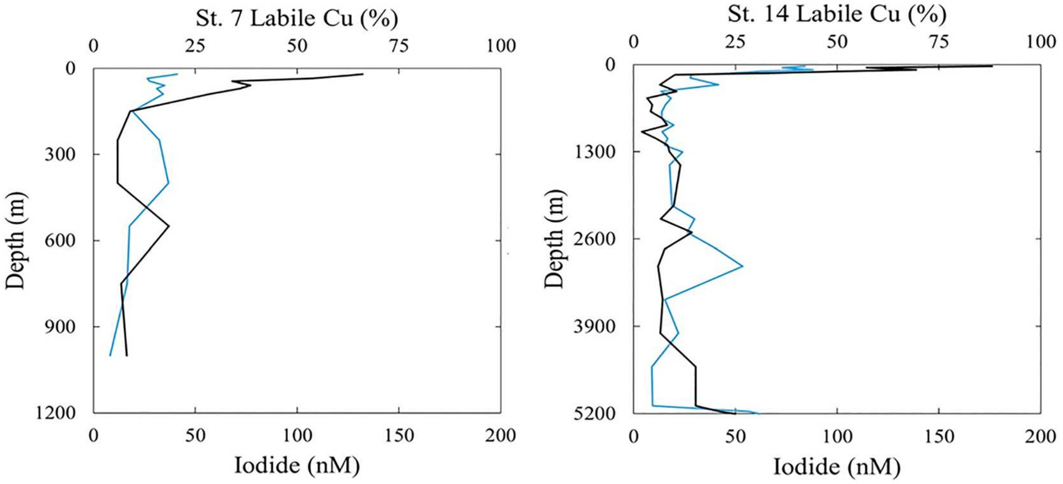

Figure 6. Depth profiles of % labile Cu(green) and iodide(black) at Sta. 7 (a) and Sta. 14 (b).

the large estimates. Moffett (2019) argued that this approach was questionable because other databases show that Fe and Cu do not correlate well. In order to assess how inert Cu may influence this debate, we must find out whether inert Cu is conservative across the salinity gradient in the outflow of the Columbia River, or is removed by flocculation along with most terrestrial organic matter and dissolved iron. This could be addressed by further observations along with flocculation process studies.

5.4. Contrasting Behavior of Labile Cu on the GA03 Atlantic and GP15 Pacific Sections

Compared to the Pacific, the general trend seen in the North Atlantic was higher labile Cu fractions at all depths (Figure 4). Since we have shown that labile Cu is higher in the more ventilated waters of the North Pacific above the $\sigma_\theta = 26.8$ isopycnal (Jenkins et al., 2019), one might expect that NADW Formation carries labile Cu to greater depths on the GA03 transect compared to the GP15 transect. Indeed, tritium/helium-3 age data for GA03 (Figure S20 in Supporting Information S1, from Jenkins, Lott, et al. (2015)) shows substantial penetration of NADW on the western end of the transect, where high labile Cu was reported throughout the water column. However, labile Cu displayed similar high values in deep waters in the central and western stations, which were well below the influence of NADW. An alternative explanation for the higher values of labile Cu in GAO3 compared with GP15 is the much higher atmospheric deposition of Cu to the North Atlantic compared with the Pacific from natural and anthropogenic sources (Paytan et al., 2009). This may increase the concentration of Cu on sinking particles, which might elevate the steady state levels of labile Cu at depth arising from reversible exchange (Figure 5).

There are only two stations in GA03 with data near the seafloor: Station 22 and Station 3. In each case, there is a strong increase in labile Cu that can only partially be accounted for by an increase in total Cu. This increase may reflect local processes occurring at both stations, or transport from elsewhere. At Station 22, the deepest samples are embedded within the Iceland Scotland Overflow Water, whilst at shallower Station 3, the deepest sample contains a mixture of Denmark Overflow water and Iceland Scotland Water (Jenkins, Smethie, et al., 2015). It is possible that the elevated labile Cu and slightly diminished inert Cu reflect processes associated with the origin of those water masses.

5.5. Comparative Distributions of Labile Cu and Iodide on GP15

The distribution of labile Cu in surface waters on the cruise track is similar to iodide (Moriyasu et al., 2023). Iodide, like labile Cu, is produced in situ from light-dependent processes, and shows stronger mixed-layer accumulation in the permanently stratified sub-tropics than further north. At Sta. 14, the surface maxima are remarkably similar (Figure 6). However, at Sta 7, the iodide maximum is much more pronounced than the labile Cu maximum (Figure 6). Evidently, iodide accumulates more quickly in this seasonally stratified regime. The difference reflects the fact that each element is controlled by completely different light-dependent processes. Iodide is produced by phytoplankton-mediated reduction of iodate, and iodide re-oxidation is slow. Labile Cu photo-production is presumably independent of phytoplankton activity. However, Cu, unlike iodide, is readily taken up by phytoplankton, particularly iron-stressed diatoms that are characteristic of North Pacific surface waters (Maldonado et al., 2006). Therefore, labile Cu may have a shorter residence time in the North Pacific than in the oligotrophic sub-tropical waters like station 14, as we argued previously. Comparative modeling of the distribution of both elements may be extremely useful in the future as we learn more about the rate processes involved.

