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Effect of Ocean Acidification on Organic and Inorganic Speciation of Trace Metals

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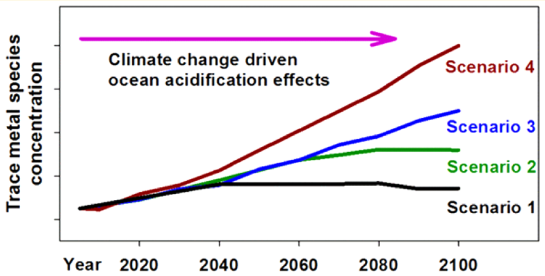
ABSTRACT: Rising concentrations of atmospheric carbon dioxide are causing acidification of the oceans. This results in changes to the concentrations of key chemical species such as hydroxide, carbonate and bicarbonate ions. These changes will affect the distribution of different forms of trace metals. Using IPCC data for $p\mathrm{CO_2}$ and pH under four future emissions scenarios (to the year 2100) we use a chemical speciation model to predict changes in the distribution of organic and inorganic forms of trace metals. Under a scenario where emissions peak after the year 2100, predicted free ion Al, Fe, Cu, and Pb concentrations increase by factors of up to approximately 21, 2.4, 1.5, and 2.0 respectively. Concentrations of organically complexed metal typically have a lower sensitivity to ocean acidification induced changes. Concentrations of organically complexed Mn, Cu, Zn, and Cd fall by up to 10%, while those of organically complexed Fe, Co, and Ni rise by up to 14%. Although modest, these changes may have significance for the biological availability of metals given the close adaptation of marine microorganisms to their environment.



INTRODUCTION

The burning of fossil fuels in the industrial era and the subsequent increase in atmospheric carbon dioxide ($p\mathrm{CO_2}$) have caused an observable pH decline in the surface oceans.[1−3] Earth's oceans are estimated to have been a sink for almost half of the $p\mathrm{CO_2}$ emissions post industrialization[4] and this trend in pH is expected to continue as anthropogenic emissions continue and $p\mathrm{CO_2}$ rises.[5]

Marine ecosystems and biogeochemical processes are sensitive to these changes because of the critical role that pH plays in mediating both chemical and physiological processes. Marine organisms possessing a skeleton of calcium carbonate are particularly sensitive to pH changes as the skeleton can dissolve when it reacts with free hydrogen ions.[6,7] These changes may also have secondary and tertiary effects on ocean biogeochemistry in terms of organic matter fluxes and cycling through the water column and on ocean oxygen minima zones.[8] Increasing $p\mathrm{CO_2}$ results in an increase in the total concentration of dissolved carbonate species. Resulting changes are a decrease in pH and $[\mathrm{CO_3}^{2-}]$ and an increase in $[\mathrm{HCO_3}^{-}]$ (Figure 1 shows these projected changes for a scenario where atmospheric carbon emissions peak after the year 2100).

Trace metals such as Mn, Fe, Co, Ni, Cu, and Zn are essential nutrients for biological functions and the concentration and chemical speciation of these metals may directly influence the distribution of phytoplankton species in ocean and neritic environments.[9−11] Biological uptake and utilization is related to competing chemical interactions, which include interactions with the organisms themselves. Cell membrane permeability is also affected by pH.[12] Hoffmann et al.,[13] recognized that further investigation into the influence of ocean acidification (OA) on trace metal biogeochemistry is necessary, particularly given that pH is a master variable in chemical and biological processes. Changes to hydrogen ion, carbonate, and hydroxide concentrations will directly affect the speciation of inorganic metal complexes and changes in hydrogen ion and metal free ion concentrations will affect the speciation of metal complexes with dissolved organic matter. Evaluation of the magnitude of chemical speciation responses to OA is necessary to assess the effects on the amount of metal available for biological uptake.

Millero et al.[14] modeled changes to the inorganic speciation of over 25 cationic metal species, projected to the year 2250 using the $p\mathrm{CO_2}$ and pH projections of Caldeira and Wickett.[5] They also estimated the effect on the organic speciation of Cu by adjusting conditional stability constants based on organic matter protonation data of Louis et al.[15] Under the assumption that increased protonation of organic ligands at lower pH lowered the concentration of unprotonated ligand binding sites available to complex Cu, they concluded that there may be a decrease of 25% in the effective concentration of organic ligand sites available for binding, but emphasized that the estimate was rudimentary and that further work on organic matter

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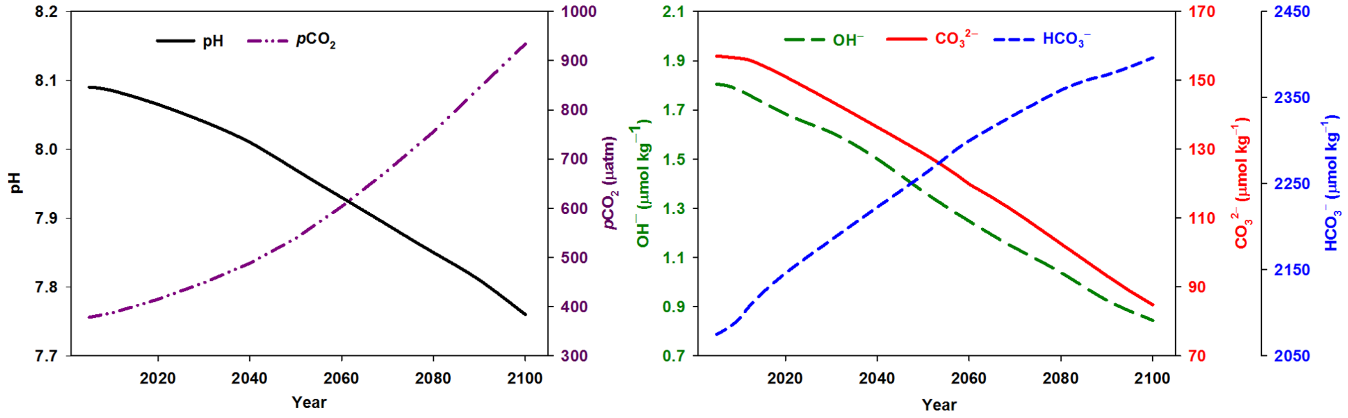

