Review

Impacts of Aerosol Copper on Marine Phytoplankton: A Review

Tianjiao Yang [1], Ying Chen [1,2,*], Shengqian Zhou [1] and Haowen Li [1]

[1]   Shanghai Key Laboratory of Atmospheric Particle Pollution Prevention, Department of Environmental Science & Engineering, Fudan University Jiangwan Campus, Shanghai 200438, China

[2]   Institute of Eco-Chongming (SIEC), No.3663 Northern Zhongshan Road, Shanghai 200062, China

*   Correspondence: yingchen@fudan.edu.cn; Tel.: +86-21-31245497

check for
updates

Abstract: Atmospheric deposition brings both nutrients and toxic components to the surface ocean, resulting in important impacts on phytoplankton. Field and lab studies have been done on the iron (Fe) fertilization on marine phytoplankton. However, studies on other trace metals are limited. Both bioassay experiments and field observations have suggested that aerosols with high copper (Cu) concentrations can negatively affect the primary productivity and change phytoplankton community structure. Note that with increasing human activities and global environmental changes (e.g., ocean acidification, warming, deoxygenation, etc.), the input of aerosol Cu could exceed toxicity thresholds at certain times or in some sensitive oceanic regions. Here, we provide a comprehensive review on aerosol Cu and marine phytoplankton studies by summarizing (1) physiological effects and toxicity thresholds of Cu to various phytoplankton taxa, (2) interactions between Cu and other metals and major nutrients, and (3) global distribution of surface seawater Cu and atmospheric Cu. We suggest that studies on aerosols, seawater chemistry, and phytoplankton should be integrated for understanding the impacts of aerosol Cu on marine phytoplankton, and thereafter the air–sea interaction via biogeochemical processes.

Keywords: aerosol; Copper; speciation; marine phytoplankton; toxicity threshold

1. Introduction

Atmospheric deposition plays an important role in providing both nutrients and toxicants to the ocean ecosystem [1–4], particularly for the case of increasing sea surface temperature and stratification [5,6]. Studies about aerosol effects on marine phytoplankton have focused on natural aerosols, e.g., volcanic ash [7] and dust [8,9]. With the enhancement of anthropogenic activities, more chemical components are emitted and transported to oceans [10–12], modifying the seawater chemistry and affecting phytoplankton growth [2,7,13]. One of the representative chemicals emitted by human is copper (Cu). According to ice-core based assessments in the former Soviet Union, anthropogenic emissions of Cu showed a significant increase from the year 1935 and culminated in the 1970s (5300–8600 tons per year, briefly t yr^{-1}), which was mostly attributed to the development of non-ferrous metallurgy [14]. In China, the primary anthropogenic emission of Cu is still growing, rising up to 9548 t yr^{-1} in 2012, which is mainly from coal combustion, brake and tire wear, metal smelting, etc. (Figure 1) [15].
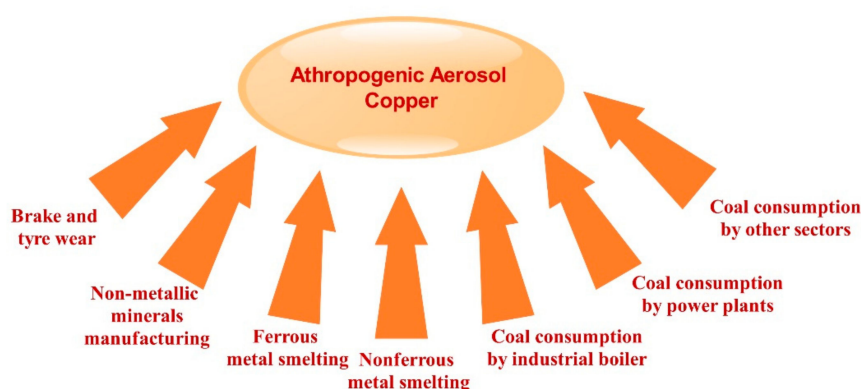
Figure 1. Anthropogenic sources of aerosol copper (Cu) in China (Data quoted from Tian et al. [15]).

Metal-containing aerosols exhibit profound impacts on ocean biogeochemistry and climate [16–19]. Dust transported to the high nutrient, low chlorophyll (HNLC) oceans could fertilize phytoplankton growth due to their supply of iron (Fe) [20]. Unlike Fe, Cu is a key metal for living organisms, which manifests positive and negative effects on marine phytoplankton at low and high concentrations, respectively [21,22]. Atmospheric deposition is one of the most important sources of external Cu to the ocean, and some studies have found that its flux is the same order of magnitude as fluxes from riverine input and upwelling waters [23]. Paytan et al. suggested that aerosols with high concentrations of Cu might inhibit phytoplankton growth, and that the responses varied across different phytoplankton taxa [10]. They also estimated the global distribution of atmospheric Cu fluxes via numerical simulations and pointed out two hot spots (the Bay of Bengal and small areas in the western Pacific, downwind of Asian industrial regions) for anthropogenic Cu deposition, though the solubility of Cu used in the model was questioned by Sholkovitz et al. [24]; the solubility can be affected by the source, transport pathway and physicochemical characters of aerosols [25,26]. Aerosol Cu toxicity to phytoplankton studied in the Sargasso Sea and the western Mediterranean Sea [4,6] further strengthened former results. The toxicity thresholds of Cu are distinct with different seawater chemistry and phytoplankton taxa [27]. In the East China Sea (ECS), soluble Cu and Fe were found to be the most significant predictors among components in atmospheric deposition responsible for changes in chlorophyll a [28]. However, the interaction of Cu with other components in the aerosol further complicates understanding the effect of Cu on plankton (Figure 2). Additionally, Cu's ions can outcompete lower complexing stability cations (e.g., zinc (Zn), manganese (Mn)) for organic ligands [29], which extends Cu's lifetime in the ocean by preventing particulate scavenging [30].

The main body of this review is organized as follows. The first subsection will talk about physiological functions and toxicity of Cu, including toxicity thresholds for different phytoplankton taxa. Interactions between Cu and other components, as well as their bioavailability, are briefly described in the following Sections 2.2 and 2.3. Then, information about the distribution and speciation of oceanic Cu are provided in Sections 2.4 and 2.5. The final two subsections point out the great contribution of atmospheric input to ocean Cu, and summarize the sources and characteristics of aerosol Cu. This integrated study of Cu behaviors in phytoplankton, aerosols, and seawater provide a comprehensive view of aerosol Cu impacts on marine phytoplankton.
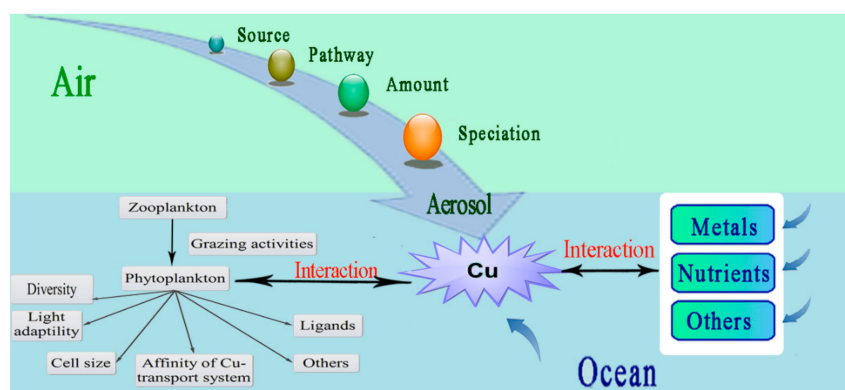
Figure 2. Factors affecting the Cu toxicity for marine phytoplankton.

2. Perspectives

Atmospheric deposition, hydrothermal vent, sediment, and riverine input are important sources of oceanic Cu (Figure 3). Surface ocean receives a large fraction of Cu from the atmosphere, especially during seasonal stratification [23,31,32]. When stratification occurs, nutrient supply from the depth decreases, and impacts of the same magnitude of atmospheric input can be amplified within the shallower mixed layer. The western Pacific Ocean and the southeast Indian Ocean receive aerosols with the highest dissolved Cu (See more information in Section 2.7). Although Cu is required as a co-factor in important enzymes of phytoplankton (Figure 3), high Cu may impede metabolic activities by substituting for other essential intracellular metals, interfering with cell permeability, and catalyzing the production of reactive oxygen species (ROS), etc. [33–35]. Phytoplankton respond differently to Cu concentrations, depending on their sizes, habitats, and light adaptability [27,35,36]. Copper toxicity to marine phytoplankton is also influenced by other metals (e.g., Fe) and nutrient status (e.g., nitrogen (N) limitation).
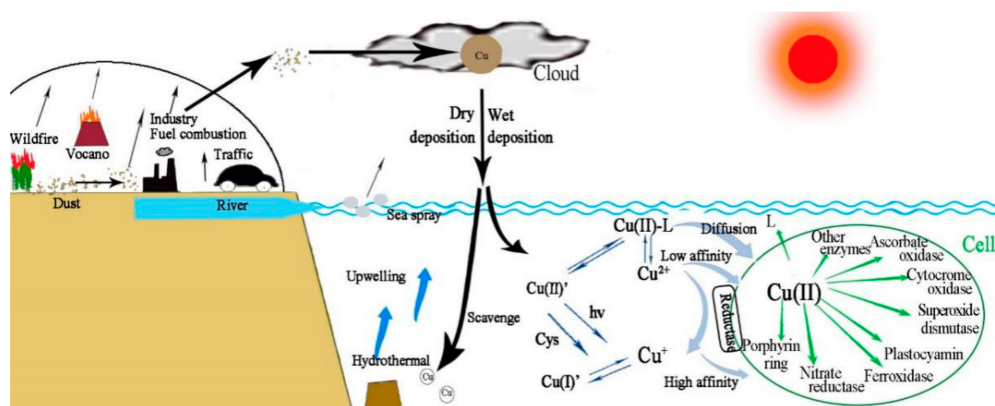

Figure 3. The scheme of Cu sources, transport, and transformation in marine ecosystems. Natural and anthropogenic sources of Cu, as well as their relative transport processes, are illustrated. The detailed description can be seen in relevant sections. After aerosol Cu is deposited into the seawater, some of it is scavenged, while some is taken up by phytoplankton. The uptake pathways are also shown as diffusion as well as low- and high-affinity transports in the figure.

2.1. Physiological Functions and Toxicity of Cu

Many biotic activities are related to cellular Cu concentrations, because Cu is required as a co-factor in important enzymes of phytoplankton [37], such as plastocyanin, cytochrome oxidase, ascorbate oxidase, superoxide dismutase (SOD), laccase, and ferroxidase (Figure 3). Plastocyanin is a kind of cuproprotein (proteins that are unable to substitute other metal ions for Cu) found in many cyanobacteria species, and is involved in the electron transport system in photosynthetic process [38].

Thus, Cu has an important effect on cyanobacteria growth. Cytochrome oxidase, with both Fe and Cu, is a terminal protein responsible for mitochondrial electron transport, reducing O_2 to H_2O [30]. Nitrate reductase, an essential reductive enzyme responsible for the conversion of NO_3^- into NH_4^+, is sensitively affected by Cu [39]. Nitrous oxide reductase also needs Cu in denitrification activity [40].

Nonetheless, high concentrations of Cu may interfere with (1) phytoplankton cell permeability; (2) uptake of nutrients and essential metals; (3) carbon fixation; (4) biosynthesis of lipids, cytochromes, and enzymes; and (5) impair chloroplast ultrastructure [33–35]. High concentrations of Cu may curb HCO_3^- intake by reducing carbonic anhydrate activities [34]. The xanthophyll cycle, which is mainly comprised of diadinoxanthin and diatoxanthin in diatoms, was reported to be vulnerable to high Cu concentration. The inversion of diadinoxanthin to diatoxanthin could be hindered by high Cu levels, resulting in a rise of the DT index (DT index refers to [diatoxanthin]/([diatoxanthin] + [diadinoxanthin])) [34]. Copper could also catalyze the production of reactive oxygen species [38,41]. Chlorophyll molecules could be destroyed when Cu^{2+} replaces Mg^{2+} in the porphyrin ring [34]. Transcription of photosynthesis-related genes decreased under Cu stress [36], and photosynthetic rates declined when Cu inhibited the first step of chlorophyll photosynthesis, accumulation, and function [42]. Under acute Cu stress, the major energy metabolic protein, ATP synthase, was inhibited in *Sargassum fusiforme*, while carbohydrate metabolism, protein destination, RNA degradation, and signaling regulation were induced [22]. Ritter et al. reported that proteins related to energy production (e.g., pentose phosphate pathway) accumulated at high Cu concentrations [43]. It should be noticed that acute stress of Cu seemed to increase phytoplankton reproduction rates in the short-term; however, these effects were more likely due to hormesis rather than any evidence for Cu limitation [27,44].