6. Conclusion

The predominance of inert Cu in the interior of the ocean basin requires a re-evaluation of our knowledge of Cu chemistry in seawater. It is not dominated by strong but labile complexes spanning a broad range of binding strengths. Rather, there is an abrupt transition between a kinetically labile fraction and an inert fraction that is unchanged by increasing the concentration of competing ligand or equilibration period. Previous studies assigning binding constants and ligand concentrations based on assumptions of labile complexes at equilibrium need to be evaluated, as argued in our previous study (Moriyasu and Moffett 2022). The distribution of inert Cu revealed by the study may help explain existing observations about Cu geochemistry. For instance, the large fraction of inert Cu in deep waters can help account for the linear increase with depth—in contrast with other elements that undergo scavenging, such as aluminum. Indeed, the distribution of the labile fraction actually does look similar to aluminum or other "scavenged" type elements. Scavenged elements are characterized by a surface source, such as dust. For labile Cu, the "source" is the release of inert Cu by a photochemical process. Throughout most of the water column below the euphotic zone, the chemistries of inert Cu and labile Cu may be largely decoupled. Near the seafloor, they appear to be connected with a modest but significant source of labile Cu from sediments that is consistent with several models of Cu cycling. This labile Cu appears to exchange with inert Cu by a mechanism we are unsure of, and it is not possible for us to fully assess its significance from our data alone.

Our data are consistent with the hypothesis of a reversible scavenging contribution to Cu cycling, which is included in recent models of Cu in the ocean (Cui & Gnanadesikan, 2022; Little et al., 2014; Richon & Tagliabue, 2019; Roshan et al., 2020). Our data also help explain a persistent question that is hard for such models to address. Why is there always a fairly high concentration of Cu in surface waters, even in areas where the biological demand for Cu is high? This can be explained by the persistence of inert Cu in the euphotic zone after most of the labile Cu has been drawn down. Photochemical degradation, rather than biological uptake, is the rate limiting step for Cu removal from the euphotic zone when biological demand is high.

Copper is an essential requirement for enzymes associated with iron transport in diatoms (Maldonado et al., 2006), nitrous oxide reduction by denitrifiers (Granger & Ward, 2003) and ammonia oxidation by archaea (Amin et al., 2013). Previous studies have shown that biologically available Cu is primarily the free cupric ion Cu^{2+} (Brand et al., 1986; Sunda & Huntsman, 1998). More recently, it has been proposed that chelators called chalkophores may enhance Cu bioavailability by exchanging Cu from naturally occurring labile complexes to form bioavailable ones (Dispirito et al., 2016). Both of these pathways are unlikely to be important for inert Cu, which, by our definition, is resistant to both ligand exchange and dissociation into the free cupric ion. Because labile Cu is frequently a small fraction of total dissolved Cu, the rates of these important processes might be constrained if the rate of labile Cu consumption exceeds its production.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

All data reported here are or will be available in a public repository - the Biological and Chemical Oceanography Data Management Office, available at (https://www.bco-dmo.org/dataset/777951 (Casciotti et al., 2020); https://www.bco-dmo.org/dataset/778168/data; https://www.bco-dmo.org/dataset/873193; https://www.bco-dmo.org/dataset/873183) (Moffett & Moriyasu, 2022); https://www.bco-dmo.org/dataset/885319; https://www.bco-dmo.org/dataset/885335 (Bian et al., 2022a, 2022b);(https://www.bco-dmo.org/dataset/862220; https://www.bco-dmo.org/dataset/862182 (Jenkins, 2023).

Acknowledgments

Sampling for this data set was made possible by the scientists and crew participating in the GEOTRACES GP15 cruise. We would also like to thank the crew of the R/V *Roger Revelle* who participated in the RR1814 and RR1815 cruises (the first and second legs of the GP15 transect). Funding for this project was made possible by the National Science Foundation, OCE-1756415, and awarded to James W. Moffett and OCE-1736896 to Seth G. John. Finally, the International GEOTRACES Program is possible, in part, thanks to the support from the U.S. National Science Foundation (Grant OCE-1840868) to the Scientific Committee on Oceanic Research (SCOR).

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