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1 **The effect of ocean acidification on organic and inorganic speciation of trace metals**

2

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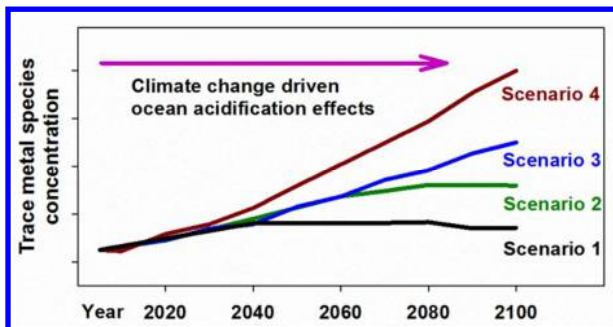
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14



16 Abstract

17 Rising concentrations of atmospheric carbon dioxide are causing acidification of the oceans.
18 This results in changes to the concentrations of key chemical species such as hydroxide,
19 carbonate and bicarbonate ions. These changes will affect the distribution of different forms
20 of trace metals. Using IPCC data for $p\text{CO}_2$ and pH under four future emissions scenarios (to
21 the year 2100) we use a chemical speciation model to predict changes in the distribution of
22 organic and inorganic forms of trace metals. Under a scenario where emissions peak after
23 the year 2100, predicted free ion Al, Fe, Cu and Pb concentrations increase by factors of up
24 to approximately 21, 2.4, 1.5 and 2.0 respectively. Concentrations of organically complexed
25 metal typically have a lower sensitivity to ocean acidification induced changes.
26 Concentrations of organically-complexed Mn, Cu, Zn and Cd fall by up to 10%, while those
27 of organically-complexed Fe, Co and Ni rise by up to 14%. Although modest, these changes
28 may have significance for the biological availability of metals given the close adaptation of
29 marine microorganisms to their environment.

30

31 Introduction

32 The burning of fossil fuels in the industrial era and the subsequent increase in atmospheric
33 carbon dioxide ($p\text{CO}_2$) have caused an observable pH decline in the surface oceans.¹⁻³
34 Earth's oceans are estimated to have been a sink for almost half of the $p\text{CO}_2$ emissions post
35 industrialisation⁴ and this trend in pH is expected to continue as anthropogenic emissions
36 continue and $p\text{CO}_2$ rises.⁵

37

38 Marine ecosystems and biogeochemical processes are sensitive to these changes because
39 of the critical role that pH plays in mediating both chemical and physiological processes.
40 Marine organisms possessing a skeleton of calcium carbonate are particularly sensitive to
41 pH changes as the skeleton can dissolve when it reacts with free hydrogen ions.^{6, 7} These

42 changes may also have secondary and tertiary effects on ocean biogeochemistry in terms of
43 organic matter fluxes and cycling through the water column and on ocean oxygen minima
44 zones.⁸ Increasing $p\text{CO}_2$ results in an increase in the total concentration of dissolved
45 carbonate species. Resulting changes are a decrease in pH and $[\text{CO}_3^{2-}]$ and an increase in
46 $[\text{HCO}_3^-]$ (Fig. 1 shows these projected changes for a scenario where atmospheric carbon
47 emissions peak after the year 2100).

48

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

62

63 Millero et al.¹⁴ modelled changes to the inorganic speciation of over 25 cationic metal
64 species, projected to the year 2250 using the $p\text{CO}_2$ and pH projections of Caldeira and
65 Wickett⁵. They also estimated the effect on the organic speciation of Cu by adjusting
66 conditional stability constants based on organic matter protonation data of Louis et al.¹⁵
67 Under the assumption that increased protonation of organic ligands at lower pH lowered the
68 concentration of unprotonated ligand binding sites available to complex Cu, they concluded