Phytoplankton respond differently to Cu concentrations. Smaller phytoplankton are less tolerant to Cu, as they have large surface area to volume ratios and thereby possibly faster uptake rates [27,35]. In general, cyanobacteria are very sensitive to Cu additions, while diatoms are the least sensitive [27,45]. For example, the abundance of *Skeletonema costatum* dominates over *Synechococcus* when free Cu^{2+} concentration is up to 100 pM [46]. However, Levy et al. noted that cell size may not be related to Cu sensitivity [47]; in Fe-limited situations, the larger phytoplankton (>5 μm) may be more susceptible to Cu toxicity [48]. Researchers also found that the Cu tolerance of phytoplankton was higher in coastal regions than in offshore and open oceans [34,49]. In the East China Sea, chlorophyll a increased and decreased with enhanced Cu deposition in coastal and remote areas, respectively [28]. On the Visakhapatnam coast (coastal embayment of the Bay of Bengal), mesocosm experiments showed that Cu (5, 10, 25, and 50 nM) first hindered, then stimulated phytoplankton growth, suggesting that coastal phytoplankton had potentially high Cu tolerance [34]. Under excess Cu stress, both coastal and open-ocean *Synechococcus* reduce their photosynthesis-related gene transcripts; coastal strains demonstrate higher metal and oxidative adaptation, whilst open ocean strains show a general stress response in their activated genes [36]. Some phytoplankton produce polyphenols and exudates against Cu. For example, the green algae *Dunaliella tertiolecta* produces phenolic compounds (e.g., gentisic acid, (+) catechin and (−) epicatechin) under Cu stress, which can lower the solubility and bioavailability of Cu [50]. Light adaptability is also an important factor affecting Cu tolerance, and high-light-adapted species are more resistant to toxic Cu than low-light-adapted ones [35].

Toxicity thresholds of Cu for different phytoplankton taxa are listed in Table 1. Several parameters have been chosen for assessing Cu toxicity. Hall et al. suggested that growth rate was the most sensitive toxicity indicator in N-limited cultures [51], whereas final yield ranked the most susceptible in P-limited cultures. Some studies have shown that final yield and growth rate decrease but cell size increases with increasing Cu concentrations [35,52,53], possibly owing to the uncoupling between photosynthesis and cell division, resulting in the continuous accumulation of carbon fixation within the cell and mediation of membrane [51,53]. Copper may also affect phytoplankton by weakening the grazing activities of zooplankton (e.g., ciliate) [21,54]. However, grazers such as copepods have different sensitivity to Cu at different life stages [55], and the combined impacts of grazing activities and Cu addition on phytoplankton remain uncertain.

Table 1. Toxicity thresholds of Cu for different phytoplankton taxa.

Phytoplankton	Threshold	Speciation	Indicator	Reference
Pyrrophyta	**(nM)**			
Gonyaulax tamarensis	0.0001	Cu^{2+} ions	Inhibited growth	[56]
Peridinium sp. (A1572)	0.001	Cu^{2+} ions	Reduced reproduction rates	[27]
Prorocentrum sp. (R1568)	0.001	Cu^{2+} ions	Reduced reproduction rates	[27]
Gonyaulax tamarensis	0.04	Cu^{2+} ions	50% nonmotile	[57]
Gonyaulax tamarensis	0.2	Cu^{2+} ions	100% nonmotile	[57]
Cyanobacteria	**(nM)**			
Cyanobacteria	0.001	Cu^{2+} ions	Reduced reproduction rates	[27]
Synechococcus bacilaris	0.003	Cu^{2+} ions	50% inhibition of reproduction rate	[27]
Synchrococcus	0.112	Cu^{2+} ions	Reduced cell division rate	[35]
Synechrococcus (Red sea)	0.2-2*	Total Cu	Impaired cell growth	[10]
Bacillariophyta	**(µM)**			
Asterionella glacialis	0.1	Cu^{2+} ions	Dead	[27]
Bacteriastrum delicatulum	0.1	Cu^{2+} ions	Dead	[27]
Hentiuulus sinensi	0.1	Cu^{2+} ions	Dead	[27]
Rhizosolenia setigera	0.1	Cu^{2+} ions	Dead	[27]
Thalassiosira oceanica (Bering Sea)	0.001	Dissolved Cu	unable to grow	[49]
Thalassiosira sp. (Adriatic Sea)	0.31–0.78	Dissolved Cu	Inhibited growth	[58]
Thalassiosira decipiens (SW Bay)	1.00	Dissolved Cu	Abundance	[34]
Phaeodactylum tricornutum	1.6	Dissolved Cu	50% growth reduction	[59]
	15.7	Dissolved Cu	Inhibited growth	[59]
Cylindrotheca closterium (Adriatic Sea)	3.13–7.81	Dissolved Cu	Inhibited growth	[58]
Achnanthes brevipes	3.13–7.81	Dissolved Cu	Inhibited growth	[58]
Skeleonema costatum	0.0002	Cu^{2+} ions	Cell division rates reduced	[27]
Chlorophyta	**(µM)**			
Chlorella pyrenoidosa	4.13	Dissolved Cu	Biosorption capacities	[60]
Chlamydomonas geitleri Ettl	10	Cu^{2+} ions	50% reduction in growth rate	[51]
Chlorella vulgaris Beyerinck	10	Cu^{2+} ions	50% reduction in growth rate	[51]
Ochrophyta	**(µM)**			
Ectocarpus siliculosus (Southern Peru)	0.78	Dissolved Cu	Chlorophyll drop to 70% of chlorophyll autofluorescence	[43]
Ectocarpus siliculosus (Northern Chile)	3.91	Dissolved Cu	Chlorophyll decay of cell-autofluorescence	[43]
Haptophyta	**(µM)**			
Hymenomonus corterae	0.0007	Cu^{2+} ions	Dead	[27]
Emiliania huxleyi	0.3	Dissolved Cu	Inhibited growth	[33]
Emiliania huxleyi (Mediterranean strain)	0.32	Dissolved Cu	EC50	[33]
Gephyrocapsa oceanica	0.4	Dissolved Cu	EC50	[33]

Note: * Units: mg Cu/mg Chl a.

2.2. Interactions between Cu and Other Metals and Nutrients

Copper toxicity may be affected by other metals. Researchers have found a co-limitation of growth by Cu and Fe in phytoplankton [21,34,49]. Under Fe-limiting conditions, some phytoplankton increase Cu uptake and use plastocyanin, Cu/ZnX–SOD, and others as a substitute for Fe-containing enzymes (e.g., cytochrome c6 and Fe-SOD, [54,61]). In the N cycle, Fe and Cu can be incorporated into enzymes and interchangeably used for ammonium oxidation and denitrification [62]. In this case, Fe additions may reduce Cu toxicity [28]. Indeed *Thalassiosira oceanica* relies solely on the Cu-containing plastocyanin, instead of the Fe-containing cytochrome c_6; the photosynthesis rates of *T. oceanica* are hindered under low Cu, and when Cu hindered cells are exposed to 10 nmol L^{-1} Cu, their Fe uptake rates are enhanced by 1.5-fold [49,61]. Maldonano et al. also found that Fe uptake

rates closely depended on Cu availability in Fe-limited *T. oceanica*, and Fe transport improved with Cu addition, indicating that the inducible Fe transport system was consisted of multiple Cu oxidases [63]. The Cu-dependent upregulation of the high-affinity Fe uptake system was also reported by Annett et al. [64]. Both oceanic and coastal *Thalassiosira* showed obvious enhancement in Cu demands under Fe limitation. Semeniuk et al. suggested that larger Fe-limited phytoplankton were more susceptible to Cu limitation and the complex interaction between Fe and Cu was also related to grazing pressure and light [48].

Researchers found that Zn and Cu also have an interactive influence on the silicic acid uptake by *Thalassiosira pseudonana,* showing as a Zn-dependent system for silicic acid uptake that is inactivated by Cu [65]. Zn and Nickel (Ni) can be part of the SOD enzyme alleviating the demand for Cu [30]. Cupric ion and Mn^{2+} show competitive interaction on the cellular growth of *Thalassiosira*, and Cu can competitively hinder the cellular Mn^{2+} uptake or binding [66].

Nutrient status is an important determinant of phytoplankton tolerance to Cu toxicity [3,67]. Phosphate bodies may act as sites for complexing and detoxifying Cu, and thereby Cu toxicity imparts a high demand for phosphorus (P) and results in P limitation [51]. Hall et al. suggested that phytoplankton were more Cu sensitive in P-limited conditions than in N-limited cells [68]. Under high Cu concentrations, inhibition on NO_3^- uptake and synthesis of nitrate reductase were observed [39]. Rijstenbil et al. argued that more Cu accumulation took place under N-enriched treatment, probably owing to impaired metal exclusion/elimination mechanisms [69]. In the South Pacific, the distribution of dissolved Cu was tightly correlated with SiO_4^{4-} in the upper 1500 m, implied the link between Cu and silicon (Si) uptake by diatoms [70].

2.3. Bioavailability and Uptake of Cu

Copper quotas in phytoplankton vary among taxa and oceanic regions. In general, the metal abundance ranking in phytoplankton follows Fe ≈ Zn > Mn ≈ Ni ≈ Cu ≈ cobalt (Co) ≈ cadmium (Cd), with Cu cellular concentration approximately 2–5 fold less than Fe [37]. Field observations of 3.5 [71], 3.8–17.9 [72,73], 1.3–4.2 [74], 27–30 (different size fractions) [75], and 13.6 (particulate Cu > 0.45 μm) [76] μmol Cu per mol C have been reported in North Atlantic plankton, North Atlantic *Trichodesmium*, northeast Pacific Ocean plankton assemblages, northeast subarctic Pacific Ocean, and Southern Ocean diatoms, respectively, which are comparable to 0.3–6.3 [64], 1.5 [72], and 0.04–6.2 μmol Cu per mol C [77] found in the lab experiments. Anthropogenic aerosol deposition may increase cellular Cu concentrations, with different-sized phytoplankton responding differently [78].

The speciation of Cu determines its bioavailability to phytoplankton. Previous studies have reported that low-molecular-weight lipophilic Cu and inorganic Cu species are available for uptake [79,80], and that free Cu ions can be absorbed directly by phytoplankton [27,81]. Copper ions are more competitive for transport sites, compared to other metals that have a lower tendency to form complexes, e.g., Fe, Zn, Mn, and Co [29,33]. High-affinity biogenic chelates alter Cu solubility and speciation, and have all been hypothesized to be Cu detoxification in the early studies [30,82,83]. However, recent studies have found that Cu bound to strong L_1 ligands could be acquired by cyanobacteria [84]. Walsh et al. reported cysteine-enhanced Cu bioavailability in Cu-limiting *Emiliania huxleyi* via cysteine-mediated reduction of Cu (II) to Cu (I) [85]. The purpose of biogenic ligand production requires further study.

There are three types of uptake (Figure 3), including diffusion and low- and high-affinity transports. The lipophilic ligands bind Cu, and neutrally charged chloro-complexes can be assimilated by diffusion [80,81]. Under high Cu concentrations, Cu^{2+} ions can pass through low-affinity transporters for uptake [86,87]. High-affinity Cu transport is usually related to the transformation of Cu(II) to Cu(I), assisted by cell membrane reductase and a photochemical process [88], as well as by cysteine-mediated reduction [85]. The mechanisms of Cu uptake seem to be different in prokaryotic and eukaryotic phytoplankton [84].

The adsorption of Cu on the cell surface is an important process that occurs rapidly (reaching a plateau in about 40 min) before cellular uptake or internalization. [47,89,90]. Most of surface adsorptions are non-specific binding—for example, the binding of Cu with carboxylic, sulfhydryl,

and phosphate groups, and other metals can also compete with Cu for these sites [47,89]. Although adsorption is non-discriminatory to cell wall type [47], cells with a mucilaginous surface bind relatively high amounts of Cu [91]. Since pH can largely affect the chemical speciation,, as well as surface sites, it plays an important role in affecting adsorption [90]. Gonzalez-Davila et al. observed adsorption of Cu in *Phaeodactylum tricornutum* only when the pH was over 4, and pH became less effective for Cu adsorption when greater than 7 [90]. Salinity can also influence the adsorption via surface charge, double-layer capacitance, and the activities of metal ions [92]. However, most of these studies were conducted under a high level of Cu addition, which was not representative of the real environment. Further studies should be developed to mimic real scenarios by using nM levels of Cu in seawater in order to improve our understanding.