Figure 1. Trends in pH, pCO_2 and associated chemical species under RCP 8.5. The left panel shows pH and pCO_2 data as reported by IPCC.[1] The right panel shown the corresponding changes to OH^-, bicarbonate, and carbonate concentrations calculated using CO2SYS[37] with a temperature of 10 °C and salinity of 35 (see Materials and Methods section for the selection of stability constants).

complexation was required. Hirose[16] modeled the effect of changes in pH (but not carbonate species concentrations) on interactions between model organic ligands and Cu. The study reported that free ion concentrations did not respond to pH changes due to buffering by organic ligands. Gledhill et al.[17] investigated OA effects on the organic speciation of Cu and Fe in estuarine waters. Modeling, using an optimized NICA-Donnan model, and experimental results indicated that organic complexation of these metals would decrease and inorganic concentrations increase, as pH decreased. A lower fraction of metal associated with organic matter does not in itself indicate a changed availability for biological uptake as the nature of the inorganic species and biotic uptake mechanisms need to be considered.

Here we evaluate OA induced changes in both organic and inorganic trace metal speciation, with the aim of examining the potential changes to the concentrations of different forms that may reflect biological availability (specifically the free ion and organic fractions). We utilize the chemical speciation modeling code WHAM/Model VII (http://www.ceh.ac.uk/products/software/wham/), focusing on the biochemically significant metals as well as others that may exhibit toxic effects at sufficient concentrations (Al, Hg, Pb). The nature of the model used allows for competitive binding effects among metals, and among protons and metals, to be considered. The choice of thermodynamic constants and their influence on predictions is also discussed.

■ MATERIALS AND METHODS

Source Data. Required model inputs include pH and the concentrations of dissolved organic carbon, trace metals, and major ions (including the carbonate system). We have sought to use the most relevant and up to date data available for the required model inputs. For this work we made some assumptions in order to constrain the scope of the study. We assume that the binding properties of marine DOC are the same as those of terrestrial material, as supported by several studies.[18−21] We also assume that metal concentrations are constant over time, the implications of which are addressed in the discussion.

Projections for future pH and atmospheric pCO_2 values were taken from the most recent IPCC assessment.[1] These data are reported for Representative Concentration Pathways (RCPs) under four different carbon emissions scenarios. The data include a value for 2005 and forward projections to the year 2100. The four scenarios represent approximate peak emissions as, already peaked (RCP 2.6), peaking 2040 (RCP 4.5), peaking 2080 (RCP 6.0) and peaking after 2100 (RCP 8.5).[1]

In order to maintain consistency with typical methods for evaluating the carbonate system in marine environments, we calculated $[CO_3^{2-}]$ using the CO2SYS model[22] with the constants describing the carbonate and sulfate equilibrium with hydrogen ions from Mehrbach et al.[23] as subsequently refitted,[24,25] pH was on the total scale and the total boron concentration from Uppström.[26] This approach was recently used by Gledhill et al.,[17] who implemented the carbonate system into modeling with measured conditional stability constants using Visual MINTEQ.

Major ion concentrations (Na, Mg, K, Ca, Sr, Cl, SO_4, and F) were taken from Dickson and Goyet,[27] at a salinity of 35‰. Dissolved organic carbon concentration was fixed at 80 μM, which is a typical value for ocean surface waters between 30°N and 30°S.[28,29] For trace elements (not Al) we use concentrations reported for the Pacific Ocean.[30] Where ranges are given we use the midpoint of the range. The values used were 1.75 nmol L^{-1}, 0.26 nmol L^{-1}, 27 pmol L^{-1}, 2 nmol L^{-1}, 0.9 nmol L^{-1}, 0.15 nmol L^{-1}, 5.5 pmol L^{-1}, 5.25 pmol L^{-1}, and 32 pmol L^{-1}, for Mn, Fe(III), Co, Ni, Cu, Zn, Cd, Hg, and Pb, respectively For Al (not included in the above reference) we use 20.5 nmol L^{-1}.[31] Additional supplementary modeling that deviates from these conditions is described in the relevant sections of the results and discussion.

WHAM/Model VII. The model comprises two components, first the inorganic speciation code from WHAM[32] and second Humic Ion Binding Model VII, described in detail in Tipping et al.[33] Previous work has described applications of the model comparing predictions with measurements of metal speciation in coastal and estuarine[34] and open ocean environments.[35] Tipping et al.[36] evaluated over 2000 data points comparing measured values of chemical speciation to model predictions across freshwater, coastal and estuarine, and open ocean environments. Agreement for open ocean data was poorer than for coastal, estuarine, and freshwater environments, particularly for the weaker binding metals. However, the modeled values do generally follow the trends of the measured data,[35] and this is particularly relevant as we are examining trends in this present work.