69 that there may be a decrease of 25% in the effective concentration of organic ligand sites
70 available for binding, but emphasised that the estimate was rudimentary and that further
71 work on organic matter complexation was required. Hirose¹⁶ modelled the effect of changes
72 in pH (but not carbonate species concentrations) on interactions between model organic
73 ligands and Cu. The study reported that free ion concentrations did not respond to pH
74 changes due to buffering by organic ligands. Gledhill et al.¹⁷ investigated OA effects on the
75 organic speciation of Cu and Fe in estuarine waters. Modelling, using an optimised NICA-
76 Donnan model, and experimental results indicated that organic complexation of these metals
77 would decrease and inorganic concentrations increase, as pH decreased. A lower fraction of
78 metal associated with organic matter does not in itself indicate a changed availability for
79 biological uptake as the nature of the inorganic species and biotic uptake mechanisms need
80 to be considered.

81

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

91

92 **Methods**

93 **Source data.** Required model inputs include pH and the concentrations of dissolved organic
94 carbon, trace metals, and major ions (including the carbonate system). We have sought to

95 use the most relevant and up to date data available for the required model inputs. For this
96 work we made some assumptions in order to constrain the scope of the study. We assume
97 that the binding properties of marine DOC are the same as those of terrestrial material, as
98 supported by several studies.¹⁸⁻²¹ We also assume that metal concentrations are constant
99 over time, the implications of which are addressed in the discussion.

100

101 Projections for future pH and atmospheric $p\text{CO}_2$ values were taken from the most recent
102 IPCC assessment.¹ These data are reported for Representative Concentration Pathways
103 (RCPs) under four different carbon emissions scenarios. The data include a value for 2005
104 and forward projections to the year 2100. The four scenarios represent approximate peak
105 emissions as, already peaked (RCP 2.6), peaking 2040 (RCP 4.5), peaking 2080 (RCP 6.0)
106 and peaking after 2100 (RCP 8.5).¹

107

108 In order to maintain consistency with typical methods for evaluating the carbonate system in
109 marine environments, we calculated $[\text{CO}_3^{2-}]$ using the CO2SYS model²² with the constants
110 describing the carbonate and sulphate equilibrium with hydrogen ions from Mehrbach et al.²³
111 as subsequently refitted,^{24, 25} pH was on the total scale and the total boron concentration
112 from Uppström.²⁶ This approach was recently used by Gledhill et al.,¹⁷ who implemented the
113 carbonate system into modelling with measured conditional stability constants using Visual
114 MINTEQ.

115

116 Major ion concentrations (Na, Mg, K, Ca, Sr, Cl, SO_4 and F) were taken from Dickson and
117 Goyet,²⁷ at a salinity of 35‰. Dissolved organic carbon concentration was fixed at 80 μM ,
118 which is a typical value for ocean surface waters between 30°N and 30°S.^{28, 29} For trace
119 elements (not Al) we use concentrations reported for the Pacific Ocean.³⁰ Where ranges are

120 given we use the mid-point of the range. The values used were, 1.75 nmol L⁻¹, 0.26 nmol
121 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
122 pmol L⁻¹, for Mn, Fe(III), Co, Ni, Cu, Zn, Cd, Hg and Pb, respectively For Al (not included in
123 the above reference) we use 20.5 nmol L⁻¹.³¹ Additional supplementary modelling that
124 deviates from these conditions is described in the relevant sections of the results and
125 discussion.

126

127 **WHAM/Model VII.** The model comprises two components, firstly the inorganic speciation
128 code from WHAM³² and secondly Humic Ion Binding Model VII, described in detail in Tipping
129 et al.³³ Previous work has described applications of the model comparing predictions with
130 measurements of metal speciation in coastal and estuarine³⁴ and open ocean
131 environments.³⁵ Tipping et al.³⁶ evaluated over 2000 data points comparing measured
132 values of chemical speciation to model predictions across freshwater, coastal and estuarine,
133 and open ocean environments. Agreement for open ocean data was poorer than for coastal,
134 estuarine, and freshwater environments, particularly for the weaker binding metals.
135 However, the modelled values do generally follow the trends of the measured data,³⁵ and
136 this is particularly relevant as we are examining trends in this present work.