2.4. Distribution of Dissolved Cu in the Ocean

The global distribution of dissolved Cu in surface seawater is shown in Figure 4. Cu concentration exhibits spatial variation, showing relatively high and low values in coastal and remote oceans, respectively, which is probably associated with upwelling [6,93], currents [94], or mesoscale eddies [95]. In some coastal areas, heavy rain may cause a sudden increase of Cu in the surface water [96]. Posacka et al. investigated the dynamic variability of dissolved Cu in the subarctic northeast Pacific during the years 2010–2012, and indicated that subsurface Cu concentration increased due to atmospheric deposition [95]. High concentrations of dissolved Cu were found in the Mediterranean Sea, East China Sea, and northeast Pacific surface seawater. Among these, some coastal areas of the Mediterranean Sea suffered from ambient industrial contamination (e.g., acid mine drainage [97]), resulting very high Cu concentrations compared to other coastal places. In the surface ocean, the lowest concentrations occur in the Atlantic and Pacific gyres, while relatively high values are found at high latitudes (Figure 4). The distribution of dissolved Cu in seawater also exhibits seasonal variability, due to seasonal cycles of stratification and upwelling. In the Gulf of Aqaba, dissolved Cu shows a slight surface enrichment in August and September, probably due to both stratification and dust storms from the Sahara Desert [30,98]. Additionally, Cu concentration may increase significantly in coastal areas with enhanced anthropogenic activities (e.g., shipping) in the summer [94,99]. The residence time of Cu was about thousand years for all the oceans (Box 1).
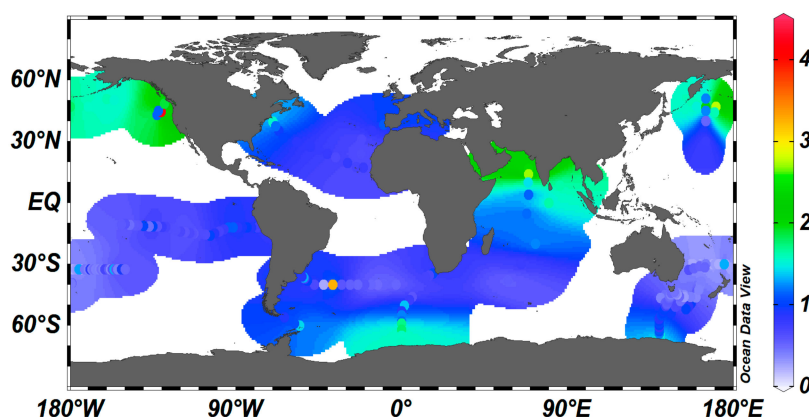

Figure 4. Dissolved Cu in surface seawater. The color bar refers to the concentration of dissolved Cu in the unit of nmol kg^{-1}. Data source: Schlitzer et al. [100]. Map was produced using Ocean Data View (Schlitzer, R., Ocean Data View, odv.awi.de, 2017). The spatial extent of the interpolation is ~800 km.

Box 1. Residence Time of Cu.

A typical removal process for metals from the mixed layer is particulate scavenging. Particulate transport was estimated to be 2.2×10^5 t yr-1 of dissolved Cu from surface to deep ocean [23]. Chen et al. estimated that the dissolved Cu from atmospheric deposition had the residence time of 32 years in the surface 50 m of the Gulf of Aqaba [101]. Atmospheric input of Cu to the Pacific Ocean had a residence time of 5000 years [102], comparable to its riverine input. Copper residence time estimated from its isotopic ratios was about 2000–3200 years for all the oceans [23,103].

As for vertical distribution, Cu shows low concentration in the surface layer, due to biological uptake [23]. Dissolved Cu in the eastern North Pacific and tropical South Pacific increases with depth, mimicking typical depth profiles of major nutrients [70,95]. Similar depth profiles of dissolved Cu were observed in the Indian and Atlantic oceans (Figure 5). This also indicates that surface phytoplankton may encounter a sharp increase of dissolved Cu during the mixing event. In the surface ocean, the lowest values occurred in the Atlantic and Pacific gyres, while relatively high concentrations were observed at high latitudes (Figure 5). At the air-sea interface, aerosol Cu may have shown different characters (Box 2).
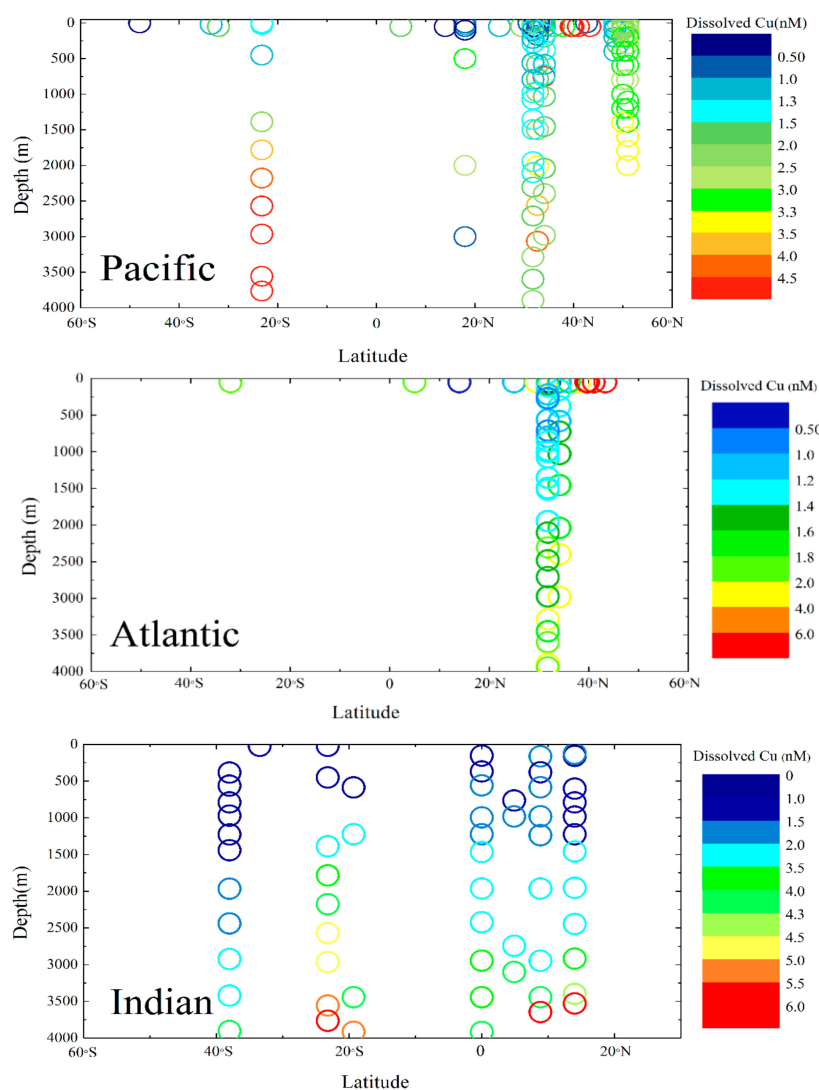

Figure 5. Latitudinal and depth distributions of dissolved Cu in the Pacific, Atlantic, and Indian oceans. Data quoted from Coale and Bruland [104], Boyle et al. [102], Chen [105], Wen et al. [106], Vance et al. [107], Chase et al. [98], Sunda [30], Vu and Sohrin [108], Lagerström et al. [109], Pinedo-Gonzalez et al. [110], Middag et al. [111], Posacka et al. [95], and Whitby et al. [112].

Box 2. Sea-Surface Microlayer (SSM).

The sea-surface microlayer (SSM) is a single hydrated gelatinous layer at the air–sea interface, which has unique physical, chemical, and biological properties differing from surface water [113–115]. Total Cu was enriched by factors of 2.8 and 16 in the SSMs of Lake Dołgie Wielkie [116] and the Mediterranean Sea [113] compared to underlying waters, and dissolved Cu showed enrichment factors of 3 and 20 in the SSMs of Bay of Villefranche [113] and the Mediterranean Sea [117], respectively. The active interactions between organics and Cu within the SSM have been observed near the Mediterranean coast and north Norwegian fjords, and the complexing capacity of ligands with Cu in the SSM vary from 230 nM to 1790 nM in the subarctic region [118], 280 nM to 940 nM in the northwest Mediterranean [119], and 52 nM to 680 nM in the eastern Mediterranean [120]. The residence time of dissolved aerosol Cu in the SSM is potentially long enough (180–210 min), compared to dissolved Fe (8.1–26 min) and Zn (10–14 min), for atmospheric deposited substances to get involved in reactions [121]. The SSM acted more like a trap for aerosol particles [117], and more work needs to be done to clarify the complex processes of biological response and Cu addition in this layer.

2.5. Copper Speciation in the Seawater

In seawater, Cu exists in both thermodynamically stable Cu (II) and unstable Cu (I). Copper (I) consists of 5%–10% of the filterable Cu [30,122], generally as chloride complexes, since natural organic ligands cannot meet Cu (I)'s requirement for tetrahedral coordination site in complexation [123]. Copper (II) can be reduced to Cu (I) via photochemical processes, ligand-to-metal charge transfer reactions, or reductions, and the Cu (I) can also be oxidized to Cu (II) (Box 3) [123,124]. The redox chemistry of Cu is closely related to Fe in the seawater (Box 3).

Box 3. Redox Chemistry of Cu.

High concentrations of dissolved organic ligands or low Cl^- concentrations are favorable to the oxidation rate of Cu (I) [123,125]. A change of pH leads to an obvious speciation change of inorganic Cu (II), since the major species of inorganic Cu (II) are carbonate complexes. Differently, the oxidation of Cu (I) is less affected by increasing acidification, because it is dominated by chloride complexes or free ions [126]. At low oxygen concentrations (<22 μM), Cu (I) oxidation depends on its reaction with H_2O_2 [127]. When the concentration of bicarbonate in seawater is under 5 mM, the oxidation rate constant of Cu (I) increases with the increase of bicarbonate concentration [125]. Ions such as Mg^{2+} and Ca^{2+} can decrease Cu (I) oxidation rate constants, possibly due to the slow exchange of Mg^{2+} or Ca^{2+} complexes with Cu^{2+} and the back-reaction of Cu (II) [125,128]. The presence of Cu (II) catalyzes the oxidation of Fe (II), and in turn Fe (II) can enhance the reduction of Cu (II) to Cu (I) under both air-saturated and anoxic conditions [129]. In contrast, Cu (I) is likely to be oxidized in the presence of Fe (III), and the oxidation rate linearly decreases with the increase of Fe (II) under oxygen saturation conditions [130]. Apart from these direct redox reactions, the current kinetic model also includes the competition between Cu and Fe by reactive oxygen species (ROS), as well as the formation of Fe–Cu species (e.g., cupric ferrite) [130].

More than 99% of dissolved Cu in the surface seawater is chelated as dissolved, low-molecular-weight organic complexes [122,131]. Abiotic factors, such as pH and temperature, can affect the complexation of Cu with organic ligands. Biota are thought to be the major source of organic ligands binding Cu (Box 4 and Table 2) [75,132]. Both the production rate and the number of Cu-binding ligands were found to be enhanced rapidly after Cu addition in seawater [6,133]. High carbohydrates were observed to be exuded by *Cylindrotheca fusiformis* (diatom) exposed to high Cu, suggesting a plausible cell protection mechanism via polysaccharide production [134]. The strong Cu-binding ligands can be produced by dinoflagellate [135] and cyanobacteria [82]. This may have partly explained why strong Cu complexes reach a peak when cyanobacteria were abundant [104,122]. Some phytoplankton also produce both low concentrations of strong ligands and high concentrations of weak ligands—for example, *Emiliania huxleyi* can produce thiols as well as carbohydrates as a Cu-complexing ligand [136,137]. Seasonal changes of Cu speciation may be partly attributed to the variation of phytoplankton community composition [138,139]. The weaker L_2 ligands (as well as L_3 ligands) may be derived from activated sludge or humus in some coastal areas [140], which contributes

to 1%–27% of the total ligand concentration in the northeast Pacific [112]. The conditional stability constants of Cu with humic acid (HA) and fulvic acid (FA) are stronger than Zn, Co, Fe, and Al [141].

Box 4. Ligands.

In general, there are two classes of ligands, the strong L_1 ligands ($K^{cond}_{CuL1,Cu2+} = 10^{12-14}$) mainly found in surface water with concentrations between 1–2 nmol kg^{-1}) and the weak L_2 ligands ($K^{cond}_{CuL2,Cu2+} = 10^{8-10}$) [122,142]. However, Hurst and Bruland [143] argued that a weaker L_3 class of ligands existed in San Francisco Bay waters ($K^{cond}_{CuL2,Cu2+} = 10^{8.3-9.3}$). Dissolved Cu was first bound by high-affinity organic ligands (L_1), and once L_1 approached upper capacity, weaker L_2 appeared to bind additional Cu [79]. In the northeast Pacific, the L_1-complexed Cu comprised of 94% dissolved Cu when ligands were sufficient in the water column [112].