Table 1. Distributions of Dominant Inorganic Species and the Organic Speciation of Trace Metals (Percent of Total Metal)[a]

	2005	2100			
RCP/Year	Baseline	RCP 2.6	RCP 4.5	RCP 6.0	RCP 8.5
Al − Inorg.	$Al(OH)_4^-$ (99.95%)	$Al(OH)_4^-$ (99.94%)	$Al(OH)_4^-$ (99.90%)	$Al(OH)_4^-$ (99.85%)	$Al(OH)_4^-$ (99.69%)
Al − Org.	0.008%	0.011%	0.018%	0.031%	0.075%
Mn − Inorg.	Mn^{2+} (45%)	Mn^{2+} (46%)	Mn^{2+} (46%)	Mn^{2+} (47%)	Mn^{2+} (48%)
	$MnCl^+$ (24%)	$MnCl^+$ (24%)	$MnCl^+$ (24%)	$MnCl^+$ (24%)	$MnCl^+$ (25%)
	$MnCO_3$ (13%)	$MnCO_3$ (12%)	$MnHCO_3^+$ (11%)	$MnHCO_3^+$ (12%)	$MnHCO_3^+$ (13%)
	$MnHCO_3^+$ (10%)	$MnHCO_3^+$ (11%)	$MnCO_3$ (11%)	$MnCO_3$ (10%)	$MnCO_3$ (7%)
	$MnSO_4$ (6%)	$MnSO_4$ (7%)	$MnSO_4$ (7%)	$MnSO_4$ (7%)	$MnSO_4$ (7%)
Mn − Org.	0.6%	0.6%	0.6%	0.6%	0.6%
Fe(III) − Inorg.	$Fe(OH)_3$ (0.95%)	$Fe(OH)_3$ (0.80%)	$Fe(OH)_3$ (0.57%)	$Fe(OH)_3$ (0.40%)	$Fe(OH)_3$ (0.23%)
	$Fe(OH)_2^-$ (0.20%)	$Fe(OH)_2^-$ (0.19%)	$Fe(OH)_2^-$ (0.16%)	$Fe(OH)_2^-$ (0.14%)	$Fe(OH)_2^-$ (0.11%)
Fe(III) − Org.	98.8%	98.9%	99.2%	99.4%	99.7%
Co − Inorg.	$CoCO_3$ (46%)	$CoCO_3$ (44%)	$CoCO_3$ (40%)	$CoHCO_3^+$ (39%)	$CoHCO_3^+$ (43%)
	$CoHCO_3^+$ (31%)	$CoHCO_3^+$ (32%)	$CoHCO_3^+$ (36%)	$CoCO_3$ (36%)	$CoCO_3$ (30%)
	Co^{2+} (15%)	Co^{2+} (16%)	Co^{2+} (16%)	Co^{2+} (17%)	Co^{2+} (19%)
Co − Org.	0.021%	0.021%	0.022%	0.022%	0.023%
Ni − Inorg.	$NiCO_3$ (53%)	$NiCO_3$ (51%)	$NiCO_3$ (47%)	$NiCO_3$ (43%)	$NiHCO_3^+$ (45%)
	$NiHCO_3^+$ (31%)	$NiHCO_3^+$ (33%)	$NiHCO_3^+$ (36%)	$NiHCO_3^+$ (40%)	$NiCO_3$ (36%)
	Ni^{2+} (10%)	Ni^{2+} (10%)	Ni^{2+} (11%)	Ni^{2+} (11%)	Ni^{2+} (13%)
Ni − Org.	0.8%	0.9%	0.9%	0.9%	0.9%
Cu − Inorg.	$CuHCO_3^+$ (4.8%)	$CuHCO_3^+$ (5.2%)	$CuHCO_3^+$ (6.1%)	$CuHCO_3^+$ (6.9%)	$CuHCO_3^+$ (8.3%)
	$CuCO_3$ (4.8%)	$CuCO_3$ (4.7%)	$CuCO_3$ (4.5%)	$CuCO_3$ (4.3%)	$CuCO_3$ (3.8%)
Cu − Org.	89.1%	88.9%	88.3%	87.9%	87.2%
Zn − Inorg.	$ZnHCO_3^+$ (43%)	$ZnHCO_3^+$ (44%)	$ZnHCO_3^+$ (47%)	$ZnHCO_3^+$ (48%)	$ZnHCO_3^+$ (50%)
	Zn^{2+} (27%)	Zn^{2+} (27%)	Zn^{2+} (26%)	Zn^{2+} (27%)	Zn^{2+} (27%)
	$ZnCO_3$ (14%)	$ZnCO_3$ (13%)	$ZnCO_3$ (11%)	$ZnCO_3$ (10%)	$ZnCl^+$ (8%)
	$ZnCl^+$ (8%)	$ZnCl^+$ (8%)	$ZnCl^+$ (8%)	$ZnCl^+$ (8%)	$ZnCO_3$ (7%)
	$ZnSO_4$ (6%)	$ZnSO_4$ (6%)	$ZnSO_4$ (6%)	$ZnSO_4$ (6%)	$ZnSO_4$ (6%)
Zn − Org.	0.75%	0.74%	0.72%	0.70%	0.67%
Cd − Inorg.	$CdCl^+$ (53%)	$CdCl^+$ (53%)	$CdCl^+$ (53%)	$CdCl^+$ (53%)	$CdCl^+$ (53%)
	$CdCl_2$ (40%)	$CdCl_2$ (40%)	$CdCl_2$ (40%)	$CdCl_2$ (40%)	$CdCl_2$ (40%)
	Cd^{2+} (4%)	Cd^{2+} (4%)	Cd^{2+} (4%)	Cd^{2+} (4%)	Cd^{2+} (4%)
Cd − Org.	0.052%	0.051%	0.050%	0.049%	0.048%
Hg − Inorg.	$HgCl_x^{(2\text{-}x)}$ (7×10^{-6} %)	$HgCl_x^{(2\text{-}x)}$ (8×10^{-6} %)	$HgCl_x^{(2\text{-}x)}$ (10^{-5} %)	$HgCl_x^{(2\text{-}x)}$ (10^{-5} %)	$HgCl_x^{(2\text{-}x)}$ (2×10^{-5} %)
Hg − Org.	100%	100%	100%	100%	100%
Pb − Inorg.	$PbCO_3$ (72%)	$PbCO_3$ (73%)	$PbCO_3$ (74%)	$PbCO_3$ (76%)	$PbCO_3$ (77%)
	$Pb(CO_3)_2^{2-}$ (23%)	$Pb(CO_3)_2^{2-}$ (21%)	$Pb(CO_3)_2^{2-}$ (19%)	$Pb(CO_3)_2^{2-}$ (17%)	$Pb(CO_3)_2^{2-}$ (13%)
Pb − Org.	0.72%	0.75%	0.80%	0.87%	1.03%