137

138 The Model VII constants are derived from 38 datasets for proton binding to humic and fulvic
139 acids (over 8000 data points) and between 3 and 39 binding datasets for each of the metals
140 covered in this study (an average of 484 data points for each metal, range 13 to 1616). The
141 model uses a structured formulation of discrete, chemically plausible, binding sites for
142 protons, to allow the creation of regular arrays of bidentate and tridentate binding sites for
143 metals. The multidentate sites are required to explain strong binding observed at low
144 metal:humic ratios. A small number of strong binding sites ('soft' ligand elements) are
145 included, the equilibrium constants for which are related to constants for metal complexation

146 with NH_3 . An important feature of the model is that cations and protons compete for
147 complexation at all the binding sites. We used the WHAM VII code to calculate chemical
148 speciation under the various RCP scenarios, with total concentrations of solution
149 components, and pH, as inputs (as described above). Concentrations of DOM were based
150 on dissolved organic carbon (DOC), assuming that DOM comprises 50% carbon and that
151 65% of it is active with respect to cation binding and can be represented by fulvic acid.³⁷ For
152 example, for a DOC concentration of $80 \mu\text{mol L}^{-1}$, this corresponds to a fulvic acid
153 concentration of 1.25 mg L^{-1} for modelling. The model predictions are those expected if
154 DOM in natural waters behaves in the same way as extracted soil and freshwater fulvic and
155 humic acids used in laboratory experiments, taking into account competition effects and
156 inorganic speciation. DOC quality is not taken into consideration here, however, this is more
157 likely to vary with depth, rather than spatially in the surface oceans, although more
158 recalcitrant DOC at depth can be recirculated into surface waters.³⁸

159

160 We use the default WHAM/Model VII database, which includes thermodynamic (ΔH) data for
161 a large number of the trace metal chloride and sulfate complexes, however, these data are
162 largely absent for hydroxide and carbonate complexes. Ionic strength is handled using the
163 default WHAM/Model VII option, the Extended Debye–Hückel equation. Previous work³⁵
164 examined the differences in activities derived using this approach and the Pitzer equations.
165 Differences in the free ion activities calculated using the two methods were within $\pm 16\%$.

166

167 **Results and Discussion**

168 The chemical speciation behaviour of the ten metals of interest in surface seawater can be
169 broken down into three distinct groups with respect to chemical speciation. 1) Strongly
170 ($>85\%$) associated with organic complexes (Fe, Cu, Hg). 2) Weakly (0.5-1%) associated with
171 organic complexes together with significant complexation with (bi)carbonate (Mn, Ni, Zn,

172 Pb). 3) low organic complexation (<0.1%), plus hydroxide dominated (Al), or carbonate
173 dominated (Co), or chloride speciation dominated (Cd). Table 1 details the fraction of organic
174 complexation and most prevalent inorganic species for each of these metals, for the year
175 2005 and for each RCP scenario, the year 2100.

176

177 The potential of metals in solution to interact with aquatic organisms can be considered in
178 terms of binding to organic ligands. This is the case with the widely used biotic ligand model
179 (BLM), which takes into account metal speciation, including competition, and employs a
180 specific biological ligand (typically based on a fish gill) as a predictor of metal free ion
181 interactions with an organism.³⁹ More generally, correlations between model predictions of
182 metal binding to humic acid (using WHAM/Model VI) and the measured total body burden of
183 freshwater⁴⁰ and soil organisms⁴¹ have been demonstrated. In the modelling here we
184 assume that such relationships also hold for marine organisms. Whilst these different
185 environments contrast in their relative dominance of diatoms and green algae, there is
186 evidence to suggest that for some species cellular copper/carbon ratios,⁴² and trends in
187 initial copper uptake rates (in exposure experiments)⁴³ are comparable between freshwater
188 and marine algae, at least for some species, although further comparison work is clearly
189 desirable. Thus, we consider the measure of organically bound metal to represent a proxy
190 for organism interactions with dissolved metal, which accounts for increasing proton
191 competition due to acidification. Nevertheless, organism-metal interactions will also be
192 closely related to metal free ion concentrations (with the additional consideration of
193 competition effects), therefore we examine trends in both metal free ion and fulvic acid
194 bound concentrations (Table 2).