Table 2. Copper-complexing ligands produced by phytoplankton.

Ligand Producer	Taxa	Class	Reference
Cylindrotheca fusiformis	Diatom	Strong ligands	[134]
Amnphidiniumn carterae	Dinoflagellate	Strong ligands	[135]
Synechococcu. spp	Cyanobacteria	Strong ligands	[82,135]
Emiliania huxleyi	Haptophyta	Both strong and weak ligands	[136,137]
Hymnenoinonas carterae	Coccolithophorid	Weak ligands	[135]

2.6. Atmospheric Contribution to Oceanic Cu

Atmospheric deposition is one of the most important sources for oceanic Cu, in conjunction with hydrothermal vents, sediment, rivers, and other sources. Duce et al. elucidated that global atmospheric deposition and riverine input of dissolved Cu were comparable [31]. An isotopic study showed that rivers and dust contributed 4.6×10^4 and 3.4×10^3 t yr^{-1} of Cu to the oceans, respectively [144]. With regard to wet deposition, which is often more important than dry deposition over oceanic regions [32], Takano et al. reported that 6.1×10^4 t yr^{-1} of dissolved Cu came from the atmosphere, higher than rivers (4.8×10^4 t yr^{-1}) and but less than upwelling (1.9×10^5 t yr^{-1}) inputs [23]. In addition, the majority of riverine input of metals deposits in the estuaries and mainly influence the coastal area, whilst atmospheric deposition can reach remote oceans [31].

Hydrothermal fluids were found to account for 14% of dissolved Cu in the deep ocean [145]. The decomposition of biogenic sinking particles in the benthos also releases Cu, and upwelling or vertical mixing can bring Cu to the surface. In shelf waters, sediment may dominantly contribute to Cu concentration. In the Irish Sea, sediment Cu flux (160 t yr^{-1}) was significantly higher than atmospheric deposition (26 t yr^{-1}) and riverine input (38 t yr^{-1}) [146]. Sediment flux of Cu in the south Yellow Sea was 5.4×10^3 t yr^{-1}, which was comparable to Cu dry deposition of 2.8×10^3 t yr^{-1} [147] and Yellow River input of 13.2×10^3 t yr^{-1} [148]. However, the surface ocean receives larger fractions of Cu from the atmosphere during the seasonal stratification, due to shallowed mixed layer and reduced upwelling inputs [4,6,149].

2.7. Sources, Solubility, and Deposition of Atmospheric Cu

Atmospheric Cu has both natural and anthropogenic sources. Volcanic emission (e.g., [150]), sea spray (e.g., [151] and [152]), and dust (e.g., [153] and [154]) are typical natural sources. Anthropogenic sources include fuel combustion (e.g., coal and furnace oil), industry (e.g., industrial boiler, iron and steel production, nonferrous metal smelting, and cement production), traffic emissions (e.g., brake and tire wear), and incineration of waste [155–157]. Aerosol Cu derived from anthropogenic emissions is predominantly distributed in fine particles [15]. Asia has the largest anthropogenic emission of trace metals, attributed to its soaring demand for energy in the process of industrial development [158].

Cu associated with dust can be transported over a long distance to the ocean. Surface particles in dry and sparsely vegetated soil start to saltate in a horizontal flux when the wind speed exceeds

threshold friction velocity. Next, small particles are dislodged, lifted into the air, and carried downstream [32,159]. Some of them can reach the free troposphere and be transported for thousands of kilometers. For example, Asian dust is carried to Hawaii [154] and remote high-altitude sites in North America [153]; African dust is transported to the eastern Mediterranean [160], Florida [8], and Amazon [161]. It has been indicated that the western Mediterranean Sea receives high fluxes of aerosols, and Sahara dust is the largest natural contributor [4,162]. Prevailing winds, convective processes, and adiabatic vertical motion associated with fronts also play roles in the transport of dust. During this transport process, interactions with clouds and interactions between Cu and other aerosol components (e.g., acidic components) take place, resulting in changes in physicochemical characters of Cu.

The metal solubility in aerosols is closely dependent upon aerosol sources [26]. Sholkovitz et al. showed that Cu solubility in dust-derived aerosols was 1%–7% (Table 3), far lower than that of anthropogenic aerosols (10%–100%) [24]. During transport, Cu solubility is also affected by chemical and photochemical reactions. Redox reactions between Cu and oxidants (e.g., HO_X) during cloud processing are more rapid than those between Fe and oxidants, and these reactions are quite important in affecting Cu speciation and solubility [163,164]. Due to the large emissions of acidic components (represented by CO_2, SO_2, NO_2, etc.) into the atmosphere, high acidity of aerosol and low pH cloud water have been observed, which could increase Cu solubility and change Cu speciation [5,165]. For example, atmospheric hygroscopic sulfate is capable of enhancing Cu dissolution [166]. The dissolution rate of Cu elevates rapidly in the first 20 min, then stabilizes to lower values in the atmospheric aqueous condition [167]. In marine precipitation, over 80% of the total Cu exists in dissolved form when pH < 5 [168]. Furthermore, Cu is more soluble in rainwater than in seawater, and Chen et al. measured the Cu solubility of 66% and 49% in pure water and seawater (Table 3), respectively [25].

Table 3. Fractional solubility of aerosol Cu over the global oceans.

Ocean	Seawater	Pure Water	Sample Types	References
East China Sea		51%	Non-dust event days	[169]
An island in Taiwan Strait	42%		Aerosol samples	[170]
Coastal site in Taiwan Strait	27%		Aerosol samples	[170]
North Atlantic (Bermuda)		84%	Rain samples	[168]
Atlantic		40%	Aerosol samples	[10]
German Bight		41%	Aerosol samples	[171]
Gulf of Aqaba	49%	66%	Aerosol samples	[25]
Mediterranean Sea (Corsica)		48%	Rain samples	[168]
Western Mediterranean		76%	Rain samples	[172]
Sargasso Sea and Bermuda		1–7%	Dust source	[24]
Sargasso Sea		10–100%	Anthropogenic source	[24]

Due to gravitational settling, turbulent dry deposition, and rain scavenging, Cu in the atmosphere will deposit in the marine boundary layer after long-range transport [159]. The dry deposition flux can be calculated by multiplying the Cu concentration by a size-dependent dry deposition velocity under the Williams model [173]. With fewer uncertainties, recent studies provide more promising approaches, using radionuclide beryllium-7 as a tracer to calculate the deposition of various chemical species from the atmosphere [174]. Submicron particles are largely affected by precipitation, and wet deposition usually dominates the deposition in remote oceans [32].

According to the atmospheric concentrations of dissolved Cu obtained from GEOTRACES Intermediate Data Product 2017 (IDP2017, [100]), published papers, and our measurements over the western North Pacific, we showed a global distribution of dissolved aerosol Cu over the ocean (Figure 6). Aerosol sampling methods followed Fu et al. [175]. We calculate dry deposition fluxes of Cu using an empirical deposition velocity of 1 cm s^{-1}. Human activities can significantly increase the atmospheric emission flux of dissolved Cu and impact the growth of marine phytoplankton, and the

deposition of anthropogenic Cu has the greatest probability to be "toxic" in the western North Pacific and the southeast Indian Ocean [10–12], due to rapid economic development, the increase of human activities, and growing energy consumption in adjacent continents [15,157,158,176].
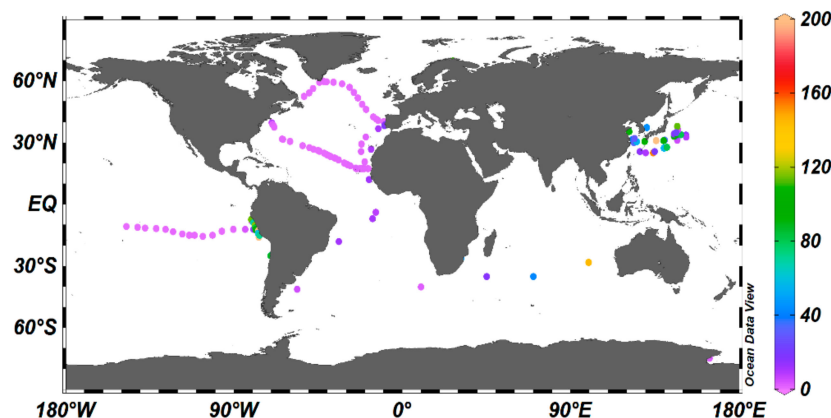

Figure 6. Global distributions of dissolved aerosol Cu over the global oceans. The color bar refers to the concentration of dissolved aerosol Cu in the unit of pmol m^{-3}. Data sources: Maenhaut and Cafmeyer [177], Virkkula et al. [178], Witt et al. [179], Chand et al. [180], Hsu et al. [169], Kang et al. [181], Laing et al. [182], Chance et al. [183], Illuminati et al. [184], Baker et al. [185], Wang et al. [28], Schlitzer et al. [100], and our unpublished data. Figures were produced using Ocean Data View (Schlitzer, R., Ocean Data View, odv.awi.de, 2017).

3. Remarks

To better understand aerosol Cu effects on marine phytoplankton, studies on aerosols, seawater chemistry, and phytoplankton should be integrated. In the future, an urgent priority is to accurately estimate the contribution of atmospheric Cu to the oceanic bioavailable Cu pool, and the application of isotopic analyses will promote such studies. Bioassay studies should be carried out with Cu concentrations in the same order of magnitude as seawater (nM levels), in order to simulate the virtual scenario. The purpose of organic ligands produced by phytoplankton, whether is for self-protection or for other reasons, remains to be investigated among different taxa. In addition, Cu impacts on primary productivity under different nutrient conditions, as well as the synergistic or antagonistic effects of aerosol Cu and other metals on phytoplankton growth, should be further studied.

In future decades, changes of the global environment, such as ocean acidification, warming, and deoxygenation may amplify the impacts of metals. The presumed pH of global ocean will be 7.7 by the year 2100, and this will result in a 30% augmentation of free ionic forms of Cu in the seawater [126]. Researchers have already seen that Cu toxicity to marine organisms (coastal benthic species) would increase under ocean acidification [186]. The reduction of Cu (II) to Cu (I) will increase with the warming and lowered oxygen [5]. Adverse synergistic interactions between abiotic stressors and Cu are more likely to take place in future oceans [187]. Attendant with the growing human activity, the implication of anthropogenic aerosol Cu to the marine ecosystem should be highly concerning.