[a] Data are shown for the 2005 "baseline" year and for 2100 for the four RCP scenarios.

The Model VII constants are derived from 38 data sets for proton binding to humic and fulvic acids (over 8000 data points) and between 3 and 39 binding data sets for each of the metals covered in this study (an average of 484 data points for each metal, range 13−1616). The model uses a structured formulation of discrete, chemically plausible, binding sites for protons, to allow the creation of regular arrays of bidentate and tridentate binding sites for metals. The multidentate sites are required to explain strong binding observed at low metal:humic ratios. A small number of strong binding sites ("soft" ligand elements) are included, the equilibrium constants for which are related to constants for metal complexation with NH_3. An important feature of the model is that cations and protons compete for complexation at all the binding sites. We used the WHAM VII code to calculate chemical speciation under the various RCP scenarios, with total concentrations of solution components, and pH, as inputs (as described above). Concentrations of DOM were based on dissolved organic carbon (DOC), assuming that DOM comprises 50% carbon and that 65% of it is active with respect to cation binding and can be represented by fulvic acid.[37] For example, for a DOC concentration of 80 μmol L^{-1}, this corresponds to a fulvic acid concentration of 1.25 mg L^{-1} for modeling. The model predictions are those expected if DOM in natural waters behaves in the same way as extracted soil and freshwater fulvic and humic acids used in laboratory experiments, taking into account competition effects and inorganic speciation. DOC quality is not taken into consideration here, however, this is more likely to vary with depth, rather than spatially in the surface oceans, although more recalcitrant DOC at depth can be recirculated into surface waters.[38]

We use the default WHAM/Model VII database, which includes thermodynamic (ΔH) data for a large number of the trace metal chloride and sulfate complexes, however, these data are largely absent for hydroxide and carbonate complexes. Ionic strength is handled using the default WHAM/Model VII option, the Extended Debye−Hückel equation. Previous work[35] examined the differences in activities derived using this approach and the Pitzer equations. Differences in the free ion activities calculated using the two methods were within ±16%.

Table 2. WHAM/Model VII Calculated Metal Free Ion and Organically Bound Concentrations (Moles Per Gram of Organic Matter) For the Years 2005 and 2100 for the Four RCP Scenarios, Including the Percentage Change from the 2005 Baseline (Nc Denotes No Change)