Author Contributions: Conceptualization, Y.C.; methodology, Y.C. and T.Y.; software, T.Y., S.Z.; validation, Y.C., S.Z., and H.L.; formal analysis, Y.C. and T.Y.; investigation, T.Y.; resources, Y.C., S.Z., and H.L.; data curation, Y.C., S.Z., and H.L.; writing—original draft preparation, T.Y.; writing—review and editing, Y.C.; visualization, T.Y.; supervision, Y.C.; project administration, Y.C.; funding acquisition, Y.C.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Gallisai, R.; Peters, F.; Volpe, G.; Basart, S.; Baldasano, J.M. Saharan Dust Deposition May Affect Phytoplankton Growth in the Mediterranean Sea at Ecological Time Scales. *PLoS ONE* **2014**, *9*, e110762. [CrossRef] [PubMed]
2. Mahowald, N.M.; Hamilton, D.S.; Mackey, K.R.M.; Moore, J.K.; Baker, A.R.; Scanza, R.A.; Zhang, Y. Aerosol Trace Metal Leaching and Impacts on Marine Microorganisms. *Nat. Commun.* **2018**, *9*, 2614. [CrossRef] [PubMed]
3. Kim, I.N.; Lee, K.; Gruber, N.; Karl, D.M.; Bullister, J.L.; Yang, S.; Kim, T.W. Increasing Anthropogenic Nitrogen in the North Pacific Ocean. *Science* **2014**, *346*, 1102–1106. [CrossRef] [PubMed]
4. Jordi, A.; Basterretxea, G.; Tovar-Sanchez, A.; Alastuey, A.; Querol, X. Copper Aerosols Inhibit Phytoplankton Growth in the Mediterranean Sea. *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 21246–21249. [CrossRef] [PubMed]
5. Hoffmann, L.J.; Breitbarth, E.; Boyd, P.W.; Hunter, K.A. Influence of Ocean Warming and Acidification on Trace Metal Biogeochemistry. *Mar. Ecol. Prog. Ser.* **2012**, *470*, 191–205. [CrossRef]
6. Mackey, K.R.; Buck, K.N.; Casey, J.R.; Cid, A.; Lomas, M.W.; Sohrin, Y.; Paytan, A. Phytoplankton Responses to Atmospheric Metal Deposition in the Coastal and Open-Ocean Sargasso Sea. *Front. Microbiol.* **2012**, *3*, 359. [CrossRef] [PubMed]
7. Duggen, S.; Croot, P.; Schacht, U.; Hoffmann, L. Subduction Zone Volcanic Ash Can Fertilize the Surface Ocean and Stimulate Phytoplankton Growth: Evidence from Biogeochemical Experiments and Satellite Data. *Geophys. Res. Lett.* **2007**, *34*. [CrossRef]
8. Walsh, J.J.; Steidinger, K.A. Saharan dust and Florida red tides: The cyanophyte connection. *J. Geophys. Res. Space Phys.* **2001**, *106*, 11597–11612. [CrossRef]
9. Chien, C.; Mackey, K.R.; Dutkiewicz, S.; Mahowald, N.M.; Prospero, J.; Paytan, A. Effects of African dust deposition on phytoplankton in the western tropical Atlantic Ocean off Barbados. *Glob. Biogeochem. Cycles* **2016**, *30*, 716–734. [CrossRef]
10. Paytan, A.; Chen, Y.; Mahowald, N.; Labiosa, R.; Mackey, K.R.M.; Lima, I.D.; Doney, S.C.; Post, A.F. Toxicity of atmospheric aerosols on marine phytoplankton. *Proc. Natl. Acad. Sci. USA* **2009**, *106*, 4601–4605. [CrossRef]
11. Krishnamurthy, A.; Moore, J.K.; Mahowald, N.; Luo, C.; Doney, S.C.; Lindsay, K.; Zender, C.S. Impacts of increasing anthropogenic soluble iron and nitrogen deposition on ocean biogeochemistry. *Glob. Biogeochem. Cycles* **2009**, *23*. [CrossRef]
12. Sholkovitz, E.R.; Sedwick, P.N.; Church, T.M. Influence of anthropogenic combustion emissions on the deposition of soluble aerosol iron to the ocean: Empirical estimates for island sites in the North Atlantic. *Geochim. Cosmochim. Acta* **2009**, *73*, 3981–4003. [CrossRef]
13. Jickells, T. Atmospheric inputs of metals and nutrients to the oceans: Their magnitude and effects. *Mar. Chem.* **1995**, *48*, 199–214. [CrossRef]
14. Eichler, A.; Tobler, L.; Eyrikh, S.; Malygina, N.; Papina, T.; Schwikowski, M. Ice-Core Based Assessment of Historical Anthropogenic Heavy Metal (Cd, Cu, Sb, Zn) Emissions in the Soviet Union. *Environ. Sci. Technol.* **2014**, *48*, 2635–2642. [CrossRef]
15. Tian, H.Z.; Zhu, C.Y.; Gao, J.J.; Cheng, K.; Hao, J.M.; Wang, K.; Hua, S.B.; Wang, Y.; Zhou, J.R. Quantitative assessment of atmospheric emissions of toxic heavy metals from anthropogenic sources in China: Historical trend, spatial distribution, uncertainties, and control policies. *Atmos. Chem. Phys. Discuss.* **2015**, *15*, 10127–10147. [CrossRef]
16. Jickells, T.D.; An, Z.S.; Andersen, K.K.; Baker, A.R.; Bergametti, G.; Brooks, N.; Cao, J.J.; Boyd, P.W.; Duce, R.A.; Hunter, K.A.; et al. Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science* **2005**, *308*, 67–71. [CrossRef] [PubMed]
17. Guerzoni, S.; Chester, R.; Dulac, F.; Herut, B.; Loÿe-Pilot, M.-D.; Measures, C.; Migon, C.; Molinaroli, E.; Moulin, C.; Rossini, P.; et al. The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea. *Prog. Oceanogr.* **1999**, *44*, 147–190. [CrossRef]

18. Hooper, J.; Mayewski, P.; Marx, S.; Henson, S.; Potocki, M.; Sneed, S.; Handley, M.; Gassó, S.; Fischer, M.; Saunders, K.M. Examining links between dust deposition and phytoplankton response using ice cores. *Aeolian Res.* **2019**, *36*, 45–60. [CrossRef]

19. Wang, R.; Balkanski, Y.; Bopp, L.; Aumont, O.; Boucher, O.; Ciais, P.; Gehlen, M.; Peñuelas, J.; Ethé, C.; Hauglustaine, D.; et al. Influence of anthropogenic aerosol deposition on the relationship between oceanic productivity and warming. *Geophys. Res. Lett.* **2015**, *42*, 10745–10754. [CrossRef]

20. Yoon, J.E.; Yoo, K.C.; Macdonald, A.M.; Yoon, H.I.; Park, K.T.; Yang, E.J.; Kim, H.C.; Lee, J.I.; Lee, M.K.; Jung, J.; et al. Reviews and Syntheses: Ocean Iron Fertilization Experiments-Past, Present, and Future Looking to a Future Korean Iron Fertilization Experiment in the Southern Ocean (Kskies Project). *Biogeosciences* **2018**, *15*, 5847–5889. [CrossRef]

21. Coale, K.H. Effects of iron, manganese, copper, and zinc enrichments on productivity and biomass in the subarctic Pacific. *Limnol. Oceanogr.* **1991**, *36*, 1851–1864. [CrossRef]

22. Zou, H.-X.; Pang, Q.-Y.; Zhang, A.-Q.; Lin, L.-D.; Li, N.; Yan, X.-F. Excess copper induced proteomic changes in the marine brown algae Sargassum fusiforme. *Ecotoxicol. Environ. Saf.* **2015**, *111*, 271–280. [CrossRef]

23. Takano, S.; Tanimizu, M.; Hirata, T.; Sohrin, Y. Isotopic constraints on biogeochemical cycling of copper in the ocean. *Nat. Commun.* **2014**, *5*, 5663. [CrossRef]

24. Sholkovitz, E.R.; Sedwick, P.N.; Church, T.M. 24. On the fractional solubility of copper in marine aerosols: Toxicity of aeolian copper revisited. *Geophys. Res. Lett.* **2010**, *37*, 20601. [CrossRef]

25. Chen, Y.; Street, J.; Paytan, A. Comparison between pure-water- and seawater-soluble nutrient concentrations of aerosols from the Gulf of Aqaba. *Mar. Chem.* **2006**, *101*, 141–152. [CrossRef]

26. Chester, R.; Murphy, K.; Lin, F.; Berry, A.; Bradshaw, G.; Corcoran, P. Factors controlling the solubilities of trace metals from non-remote aerosols deposited to the sea surface by the 'dry' deposition mode. *Mar. Chem.* **1993**, *42*, 107–126. [CrossRef]

27. Brand, L.E.; Sunda, W.G.; Guillard, R.R. Reduction of marine phytoplankton reproduction rates by copper and cadmium. *J. Exp. Mar. Boil. Ecol.* **1986**, *96*, 225–250. [CrossRef]

28. Wang, F.J.; Chen, Y.; Guo, Z.G.; Gao, H.W.; Mackey, K.R.; Yao, X.H.; Zhuang, G.S.; Paytan, A. Combined effects of iron and copper from atmospheric dry deposition on ocean productivity. *Geophys. Res. Lett.* **2017**, *44*, 2546–2555. [CrossRef]

29. Irving, H.; William, R.J.P. The stability of transition-metal complexes. *J. Chem. Soc.* **1953**, *637*, 3192–3210. [CrossRef]

30. Sunda, W.G. Feedback interactions between trace metal nutrients and phytoplankton in the ocean. *Front. Microbiol.* **2012**, *3*, 204. [CrossRef]

31. Duce, R.A.; Liss, P.S.; Merrill, J.T.; Atlas, E.L.; Buat-Menard, P.; Hicks, B.B.; Miller, J.M.; Prospero, J.M.; Arimoto, R.; Church, T.M.; et al. The atmospheric input of trace species to the world ocean. *Glob. Biogeochem. Cycles* **1991**, *5*, 193–259. [CrossRef]

32. Mahowald, N.M.; Baker, A.R.; Bergametti, G.; Brooks, N.; Duce, R.A.; Jickells, T.D.; Kubilay, N.; Prospero, J.M.; Tegen, I. Atmospheric global dust cycle and iron inputs to the ocean. *Glob. Biogeochem. Cycles* **2005**, *19*. [CrossRef]

33. Echeveste, P.; Croot, P.; von Dassow, P. Differences in the sensitivity to Cu and ligand production of coastal vs offshore strains of *Emiliania huxleyi*. *Sci. Total Environ.* **2018**, *625*, 1673–1680. [CrossRef] [PubMed]

34. Biswas, H.; Bandyopadhyay, D. Physiological responses of coastal phytoplankton (Visakhapatnam, SW Bay of Bengal, India) to experimental copper addition. *Mar. Environ. Res.* **2017**, *131*, 19–31. [CrossRef] [PubMed]

35. Mann, E.L.; Ahlgren, N.; Moffett, J.W.; Chisholm, S.W. Copper toxicity and cyanobacteria ecology in the Sargasso Sea. *Limnol. Oceanogr.* **2002**, *47*, 976–988. [CrossRef]

36. Stuart, R.K.; Dupont, C.L.; Johnson, D.A.; Paulsen, I.T.; Palenik, B. Coastal strains of marine *Synechococcus* species exhibit increased tolerance to copper shock and a distinctive transcriptional response relative to those of open-ocean strains. *Appl. Environ. Microb.* **2009**, *75*, 5047–5057. [CrossRef] [PubMed]

37. Twining, B.S.; Baines, S.B. The trace metal composition of marine phytoplankton. *Annu. Rev. Mar. Sci.* **2013**, *5*, 191–215. [CrossRef]

38. Ridge, P.G.; Zhang, Y.; Gladyshev, V.N. Comparative genomic analyses of copper transporters and cuproproteomes reveal evolutionary dynamics of copper utilization and its link to oxygen. *PLoS ONE* **2008**, *3*, e1378. [CrossRef]

39. Harrison, W.; Eppley, R.; Renger, E. Phytoplankton nitrogen metabolism, nitrogen budgets, and observations on copper toxicity: Controlled ecosystem pollution experiment. *Bull. Mar. Sci.* **1977**, *27*, 44–57.

40. Magalhães, C.M.; Machado, A.; Matos, P.; Bordalo, A.A. Impact of copper on the diversity, abundance and transcription of nitrite and nitrous oxide reductase genes in an urban European estuary. *FEMS Microbiol. Ecol.* **2011**, *77*, 274–284. [CrossRef]

41. Lopez, J.S.; Lee, L.; Mackey, K.R.M. The toxicity of copper to *Crocosphaera watsonii* and other marine phytoplankton: A systematic review. *Front. Mar. Sci.* **2018**, *5*, 511. [CrossRef]

42. Baron, M.; Arellano, J.B.; Gorge, J.L. Copper and photosystem-II: A controversial relationship. *Physiol. Plant.* **1995**, *94*, 174–180. [CrossRef]

43. Ritter, A.; Ubertini, M.; Romac, S.; Gaillard, F.; Delage, L.; Mann, A.; Cock, J.M.; Tonon, T.; Correa, J.A.; Potin, P. Copper stress proteomics highlights local adaptation of two strains of the model brown alga *Ectocarpus siliculosus*. *Proteomics* **2010**, *10*, 2074–2088. [CrossRef]

44. Perez, P.; Estevez-Blanco, P.; Beiras, R.; Fernandez, E. Effect of copper on the photochemical efficiency, growth, and chlorophyll a biomass of natural phytoplankton assemblages. *Environ. Toxicol. Chem.* **2006**, *25*, 137–143. [CrossRef]

45. Miao, A.J.; Wang, W.X.; Juneau, P. Comparison of Cd, Cu, and Zn toxic effects on four marine phytoplankton by pulse-amplitude-modulated fluorometry. *Environ. Toxicol. Chem.* **2005**, *24*, 2603–2611. [CrossRef]

46. Moffett, J.W.; Brand, L.E.; Croot, P.L.; Barbeau, K.A. Cu speciation and cyanobacterial distribution in harbors subject to anthropogenic Cu inputs. *Limnol. Oceanogr.* **1997**, *42*, 789–799. [CrossRef]

47. Levy, J.L.; Stauber, J.L.; Jolley, D.F. Sensitivity of marine microalgae to copper: The effect of biotic factors on copper adsorption and toxicity. *Sci. Total Environ.* **2007**, *387*, 141–154. [CrossRef]