	2005	2100			
	"baseline"	RCP 2.5	RCP 4.5	RCP 6.0	RCP 8.5
Organically Bound Metal/H^+ (nmol g^{-1} unless Otherwise Stated)					
H (mmol g^{-1})	1.39	1.40 (+1%)	1.44 (+4%)	1.48 (+7%)	1.54 (+11%)
Al	1.36	1.77 (+31%)	3.02 (+123%)	5.15 (+280%)	12.2 (+802%)
Mn	8.67	8.64 (−0.3%)	8.53 (−1.6%)	8.44 (−2.7%)	8.28 (−4.5%)
Fe	205	206 (+0.2%)	206 (+0.5%)	207 (+0.7%)	207 (+0.9%)
Co (pmol g^{-1})	4.51	4.60 (+2%)	4.65 (+3%)	4.76 (+6%)	4.95 (+10%)
Ni	1.33	1.36 (+3%)	1.39 (+5%)	1.44 (+8%)	1.52 (+14%)
Cu	642	640 (−0.2%)	636 (−0.9%)	633 (−1.4%)	628 (−2.1%)
Zn	0.90	0.89 (−1%)	0.86 (−4%)	0.84 (−7%)	0.81 (−10%)
Cd (pmol g^{-1})	2.28	2.26 (−1%)	2.22 (−3%)	2.17 (−5%)	2.10 (−8%)
Hg	4.20	4.20 (nc)	4.20 (nc)	4.20 (nc)	4.20 (nc)
Pb	0.18	0.19 (+5%)	0.20 (+11%)	0.22 (+21%)	0.26 (+43%)
Free Ion Concentration (mol L^{-1})					
Al	4.2×10^{-16}	6.0×10^{-16} (+45%)	1.3×10^{-15} (+202%)	2.6×10^{-15} (+530%)	8.7×10^{-15} (+1980%)
Mn	7.9×10^{-10}	8.0×10^{-10} (+1%)	8.1×10^{-10} (+2%)	8.2×10^{-10} (+3%)	8.3×10^{-10} (+5%)
Fe	5.3×10^{-22}	5.9×10^{-22} (+11%)	7.2×10^{-22} (+36%)	8.9×10^{-22} (+68%)	1.3×10^{-21} (+137%)
Co	4.2×10^{-12}	4.3×10^{-12} (+3%)	4.4×10^{-12} (+6%)	4.6×10^{-12} (+11%)	5.0×10^{-12} (+19%)
Ni	2.0×10^{-10}	2.1×10^{-10}(+4%)	2.2×10^{-10} (+8%)	2.3×10^{-10} (+11%)	2.5×10^{-10} (+25%)
Cu	8.7×10^{-13}	9.2×10^{-13} (+6%)	1.0×10^{-12} (+16%)	1.1×10^{-12} (+28%)	1.3×10^{-12} (+48%)
Zn	4.1×10^{-11}	4.1×10^{-11} (nc)	4.1×10^{-11} (nc)	4.1×10^{-11} (nc)	4.1×10^{-11} (+2%)
Cd	2.4×10^{-13}	2.4×10^{-13} (nc)	2.4×10^{-13} (nc)	2.4×10^{-13} (nc)	2.4×10^{-13} (nc)
Hg	2.1×10^{-33}	2.4×10^{-33} (+11%)	2.9×10^{-33} (+36%)	3.6×10^{-33} (+68%)	5.1×10^{-33} (+137%)
Pb	1.7×10^{-13}	1.8×10^{-13} (+9%)	2.1×10^{-13} (+26%)	2.5×10^{-13} (+49%)	3.3×10^{-13} (+97%)

■ RESULTS AND DISCUSSION

The chemical speciation behavior of the 10 metals of interest in surface seawater can be broken down into three distinct groups with respect to chemical speciation. (1) Strongly (>85%) associated with organic complexes (Fe, Cu, Hg). (2) Weakly (0.5−1%) associated with organic complexes together with significant complexation with (bi)carbonate (Mn, Ni, Zn, Pb). (3) low organic complexation (<0.1%), plus hydroxide dominated (Al), or carbonate dominated (Co), or chloride speciation dominated (Cd). Table 1 details the fraction of organic complexation and most prevalent inorganic species for each of these metals, for the year 2005 and for each RCP scenario, the year 2100.

The potential of metals in solution to interact with aquatic organisms can be considered in terms of binding to organic ligands. This is the case with the widely used biotic ligand model (BLM), which takes into account metal speciation, including competition, and employs a specific biological ligand (typically based on a fish gill) as a predictor of metal free ion interactions with an organism.[39] More generally, correlations between model predictions of metal binding to humic acid (using WHAM/Model VI) and the measured total body burden of freshwater[40] and soil organisms[41] have been demonstrated. In the modeling here we assume that such relationships also hold for marine organisms. While these different environments contrast in their relative dominance of diatoms and green algae, there is evidence to suggest that for some species cellular copper/carbon ratios,[42] and trends in initial copper uptake rates (in exposure experiments)[43] are comparable between freshwater and marine algae, at least for some species, although further comparison work is clearly desirable. Thus, we consider the measure of organically bound metal to represent a proxy for organism interactions with dissolved metal, which accounts for increasing proton competition due to acidification. Nevertheless, organism−metal interactions will also be closely related to metal free ion concentrations (with the additional consideration of competition effects), therefore we examine trends in both metal free ion and fulvic acid bound concentrations (Table 2).

Table 2 details the modeled concentrations of the organic bound metal (mol g^{-1}) and free ion concentrations (mol L^{-1}) detailing the relative change from the 2005 "baseline" year 2100 for each RCP scenario. Free ion concentrations (except Cd which is unchanged) are universally predicted to be higher for all RCP scenarios, and are predicted to rise as a result of ocean acidification. For RCP 8.5 predicted free ion Al, Fe, Cu and Pb concentrations increase by factors of approximately 21, 2.4, 1.5, and 2.0 respectively. Concentrations of organically complexed metal typically have a lower sensitivity to ocean acidification induced changes. The concentrations of organically complexed Mn, Cu, Zn, and Cd fall by up to 10%, while organically complexed Fe, Co, and Ni rise by up to 14%. Marine microorganisms have evolved efficient uptake systems and they take up trace metals close to the maximum allowed by chemistry and physics.[10] Given this behavior, small changes to the availability of metals may have significant impacts on organism function. Additionally, the interdependency between some metals (e.g., Cu and Fe),[10,44] means that falls in the availability of one metal and the simultaneous rise in another results in further uncertainty in predicting organism responses.