48. Semeniuk, D.M.; Taylor, R.L.; Bundy, R.M.; Johnson, W.K.; Cullen, J.T.; Robert, M.; Barbeau, K.A.; Maldonado, M.T. Iron-copper interactions in iron-limited phytoplankton in the northeast subarctic Pacific Ocean. *Limnol. Oceanogr.* **2016**, *61*, 279–297. [CrossRef]

49. Peers, G.; Quesnel, S.A.; Price, N.M. Copper requirements for iron acquisition and growth of coastal and oceanic diatoms. *Limnol. Oceanogr.* **2005**, *50*, 1149–1158. [CrossRef]

50. López, A.; Rico, M.; Santana-Casiano, J.M.; González, A.G.; González-Dávila, M. Phenolic profile of Dunaliella tertiolecta growing under high levels of copper and iron. *Environ. Sci. Pollut. Res.* **2015**, *22*, 14820–14828. [CrossRef]

51. Hall, J.; Healey, F.P.; Robinson, G.G.C. The interaction of chronic copper toxicity with nutrient limitation in two chlorophytes in batch culture. *Aquat. Toxicol.* **1989**, *14*, 1–13. [CrossRef]

52. Sunda, W.G.; Huntsman, S.A. Relationships among growth rate, cellular manganese concentrations and manganese transport knetics in estuarine and oceanic species of the diatom thalassiosir. *J. Phycol.* **1986**, *22*, 259–270. [CrossRef]

53. Fisher, N.S.; Jones, G.J.; Nelson, D.M. Effects of copper and zinc on growth, morphology, and metabolism of Asterionella japonica. *J. Exp. Mar. Biol. Ecol.* **1981**, *51*, 37–56. [CrossRef]

54. Guo, C.; Yu, J.; Ho, T.Y.; Wang, L.; Song, S.; Kong, L.; Liu, H. Dynamics of phytoplankton community structure in the South China Sea in response to the East Asian aerosol input. *Biogeosciences* **2012**, *9*, 1519–1536. [CrossRef]

55. Sunda, W.; Tester, P.; Huntsman, S. Effects of cupric and zinc ion activities on the survival and reproduction of marine copepods. *Mar. Biol.* **1987**, *94*, 203–210. [CrossRef]

56. Schenck, R.C. Copper deficiency and toxicity in *Gonyaulax-Tamarensis* (Lebour). *Mar. Biol. Lett.* **1984**, *5*, 13–19.

57. Anderson, D.M.; Morel, F.M.M. Copper sensitivity of Gonyaulax-Tamarensis. *Limnol. Oceanogr.* **1978**, *23*, 283–295. [CrossRef]

58. Pistocchi, R.; Mormile, M.A.; Guerrini, F.; Isani, G.; Boni, L. Increased production of extra- and intracellular metal-ligands in phytoplankton exposed to copper and cadmium. *J. Appl. Phycol.* **2000**, *12*, 469–477. [CrossRef]

59. Cid, A.; Herrero, C.; Torres, E.; Abalde, J. Copper toxicity on the marine microalga *Phaeodactylum tricornutum*: Effects on Photosynthesis and Related Parameters. *Aquat. Toxicol.* **1995**, *31*, 165–174. [CrossRef]

60. Shi, W.; Jin, Z.; Hu, S.; Fang, X.; Li, F. Dissolved organic matter affects the bioaccumulation of copper and lead in Chlorella pyrenoidosa: A case of long-term exposure. *Chemosphere* **2017**, *174*, 447–455. [CrossRef]

61. Peers, G.; Price, N.M. Copper-containing plastocyanin used for electron transport by an oceanic diatom. *Nature* **2006**, *441*, 341–344. [CrossRef]

62. Morel, F.M.; Price, N.M. The biogeochemical cycles of trace metals in the oceans. *Science* **2003**, *300*, 944–947. [CrossRef]

63. Maldonado, M.T.; Allen, A.E.; Chong, J.S.; Lin, K.; Leus, D.; Karpenko, N.; Harris, S.L. Copper-dependent iron transport in coastal and oceanic diatoms. *Limnol. Oceanogr.* **2006**, *51*, 1729–1743. [CrossRef]

64. Annett, A.L.; Lapi, S.; Ruth, T.J.; Maldonado, M.T. The effects of Cu and Fe availability on the growth and Cu: C ratios of marine diatoms. *Limnol. Oceanogr.* **2008**, *53*, 2451–2461. [CrossRef]

65. Rueter, J.G.; Morel, F.M.M. The interaction between zinc deficiency and copper toxicity as it affects the silicic acid uptake mechanisms of *Thalassiosira pseudonana*. *Limnol. Oceanogr.* **1981**, *26*, 67–73. [CrossRef]

66. Sunda, W.G.; Huntsman, S.A. Effect of competitive interactions between manganese and copper on cellular manganese and growth in estuarine and oceanic species of the diatom *Thalassiosira*. *Limnol. Oceanogr.* **1983**, *28*, 924–934. [CrossRef]

67. Rocha, G.S.; Lombardi, A.T.; Melao Mda, G. Influence of phosphorus on copper toxicity to Selenastrum gracile (Reinsch) Korshikov. *Ecotoxicol. Environ. Saf.* **2016**, *128*, 30–35. [CrossRef]

68. Hall, J.; Healey, F.; Robinson, G. The interaction of chronic copper toxicity with nutrient limitation in chemostat cultures of Chlorella. *Aquat. Toxicol.* **1989**, *14*, 15–26. [CrossRef]

69. Rijstenbil, J.W.; Dehairs, F.; Ehrlich, R.; Wijnholds, J.A. Effect of the nitrogen status on copper accumulation and pools of metal-binding peptides in the planktonic diatom *Thalassiosira pseudonana*. *Aquat. Toxicol.* **1998**, *42*, 187–209. [CrossRef]

70. Roshan, S.; Wu, J.F. Dissolved and colloidal copper in the tropical South Pacific. *Geochim. Cosmochim. Acta* **2018**, *233*, 81–94. [CrossRef]

71. Kuss, J.; Kremling, K. Spatial variability of particle associated trace elements in near-surface waters of the North Atlantic (30 N/60 W to 60 N/2 W), derived by large volume sampling. *Mar. Chem.* **1999**, *68*, 71–86. [CrossRef]

72. Tovar-Sanchez, A.; Sanudo-Wilhelmy, S.A.; Kustka, A.B.; Agustí, S.; Dachs, J.; Hutchins, D.A.; Capone, D.G.; Duarte, C.M. Effects of dust deposition and river discharges on trace metal composition of *Trichodesmium* spp. in the tropical and subtropical North Atlantic Ocean. *Limnol. Oceanogr.* **2006**, *51*, 1755–1761. [CrossRef]

73. Nuester, J.; Vogt, S.; Newville, M.; Kustka, A.B.; Twining, B.S. The unique biogeochemical signature of the marine diazotroph *Trichodesmium*. *Front. Microbiol.* **2012**, *3*, 150. [CrossRef]

74. Semeniuk, D.M.; Cullen, J.T.; Johnson, W.K.; Gagnon, K.; Ruth, T.J.; Maldonado, M.T. Plankton copper requirements and uptake in the subarctic Northeast Pacific Ocean. *Deep Sea Res. Oceanogr. Res. Pap.* **2009**, *56*, 1130–1142. [CrossRef]

75. Semeniuk, D.M.; Bundy, R.M.; Posacka, A.M.; Robert, M.; Barbeau, K.A.; Maldonado, M.T. Using [67]Cu to study the biogeochemical cycling of copper in the northeast subarctic pacific ocean. *Front. Mar. Sci.* **2016**, *3*, 78. [CrossRef]

76. Cullen, J.T.; Chase, Z.; Coale, K.H.; Fitzwater, S.E.; Sherrell, R.M. Effect of iron limitation on the cadmium to phosphorus ratio of natural phytoplankton assemblages from the Southern Ocean. *Limnol. Oceanogr.* **2003**, *48*, 1079–1087. [CrossRef]

77. Guo, J.; Lapi, S.; Ruth, T.J.; Maldonado, M.T. The effects of iron and copper availability on the copper stoichiometry of marine phytoplankton. *J. Phycol.* **2012**, *48*, 312–325. [CrossRef]

78. Liao, W.-H.; Yang, S.-C.; Ho, T.-Y. Trace metal composition of size-fractionated plankton in the Western Philippine Sea: The impact of anthropogenic aerosol deposition. *Limnol. Oceanogr.* **2017**, *62*, 2243–2259. [CrossRef]

79. Buck, K.N.; Ross, J.R.M.; Russell Flegal, A.; Bruland, K.W. A review of total dissolved copper and its chemical speciation in San Francisco Bay, California. *Environ. Res.* **2007**, *105*, 5–19. [CrossRef]

80. Phinney, J.T.; Bruland, K.W. Uptake of lipophilic organic Cu, Cd, and Pb complexes in the coastal diatom *Thalassiosira weissflogii*. *Environ. Sci. Technol.* **1994**, *28*, 1781–1790. [CrossRef]

81. Sunda, W.G.; Huntsman, S.A. Processes regulating cellular metal accumulation and physiological effects: Phytoplankton as model systems. *Sci. Total Environ.* **1998**, *219*, 165–181. [CrossRef]

82. Moffett, J.W.; Brand, L.E. Production of strong, extracellular Cu chelators by marine cyanobacteria in response to Cu stress. *Limnol. Oceanogr.* **1996**, *41*, 388–395. [CrossRef]

83. Gordon, A.S.; Donat, J.R.; Kango, R.A.; Dyer, B.J.; Stuart, L.M. Dissolved copper-complexing ligands in cultures of marine bacteria and estuarine water. *Mar. Chem.* **2000**, *70*, 149–160. [CrossRef]

84. Semeniuk, D.M.; Bundy, R.M.; Payne, C.D.; Barbeau, K.A.; Maldonado, M.T. Acquisition of organically complexed copper by marine phytoplankton and bacteria in the northeast subarctic Pacific Ocean. *Mar. Chem.* **2015**, *173*, 222–233. [CrossRef]

85. Walsh, M.J.; Goodnow, S.D.; Vezeau, G.E.; Richter, L.V.; Ahner, B.A. Cysteine enhances bioavailability of copper to marine phytoplankton. *Environ. Sci. Technol.* **2015**, *49*, 12145–12152. [CrossRef]

86. Guo, J.; Annett, A.L.; Taylor, R.L.; Lapi, S.; Ruth, T.J.; Maldonado, M.T. Copper-uptake kinetics of coastal and oceanic diatoms. *J. Phycol.* **2010**, *46*, 1218–1228. [CrossRef]

87. Hudson, R.J.M. Which aqueous species control the rates of trace metal uptake by aquatic biota. *Sci. Total Environ.* **1998**, *219*, 95–115. [CrossRef]

88. Blaby-Haas, C.E.; Merchant, S.S. The ins and outs of algal metal transport. *BBA Mol. Cell Res.* **2012**, *1823*, 1531–1552. [CrossRef]

89. Quigg, A.; Reinfelder, J.R.; Fisher, N.S. Copper uptake kinetics in diverse marine phytoplankton. *Limnol. Oceanogr.* **2006**, *51*, 893–899. [CrossRef]

90. Gonzalez-Davila, M.; Santana-Casiano, J.M.; Laglera, L.M. Copper adsorption in diatom cultures. *Mar. Chem.* **2000**, *70*, 161–170. [CrossRef]

91. Tien, C.-J.; Sigee, D.C.; White, K.N. Copper adsorption kinetics of cultured algal cells and freshwater phytoplankton with emphasis on cell surface characteristics. *J. Appl. Phycol.* **2005**, *17*, 379–389. [CrossRef]

92. Gonzalez-Davila, M.; Santana-Casiano, J.M.; Perez-Pena, J.; Millero, F.J. Binding of Cu (II) to the surface and exudates of the alga Dunaliella tertiolecta in seawater. *Environ. Sci. Technol.* **1995**, *29*, 289–301. [CrossRef]

93. Zirino, A.; Clavell, C.; Seligman, P.F.; Barber, R.T. Copper and pH in the suface waters of the eastern tropical Pacifc Oocean and the Peruvian upwelling system. *Mar. Chem.* **1983**, *12*, 25–42. [CrossRef]

94. Martinez-Soto, M.C.; Tovar-Sanchez, A.; Sanchez-Quiles, D.; Rodellas, V.; Garcia-Orellana, J.; Basterretxea, G. Seasonal variation and sources of dissolved trace metals in Mao Harbour, Minorca Island. *Sci. Total Environ.* **2016**, *565*, 191–199. [CrossRef]

95. Posacka, A.M.; Semeniuk, D.M.; Whitby, H.; van den Berg, C.M.; Cullen, J.T.; Orians, K.; Maldonado, M.T. Dissolved Copper (Dcu) Biogeochemical Cycling in the Subarctic Northeast Pacific and a Call for Improving Methodologies. *Mar. Chem.* **2017**, *196*, 47–61. [CrossRef]