Two metals exhibit larger scale changes in the concentration of their organic complexes, namely Pb where an increase of 43% is predicted for RCP 8.5 and Al, where concentrations are predicted to increase by a factor of 8 under RCP 8.5, albeit from a very low baseline. For Pb, which is not known to play any biological function, it is unlikely that the magnitude of this change is sufficient to cause toxic effects in open ocean environments, as experiments on phytoplankton, which examined the effect of increasing Pb on natural communities from the Mediterranean and Black Seas and the North East Atlantic Ocean, found that concentrations had to increase by more than an order of magnitude from typical open ocean values for toxic effects to be evident.[45] Water quality guidelines have been developed for Al in coastal environments, with a suggested upper threshold some 40 times higher than the values used in our open ocean modeling.[46] However, data relating to the sensitivity of marine organisms to Al, including solely speciation changes, are scarce, making evaluation of the changes difficult. There is evidence to suggest that Antarctic diatoms incorporate Al when cultured with additional dissolved Al, resulting in decreases to dissolution rates and solubility of silica,[47] hence the significant speciation changes predicted here may influence such processes. The potential for increases in biologically available metals to result in toxic effects is difficult to determine and is also organism dependent.[48]

Figure 2 shows the trends in selected iron complexes. Fe(III) is not strongly complexed by carbonates so the changing speciation over time is largely as a result of the decreasing hydroxide ligand concentration (53% fall in [OH^-] over the period 2005 to 2100 under RCP 8.5). This increases the free ion concentration and simultaneously drives concentrations of the organically complexed metal higher. The increase in competition from the hydrogen ion is not sufficient to overcome the effects of the increased free ion concentration on predicted organic complexation. Thus, Fe may become more available as a result, which could have a positive effect on phytoplankton growth, particularly in Fe depleted regions of the oceans.[49] Shi and co-workers[50] conducted phytoplankton iron uptake experiments under various pCO$_2$ and pH scenarios relevant to ocean acidification, using EDTA to control inorganic iron concentrations. They found that growth rates were closely correlated to the inorganic iron, independent of pH and pCO$_2$ differences. Further data demonstrated that uptake rates in the presence of the siderophore azotochelin were not affected by variations in pH and pCO$_2$. Statistically significant differences in Fe uptake rates were only observed by Shi et al. when the full experimental pH range was considered (pH 8.4−7.8), with uptake rates reported to be up to 20% lower at the lowest pH compared to the highest, leading the authors to suggest the possibility of increased Fe stress of phytoplankton populations in some ocean areas as a result of acidification.[50] There are clearly challenges in performing experiments over the moderately small pH range predicted to occur to year 2100 (e.g., a fall of 0.35 pH units from pH 8.1 for RCP 8.5). However, such experiments are needed, including on natural seawater samples, to fully evaluate these effects.

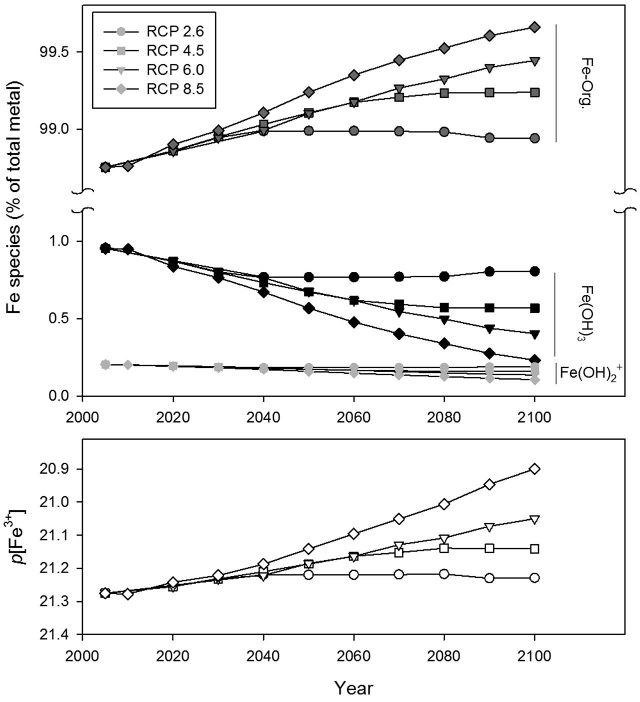

Figure 2. Trends in the speciation of Fe(III) until year 2100 under the four RCP scenarios as predicted by WHAM/Model VII. The top panel shows the three most prevalent iron species with the bottom panel showing the free ion concentration trends.