96. Blake, A.; Chadwick, D.; Zirino, A.; Rivera-Duarte, I. Spatial and temporal variations in copper speciation in San Diego Bay. *Estuaries* **2004**, *27*, 437–447. [CrossRef]

97. Braungardt, C.B.; Achterberg, E.P.; Elbaz-Poulichet, F.; Morley, N.H. Metal geochemistry in a mine-polluted estuarine system in Spain. *Appl. Geochem.* **2003**, *18*, 1757–1771. [CrossRef]

98. Chase, Z.; Paytan, A.; Beck, A.; Biller, D.; Bruland, K.; Measures, C.; Sanudo-Wilhelmy, S. Evaluating the impact of atmospheric deposition on dissolved trace-metals in the Gulf of Aqaba, Red Sea. *Mar. Chem.* **2011**, *126*, 256–268. [CrossRef]

99. Peng, S. The nutrient, total petroleum hydrocarbon and heavy metal contents in the seawater of Bohai Bay, China: Temporal-spatial variations, sources, pollution statuses, and ecological risks. *Mar. Pollut. Bull.* **2015**, *95*, 445–451. [CrossRef]

100. Schlitzer, R.; Anderson, R.F.; Dodas, E.M.; Lohan, M.; Geibert, W.; Tagliabue, A.; Bowie, A.; Jeandel, C.; Maldonado, M.T.; Landing, W.M.; et al. The Geotraces Intermediate Data Product 2017. *Chem. Geol.* **2018**, *493*, 210–223. [CrossRef]

101. Chen, Y.; Paytan, A.; Chase, Z.; Measures, C.; Beck, A.J.; Sanudo-Wilhelmy, S.A.; Post, A.F. Sources and fluxes of atmospheric trace elements to the Gulf of Aqaba, Red Sea. *J. Geophys. Res. Atmos.* **2008**, *113*, D05306. [CrossRef]

102. Boyle, E.A.; Sclater, F.R.; Edmond, J.M. The Distribution of Dissolved Copper in the Pacific. *Earth Planet. Sci. Lett.* **1977**, *37*, 38–54. [CrossRef]

103. Little, S.H.; Vance, D.; McManus, J.; Severmann, S.; Lyons, T.W. Copper Isotope Signatures in Modern Marine Sediments. *Geochim. Cosmochim. Acta* **2017**, *212*, 253–273. [CrossRef]

104. Coale, K.H.; Bruland, K.W. Spatial and Temporal Variability in Copper Complexation in the North Pacific. *Deep Sea Res.* **1990**, *37*, 317–336. [CrossRef]

105. Chen, Y. Sources and Fate of Atmospheric Nutrients over the Remote Oceans and Their Role on Controlling Marine Diazotrophic Microorganisms. Ph.D. Thesis, University of Maryland, College Park, MD, USA, 2004.

106. Wen, L.S.; Jiann, K.T.; Santschi, P.H. Physicochemical speciation of bioactive trace metals (Cd, Cu, Fe, Ni) in the oligotrophic South China Sea. *Mar. Chem.* **2006**, *101*, 104–129. [CrossRef]

107. Vance, D.; Archer, C.; Bermin, J.; Perkins, J.; Statham, P.J.; Lohan, M.C.; Ellwood, M.J.; Mills, R.A. The copper isotope geochemistry of rivers and the oceans. *Earth Planet. Sci. Lett.* **2008**, *274*, 204–213. [CrossRef]

108. Vu, H.T.D.; Sohrin, Y. Diverse stoichiometry of dissolved trace metals in the Indian Ocean. *Sci. Rep.* **2013**, *3*, 1745.

109. Lagerström, M.E.; Field, M.P.; Séguret, M.; Fischer, L.; Hann, S.; Sherrell, R.M. Automated on-line flow-injection ICP-MS determination of trace metals (Mn, Fe, Co, Ni, Cu and Zn) in open ocean seawater: Application to the GEOTRACES program. *Mar. Chem.* **2013**, *155*, 71–80. [CrossRef]

110. Pinedo-Gonzalez, P.; West, A.J.; Rivera-Duarte, I.; Sanudo-Wilhelmy, S.A. Diel changes in trace metal concentration and distribution in coastal waters: Catalina Island as a study case. *Environ. Sci. Technol.* **2014**, *48*, 7730–7737. [CrossRef]

111. Middag, R.; Seferian, R.; Conway, T.M.; John, S.G.; Bruland, K.W.; de Baar, H.J.W. Intercomparison of dissolved trace elements at the Bermuda Atlantic Time Series station. *Mar. Chem.* **2015**, *177*, 476–489. [CrossRef]

112. Whitby, H.; Posacka, A.M.; Maldonado, M.T.; van den Berg, C.M. Copper-binding ligands in the NE Pacific. *Mar. Chem.* **2018**, *204*, 36–48. [CrossRef]

113. Ebling, A.M.; Landing, W.M. Sampling and analysis of the sea surface microlayer for dissolved and particulate trace elements. *Mar. Chem.* **2015**, *177*, 134–142. [CrossRef]

114. Cunliffe, M.; Engel, A.; Frka, S.; Gasparovic, B.; Guitart, C.; Murrell, J.C.; Salter, M.; Stolle, C.; Upstill-Goddard, R.; Wurl, O. Sea surface microlayers: A unified physicochemical and biological perspective of the air-ocean interface. *Prog. Oceanogr.* **2013**, *109*, 104–116. [CrossRef]

115. Wurl, O.; Wurl, E.; Miller, L.; Johnson, K.; Vagle, S. Formation and global distribution of sea-surface microlayers. *Biogeosciences* **2011**, *8*, 121–135. [CrossRef]

116. Antonowicz, J.P.; Mudryk, Z.; Zdanowicz, M. A relationship between accumulation of heavy metals and microbiological parameters in the surface microlayer and subsurface water of a coastal Baltic lake. *Hydrobiologia* **2015**, *762*, 65–80. [CrossRef]

117. Tovar-Sánchez, A.; Arrieta, J.M.; Duarte, C.M.; Sañudo-Wilhelmy, S.A. Spatial gradients in trace metal concentrations in the surface microlayer of the Mediterranean Sea. *Front. Mar. Sci.* **2014**, *1*, 79. [CrossRef]

118. Gašparović, B.; Plavšić, M.; Ćosović, B.; Saliot, A. Organic Matter Characterization in the Sea Surface Microlayers in the Subarctic Norwegian Fjords Region. *Mar. Chem.* **2007**, *105*, 1–14. [CrossRef]

119. Plavšić, M.; Gašparović, B.; Ćosović, B. Copper Complexation and Surfactant Activity of Organic Matter in Coastal Seawater and Surface Microlayer Samples of North Norwegian Fjords and Mediterranean. *Fresenius Environ. Bull.* **2007**, *16*, 372–378.

120. Karavoltsos, S.; Kalambokis, E.; Sakellari, A.; Plavšić, M.; Dotsika, E.; Karalis, P.; Leondiadis, L.; Dassenakis, M.; Scoullos, M. Organic Matter Characterization and Copper Complexing Capacity in the Sea Surface Microlayer of Coastal Areas of the Eastern Mediterranean. *Mar. Chem.* **2015**, *173*, 234–243. [CrossRef]

121. Ebling, A.M.; Landing, W.M. Trace Elements in the Sea Surface Microlayer: Rapid Responses to Changes in Aerosol Deposition. *Elem. Sci. Anthr.* **2017**, *5*, 42. [CrossRef]

122. Coale, K.H.; Bruland, K.W. Copper complexation in the Northeast Pacific. *Limnol. Oceanogr.* **1988**, *33*, 1084–1101. [CrossRef]

123. Moffett, J.W.; Zika, R.G. Oxidation kinetics of Cu(I) in seawater: Implications for its existence in the marine environment. *Mar. Chem.* **1983**, *13*, 239–251. [CrossRef]

124. Voelker, B.M.; Sedlak, D.L.; Zafiriou, O.C. Chemistry of superoxide radical in seawater: Reactions with organic Cu complexes. *Environ. Sci. Technol.* **2000**, *34*, 1036–1042. [CrossRef]

125. González-Dávila, M.; Santana-Casiano, J.M.; González, A.; Pérez, N.; Millero, F. Oxidation of copper (I) in seawater at nanomolar levels. *Mar. Chem.* **2009**, *115*, 118–124. [CrossRef]

126. Millero, F.J.; Woosley, R.; Ditrolio, B.; Waters, J. Effect of ocean acidification on the speciation of metals in seawater. *Oceanography* **2009**, *22*, 72–85. [CrossRef]

127. Pérez-Almeida, N.; González-Dávila, M.; Santana-Casiano, J.M.; González, A.G.; Suárez de Tangil, M. Oxidation of Cu (I) in seawater at low oxygen concentrations. *Environ. Sci. Technol.* **2013**, *47*, 1239–1247. [CrossRef]

128. Sharma, V.K.; Millero, F.J. Oxidation of copper (I) in seawater. *Environ. Sci. Technol.* **1988**, *22*, 768–771. [CrossRef]

129. González, A.G.; Pérez-Almeida, N.; Santana-Casiano, J.M.; Millero, F.J.; González-Dávila, M. Redox interactions of Fe and Cu in seawater. *Mar. Chem.* **2016**, *179*, 12–22. [CrossRef]

130. Pérez-Almeida, N.; González, A.G.; Santana-Casiano, J.M.; González-Dávila, M. Iron and copper redox interactions in UV-seawater: A kinetic model approach. *Chem. Geol.* **2019**, *506*, 149–161. [CrossRef]

131. Shi, J.; Abid, A.D.; Kennedy, I.M.; Hristova, K.R.; Silk, W.K. To duckweeds (*Landoltia punctata*), nanoparticulate copper oxide is more inhibitory than the soluble copper in the bulk solution. *Environ. Pollut.* **2011**, *159*, 1277–1282. [CrossRef]

132. Moffett, J.W.; Zika, R.G.; Brand, L.E. Distribution and potential sources and sinks of copper chelators in the Sargasso Sea. *Deep Sea Res.* **1990**, *37*, 27–36. [CrossRef]

133. Mackey, K.R.; Chien, C.-T.; Post, A.F.; Saito, M.A.; Paytan, A. Rapid and gradual modes of aerosol trace metal dissolution in seawater. *Front. Microbiol.* **2015**, *5*, 794. [CrossRef]

134. Pistocchi, R.; Guerrini, F.; Balboni, V.; Boni, L. Copper toxicity and carbohydrate production in the microalgae *Cylindrotheca fusiformis* and *Gymnodinium* sp. *Eur. J. Phycol.* **1997**, *32*, 125–132. [CrossRef]

135. Croot, P.L.; Moffett, J.W.; Brand, L.E. Production of extracellular Cu complexing ligands by eucaryotic phytoplankton in response to Cu stress. *Limnol. Oceanogr.* **2000**, *45*, 619–627. [CrossRef]

136. Vasconcelos, M.T.S.D.; Leal, M.F.C.; van den Berg, C.M.G. Influence of the nature of the exudates released by different marine algae on the growth, trace metal uptake, and exudation of Emiliania huxleyi in natural seawater. *Mar. Chem.* **2002**, *77*, 187–210. [CrossRef]

137. Leal, M.F.C.; Vasconcelos, M.; van den Berg, C.M. Copper-induced release of complexing ligands similar to thiols by *Emiliania huxleyi* in seawater cultures. *Limnol. Oceanogr.* **1999**, *44*, 1750–1762. [CrossRef]

138. Croot, P.L. Seasonal cycle of copper speciation in Gullmar Fjord, Sweden. *Limnol. Oceanogr.* **2003**, *48*, 764–776. [CrossRef]

139. Whitby, H.; van den Berg, C.M. Evidence for copper-binding humic substances in seawater. *Mar. Chem.* **2015**, *173*, 282–290. [CrossRef]

140. Sedlak, D.L.; Phinney, J.T.; Bedsworth, W.W. Strongly complexed Cu and Ni in wastewater effluents and surface runoff. *Environ. Sci. Technol.* **1997**, *31*, 3010–3016. [CrossRef]

141. Yang, R.; Van den Berg, C.M. Metal complexation by humic substances in seawater. *Environ. Sci. Technol.* **2009**, *43*, 7192–7197. [CrossRef]

142. Town, R.M.; Filella, M. Dispelling the myths: Is the existence of L1 and L2 ligands necessary to explain metal ion speciation in natural waters? *Limnol. Oceanogr.* **2000**, *45*, 1341–1357. [CrossRef]