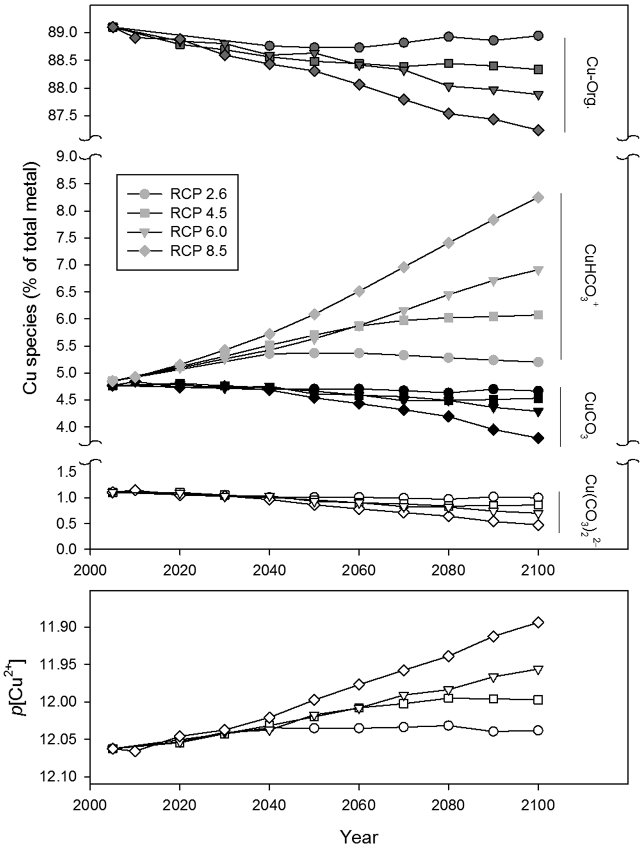

Figure 3. Trends in the speciation of Cu until year 2100 under the four RCP scenarios as predicted by WHAM/Model VII. The top panel shows the three most prevalent copper species with the bottom panel showing the free ion concentration trends.

Figure 3 shows the trends for selected Cu complexes. The small increase in the free ion concentration is not reflected in the organic speciation, due to increased competition at organic binding sites from protons. Inorganic complexes are dominated by (bi)carbonate species and changes are driven by decreases in carbonate complexes together with an increase in the bicarbonate speciation resulting from the increase in the proton concentration. The prediction of higher Cu free ion is consistent with the estimates of Millero and co-workers,[14] who calculated increases in free Cu of between 40 and 190% over the pH range 8.1−7.4 for a range of marine sites where speciation had been measured. Cyanobacterial reproduction rates have been shown to be negatively affected in the presence of copper free ion concentrations above pM levels,[51] levels that are exceeded by 2100 in all RCP scenarios except RCP 2.5. However, with predicted organic complexation of copper also being reduced, further experimental investigation is required to elucidate the effects on organisms.

Data from the RCP 2.5, 4.5, and 6.0 scenarios (Tables 1 and 2) demonstrate that effects on chemical speciation are less pronounced the lower the emissions scenario, although changes to Al are still significant for the lowest emissions scenario. Conversely, longer scale projections of Caldiera and Wickett,[5] based on an earlier IPCC emission projection, IS92a,[52] show atmospheric CO_2 peaking at 1900 ppm around the year 2300, with an associated fall in pH of 0.77 units in the surface ocean, sustained for several centuries. Thus, speciation changes could potentially be greater further into the future depending upon anthropogenic carbon emissions.

Organism sensitivity to acidification in the open oceans may be greater than in coastal environments due to low deviations in the concentrations of DOC.[38] Gledhill et al.[17] found that that for Fe and Cu in estuarine environments the concentration of DOC is more critical to chemical speciation relative to changes invoked by ocean acidification, and this is consistent with evidence of the protective effect of dissolved organic carbon on metal toxicity.[53]

In order to directly evaluate the effect of ocean acidification of the speciation of trace metals we excluded the consideration of changes in solubility of solid phase metals species, such as Fe oxides. Payten et al.[54] measured the release of metals from a desert dust addition to filtered seawater. They observed metal release in the sequence Al > Zn > Fe > Ni, Cu, Pb ≫ Cd > Co. Thus, colloidal and dust derived metal in the surface ocean, and higher solubility of acid reactive minerals, may result in higher absolute concentrations that may additionally have secondary effects on binding of other metals. Gledhill et al.[17] modeled the effects of ocean acidification including both the solubility and speciation of estuarine Fe(III). Their results indicated a decrease in iron binding by organic matter at lower pH (7.41 compared to 8.18) and a 3-fold increase in inorganic iron concentration. This contrasts with the modeling results of Hirose,[16] who concluded that acidification would increase the concentration of organically bound iron, largely driven by increased solubility of iron oxides. Understanding of the behavior of trace metals in response to elevated pCO_2 and lower pH can also be informative in the application of these elements to past climate reconstruction and understanding of the paleo-record.

Thermodynamic Constant Selection. Database selection can have significant effects on the outcome of model predictions. Here we use the WHAM default database, which is based upon several literature compilations.[32] For carbonate species the database includes the following complexes for the divalent metals included in this study (M, excluding Hg), MCO_3 and $MHCO_3^+$, all metals; and $M(CO_3)_2^{2-}$, Cu, Cd, and Pb. Despite $MgHCO_3^+$, $CaHCO_3^+$, and $NaHCO_3^0$ being important components of the pool of carbonate species in seawater,[55] previous investigations into the effects of pH variation or pCO_2 induced changes do not include trace metal $MHCO_3^+$ species in calculations.[14,56,57] Figure 4 shows the trends in the complexation of Ni, which is only weakly complexed by organic matter. There is a decrease in the concentration of the carbonate complex that is mirrored by an almost equal increase in bicarbonate complexation. This transition of complexation between carbonate species is also evident in predictions for Mn, Co, Cu, Zn, and Pb (Table 1, Figure 3). Millero et al.,[14] using the pH and pCO_2 data of Caldeira and Wickett,[5] predicted a decrease in inorganic Cu carbonate complexation from 85 to 76%, Ni from 30 to 16%, and Pb from 59 to 40% over the period 2000−2100, where bicarbonate complexation was not included in the calculations.