143. Hurst, M.P.; Bruland, K.W. The use of Nafion-coated thin mercury film electrodes for the determination of the dissolved copper speciation in estuarine water. *Anal. Chim. Acta* **2005**, *546*, 68–78. [CrossRef]

144. Little, S.; Vance, D.; Walker-Brown, C.; Landing, W. The oceanic mass balance of copper and zinc isotopes, investigated by analysis of their inputs, and outputs to ferromanganese oxide sediments. *Geochim. Cosmochim. Acta* **2014**, *125*, 673–693. [CrossRef]

145. Sander, S.G.; Koschinsky, A. Metal flux from hydrothermal vents increased by organic complexation. *Nat. Geosci.* **2011**, *4*, 145. [CrossRef]

146. Williams, M.; Millward, G.; Nimmo, M.; Fones, G. Fluxes of Cu, Pb and Mn to the North-Eastern Irish Sea: The importance of sedimental and atmospheric inputs. *Mar. Pollut. Bull.* **1998**, *36*, 366–375. [CrossRef]

147. Yuan, H.; Song, J.; Li, X.; Li, N.; Duan, L. Distribution and contamination of heavy metals in surface sediments of the South Yellow Sea. *Mar Pollut. Bull.* **2012**, *64*, 2151–2159. [CrossRef]

148. Zhang, J.; Liu, C.L. Riverine composition and estuarine geochemistry of particulate metals in China—Weathering features, anthropogenic impact and chemical fluxes. *Estuar. Coast. Shelf Sci.* **2002**, *54*, 1051–1070. [CrossRef]

149. Guieu, C.; Loÿe-Pilot, M.D.; Benyahya, L.; Dufour, A. Spatial variability of atmospheric fluxes of metals (Al, Fe, Cd, Zn and Pb) and phosphorus over the whole Mediterranean from a one-year monitoring experiment: Biogeochemical implications. *Mar. Chem.* **2010**, *120*, 164–178. [CrossRef]

150. Calabrese, S.; Aiuppa, A.; Allard, P.; Bagnato, E.; Bellomo, S.; Brusca, L.; D'Alessandro, W.; Parello, F. Atmospheric sources and sinks of volcanogenic elements in a basaltic volcano (Etna, Italy). *Geochim. Cosmochim. Acta* **2011**, *75*, 7401–7425. [CrossRef]

151. Cattell, F.C.; Scott, W.D. Copper in aerosol particles produced by the ocean. *Science* **1978**, *202*, 429–430. [CrossRef]

152. Weisel, C.; Duce, R.; Fasching, J.; Heaton, R. Estimates of the transport of trace metals from the ocean to the atmosphere. *J. Geophys. Res. Atmos.* **1984**, *89*, 11607–11618. [CrossRef]

153. VanCuren, R.A. Asian aerosols in North America: Extracting the chemical composition and mass concentration of the Asian continental aerosol plume from long-term aerosol records in the western United States. *J. Geophys. Res. Atmos.* **2003**, *108*. [CrossRef]

154. Perry, K.D.; Cahill, T.A.; Schnell, R.C.; Harris, J.M. Long-range transport of anthropogenic aerosols to the National Oceanic and Atmospheric Administration baseline station at Mauna Loa Observatory, Hawaii. *J. Geophys. Res. Atmos.* **1999**, *104*, 18521–18533. [CrossRef]

155. Duan, J.; Tan, J. Atmospheric heavy metals and arsenic in China: Situation, sources and control policies. *Atmos. Environ.* **2013**, *74*, 93–101. [CrossRef]

156. Sternbeck, J.; Sjödin, Å.; Andréasson, K. Metal emissions from road traffic and the influence of resuspension—Results from two tunnel studies. *Atmos. Environ.* **2002**, *36*, 4735–4744. [CrossRef]

157. Bhanarkar, A.; Rao, P.; Gajghate, D.; Nema, P. Inventory of SO_2, PM and toxic metals emissions from industrial sources in Greater Mumbai, India. *Atmos. Environ.* **2005**, *39*, 3851–3864. [CrossRef]

158. Pacyna, J.M.; Pacyna, E.G. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environ. Rev.* **2001**, *9*, 269–298. [CrossRef]

159. Schulz, M.; Prospero, J.M.; Baker, A.R.; Dentener, F.; Ickes, L.; Liss, P.S.; Mahowald, N.M.; Nickovic, S.; Garcia-Pando, C.P.; Rodriguez, S.; et al. Atmospheric transport and deposition of mineral dust to the ocean: Implications for research needs. *Environ. Sci. Technol.* **2012**, *46*, 10390–10404. [CrossRef]

160. Kubilay, N.; Nickovic, S.; Moulin, C.; Dulac, F. An illustration of the transport and deposition of mineral dust onto the eastern Mediterranean. *Atmos. Environ.* **2000**, *34*, 1293–1303. [CrossRef]

161. Prenni, A.J.; Petters, M.D.; Kreidenweis, S.M.; Heald, C.L.; Martin, S.T.; Artaxo, P.; Garland, R.M.; Wollny, A.G.; Pöschl, U. Relative roles of biogenic emissions and Saharan dust as ice nuclei in the Amazon basin. *Nat. Geosci.* **2009**, *2*, 402. [CrossRef]

162. Guieu, C.; Chester, R.; Nimmo, M.; Martin, J.M.; Guerzoni, S.; Nicolas, E.; Mateu, J.; Keyse, S. Atmospheric input of dissolved and particulate metals to the northwestern Mediterranean. *Deep Sea Res. Top. Stud. Oceanogr.* **1997**, *44*, 655–674. [CrossRef]

163. Mao, J.; Fan, S.; Jacob, D.J.; Travis, K.R. Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols. *Atmos. Chem. Phys.* **2013**, *13*, 509–519. [CrossRef]

164. Deguillaume, L.; Leriche, M.; Desboeufs, K.; Mailhot, G.; George, C.; Chaumerliac, N. Transition metals in atmospheric liquid phases: Sources, reactivity, and sensitive parameters. *Chem. Rev.* **2005**, *105*, 3388–3431. [CrossRef]

165. Weber, R.J.; Guo, H.; Russell, A.G.; Nenes, A. High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years. *Nat. Geosci.* **2016**, *9*, 282. [CrossRef]

166. Fang, T.; Guo, H.; Zeng, L.; Verma, V.; Nenes, A.; Weber, R.J. Highly acidic ambient particles, soluble metals, and oxidative potential: A link between sulfate and aerosol toxicity. *Environ. Sci. Technol.* **2017**, *51*, 2611–2620. [CrossRef]

167. Desboeufs, K.V.; Sofikitis, A.; Losno, R.; Colin, J.L.; Ausset, P. Dissolution and solubility of trace metals from natural and anthropogenic aerosol particulate matter. *Chemosphere* **2005**, *58*, 195–203. [CrossRef]

168. Lim, B.; Jickells, T.D.; Colin, J.L.; Losno, R. Solubilities of Al, Pb, Cu, and Zn in rain sampled in the marine environment over the North Atlantic Ocean and Mediterranean Sea. *Glob. Biogeochem. Cycles* **1994**, *8*, 349–362. [CrossRef]

169. Hsu, S.C.; Wong, G.T.F.; Gong, G.C.; Shiah, F.K.; Huang, Y.T.; Kao, S.J.; Tsai, F.J.; Lung, S.C.C.; Lin, F.J.; Lin, I.I.; et al. Sources, solubility, and dry deposition of aerosol trace elements over the East China Sea. *Mar. Chem.* **2010**, *120*, 116–127. [CrossRef]

170. Hsu, S.C.; Lin, F.J.; Jeng, W.L. Seawater solubility of natural and anthropogenic metals within ambient aerosols collected from Taiwan coastal sites. *Atmos. Environ.* **2005**, *39*, 3989–4001. [CrossRef]

171. Kersten, M.; Kriews, M.; Forstner, U. Partitioning of trace metals released from polluted marine aerosols in coastal seawater. *Mar. Chem.* **1991**, *36*, 165–182. [CrossRef]

172. Chester, R.; Nimmo, M.; Corcoran, P.A. Rain water aerosol trace metal relationships at Cap Ferrat: A coastal site in the western Mediterranean. *Mar. Chem.* **1997**, *58*, 293–312. [CrossRef]

173. Williams, R.M. A model for the dry deposition of deposition of particles to natural water surfaces. *Atmos. Environ.* **1982**, *16*, 1933–1938.

174. Kadko, D.; Landing, W.M.; Shelley, R.U. A novel tracer technique to quantify the atmospheric flux of trace elements to remote ocean regions. *J. Geophys. Res. Oceans* **2015**, *120*, 848–858. [CrossRef]

175. Fu, J.P.; Wang, B.; Chen, Y.; Ma, Q.W. The influence of continental air masses on the aerosols and nutrients deposition over the western North Pacific. *Atmos. Environ.* **2018**, *172*, 1–11. [CrossRef]

176. Witt, M.L.I.; Mather, T.A.; Baker, A.R.; De Hoog, J.C.M.; Pyle, D.M. Atmospheric trace metals over the south-west Indian Ocean: Total gaseous mercury, aerosol trace metal concentrations and lead isotope ratios. *Mar. Chem.* **2010**, *121*, 2–16. [CrossRef]

177. Maenhaut, W.; Cafmeyer, J. Long-term atmospheric aerosol study at urban and rural sites in Belgium using multi-elemental analysis by particle-induced X-ray emission spectrometry and short-irradiation instrumental neutron activation analysis. *X Ray Spectrom.* **1998**, *27*, 236–246. [CrossRef]

178. Virkkula, A.; Aurela, M.; Hillamo, R.; Mäkelä, T.; Pakkanen, T.; Kerminen, V.M.; Maenhaut, W.; François, F.; Cafmeyer, J. Chemical composition of atmospheric aerosol in the European subarctic: Contribution of the Kola Peninsula smelter areas, central Europe, and the Arctic Ocean. *J. Geophys. Res. Atmos.* **1999**, *104*, 23681–23696. [CrossRef]

179. Witt, M.; Baker, A.R.; Jickells, T.D. Atmospheric trace metals over the Atlantic and South Indian Oceans: Investigation of metal concentrations and lead isotope ratios in coastal and remote marine aerosols. *Atmos. Environ.* **2006**, *40*, 5435–5451. [CrossRef]

180. Chand, D.; Hegg, D.A.; Wood, R.; Shaw, G.E.; Wallace, D.; Covert, D.S. Source attribution of climatically important aerosol properties measured at Paposo (Chile) during VOCALS. *Atmos. Chem. Phys.* **2010**, *10*, 10789–10801. [CrossRef]

181. Kang, J.; Choi, M.-S.; Yi, H.-I.; Song, Y.-H.; Lee, D.; Cho, J.-H. A five-year observation of atmospheric metals on Ulleung Island in the East/Japan Sea: Temporal variability and source identification. *Atmos. Environ.* **2011**, *45*, 4252–4262. [CrossRef]

182. Laing, J.R.; Hopke, P.K.; Hopke, E.F.; Husain, L.; Dutkiewicz, V.A.; Paatero, J.; Viisanen, Y. Long-term particle measurements in Finnish Arctic: Part I—Chemical composition and trace metal solubility. *Atmos. Environ.* **2014**, *88*, 275–284. [CrossRef]

183. Chance, R.; Jickells, T.D.; Baker, A.R. Atmospheric trace metal concentrations, solubility and deposition fluxes in remote marine air over the south-east Atlantic. *Mar. Chem.* **2015**, *177*, 45–56. [CrossRef]

184. Illuminati, S.; Annibaldi, A.; Truzzi, C.; Libani, G.; Mantini, C.; Scarponi, G. Determination of water:soluble, acid-extractable and inert fractions of Cd, Pb and Cu in Antarctic aerosol by square wave anodic stripping voltammetry after sequential extraction and microwave digestion. *J. Electroanal. Chem.* **2015**, *755*, 182–196. [CrossRef]

185. Baker, A.R.; Thomas, M.; Bange, H.W.; Sanchez, E.P. Soluble trace metals in aerosols over the tropical south-east Pacific offshore of Peru. *Biogeosciences* **2016**, *13*, 817–825. [CrossRef]

186. Campbell, A.L.; Mangan, S.; Ellis, R.P.; Lewis, C. Ocean acidification increases copper toxicity to the early life history stages of the polychaete Arenicola marina in artificial seawater. *Environ. Sci. Technol.* **2014**, *48*, 9745–9753. [CrossRef]

187. Lewis, C.; Ellis, R.P.; Vernon, E.; Elliot, K.; Newbatt, S.; Wilson, R.W. Ocean acidification increases copper toxicity differentially in two key marine invertebrates with distinct acid-base responses. *Sci. Rep.* **2016**, *6*, 21554. [CrossRef]