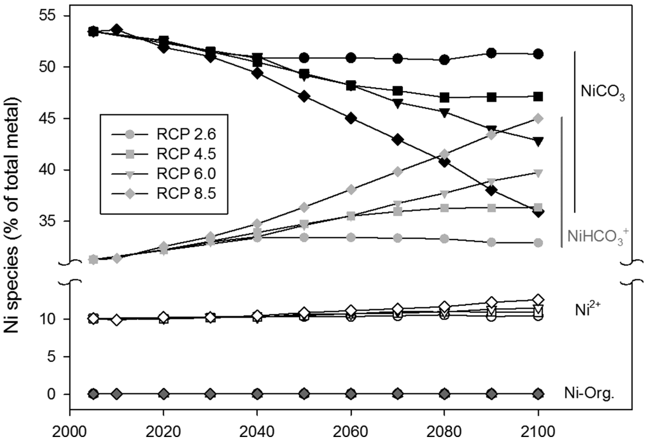

Figure 4. Trends in the modeled speciation of selected Ni species until year 2100 under the four RCP scenarios as predicted by WHAM/ Model VII.

Handling of Carbonate Complexation. For the modeling presented here we use CO2SYS to calculate the concentrations of carbonate species. Values for $[CO_3^{2-}]$ calculated using the default constants of WHAM/Model VII were ∼9% of the CO2SYS calculated values. Thus, using the default model parameters yields calculated metal carbonate and bicarbonate complex concentrations typically 9−38% of those calculated from the CO2SYS scenario. Exceptions are Pb where the values are ∼77%, and polycarbonate metals species ($M(CO_3)_2^{2-}$), which are ∼1% (7% for Pb) of the values calculated using CO2SYS. Decreased competition from lower carbonate ligand concentrations results in higher calculated values for free ion concentrations. For Al, Ca, Mn, Fe, Cu, Cd, and Hg, the values are 100−150%; for Co, Ni and Zn values are 220−440%; and for Pb the values is 870% of the values calculated using CO2SYS for carbonate speciation. The most significant variations in predicted organic matter binding occur for Ni, Zn and Pb, where the concentrations are larger by factors of four, two and eight, respectively.

These differences in calculated speciation highlight the variations obtained using different thermodynamic constants and indicate that further work is required in optimizing databases for accurate predictions. These improvements also need to include the measurement of trace metal interactions with isolated marine DOM.

Effects of Competition. WHAM/Model VII allows for competition between metals and protons and among different metals. Modeling each metal in the absence of other metals can reveal the extent of competitive effects. A previous study examined competition effects when comparing model prediction with speciation measurements of 330 data for Fe and 53 for Cu.[35] This work found that Fe speciation predictions are most sensitive to the presence/absence of Cu, and vice versa. In the present study, in the absence of competing metals more Fe is present as organic complexes (>99.93% for all years and

RCPs) and the free ion concentrations are typically 6% of the values in the presence of competing metals. However, the trend of increasing free ion over time is similar in magnitude to when other metals are included (i.e., the absolute concentration is lower but the trend on a logarithmic scale is similar in magnitude). For Cu, organic complex concentrations are ∼6% greater in the absence of competing metals and free ion concentrations are ∼54% of the values in the presence of competing metals. Hirose[16] modeled the effect of pH (range 7.5−8.5) on the speciation of marine copper with specific chelating ligands and found no change over the pH range. However, this did not include the effects of iron competition that will likely be manifest in natural systems. For metals that tend to exhibit weaker organic matter complexation, the changes are more subtle, with small increases in the extent of organic matter complexation (generally less than +1% of the total metal) and very small changes in free ion concentrations (up to a 6% reduction compared to in the presence of competing metals).

In some areas of the oceans, nutrient metal concentrations can be markedly lower than the values used in our modeling, including Fe (e.g., up to 10 times lower[49]). We ran an additional model simulation using a value of 20 pmol L^{-1} for Fe (7.7% of the mean value used for the primary modeling) while keeping all other values equal. The resulting changes to Cu speciation closely mirrored those predictions in the absence of other metals as discussed above. For Fe the organically bound fraction is 99.94% for the year 2005 and 99.98% for year 2100 RCP 8.5. The Fe free ion concentrations are lower than would be predicted solely by the lower total metal concentration. This is a reflection of higher relative occupancy of organic binding sites under conditions of lower total Fe. Trends in free ion concentrations, from a lower baseline, are of a similar magnitude to the primary modeling. The ocean acidification effect on relative biological availability is likely to be similar to that for the higher metal scenario.

The present study shows that changes to trace metal speciation as a result of acidification of the open oceans are generally modest. Changes may have significance for the biological availability of metals given the close adaptation of marine microorganisms to their environment, for example the requirement of Cu for Fe utilization. However, the magnitude of any effects will be constrained by future anthropogenic CO_2 emissions. Effects are also likely to differ depending upon location, as those in Fe depleted areas are likely to differ from other areas. Careful consideration of selection of thermodynamic data is necessary in order to achieve robust, accurate outcomes, ideally verified by measurements.

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Notes

The authors declare no competing financial interest.

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