195

196 Table 2 details the modelled absolute concentrations of the organic bound metal (mol g^{-1})
197 and free ion concentrations (mol L^{-1}) detailing the relative change from the 2005 'baseline'
198 year 2100 for each RCP scenario. Free ion concentrations (except Cd which is unchanged)

199 are universally predicted to be higher for all RCP scenarios, and are predicted to rise as a
200 result of ocean acidification. For RCP 8.5 predicted free ion Al, Fe, Cu and Pb
201 concentrations increase by factors of approximately 21, 2.4, 1.5 and 2.0 respectively.
202 Concentrations of organically complexed metal typically have a lower sensitivity to ocean
203 acidification induced changes. The concentrations of organically-complexed Mn, Cu, Zn and
204 Cd fall by up to 10%, while organically-complexed Fe, Co and Ni rise by up to 14%. Marine
205 microorganisms have evolved efficient uptake systems and they take up trace metals close
206 to the maximum allowed by chemistry and physics.¹⁰ Given this behaviour, small changes to
207 the availability of metals may have significant impacts on organism function. Additionally, the
208 interdependency between some metals (e.g., Cu and Fe),^{10, 44} means that falls in the
209 availability of one metal and the simultaneous rise in another results in further uncertainty in
210 predicting organism responses.

211

212 Two metals exhibit larger scale changes in the concentration of their organic complexes,
213 namely Pb where an increase of 43% is predicted for RCP 8.5 and Al, where concentrations
214 are predicted to increase by a factor of eight under RCP 8.5, albeit from a very low baseline.
215 For Pb, which is not known to play any biological function, it is unlikely that the magnitude of
216 this change is sufficient to cause toxic effects in open ocean environments, as experiments
217 on phytoplankton, which examined the effect of increasing Pb on natural communities from
218 the Mediterranean and Black Seas and the North East Atlantic Ocean, found that
219 concentrations had to increase by more than an order of magnitude from typical open ocean
220 values for toxic effects to be evident.⁴⁵ Water quality guidelines have been developed for Al
221 in coastal environments, with a suggested upper threshold some 40 times higher than the
222 values used in our open ocean modelling.⁴⁶ However, data relating to the sensitivity of
223 marine organisms to Al, including solely speciation changes, are scarce, making evaluation
224 of the changes difficult. There is evidence to suggest that Antarctic diatoms incorporate Al
225 when cultured with additional dissolved Al, resulting in decreases to dissolution rates and

226 solubility of silica,⁴⁷ hence the significant speciation changes predicted here may influence
227 such processes. The potential for increases in biologically available metals to result in toxic
228 effects is difficult to determine and is also organism dependent.⁴⁸

229

230 Fig. 2 shows the trends in selected iron complexes. Fe(III) is not strongly complexed by
231 carbonates so the changing speciation over time is largely as a result of the decreasing
232 hydroxide ligand concentration (53% fall in [OH⁻] over the period 2005 to 2100 under RCP
233 8.5). This increases the free ion concentration and simultaneously drives concentrations of
234 the organically complexed metal higher. The increase in competition from the hydrogen ion
235 is not sufficient to overcome the effects of the increased free ion concentration on predicted
236 organic complexation. Thus, Fe may become more available as a result, which could have a
237 positive effect on phytoplankton growth, particularly in Fe depleted regions of the oceans.⁴⁹
238 Shi and co-workers⁵⁰ conducted phytoplankton iron uptake experiments under various $p\text{CO}_2$
239 and pH scenarios relevant to ocean acidification, using EDTA to control inorganic iron
240 concentrations. They found that growth rates were closely correlated to the inorganic iron,
241 independent of pH and $p\text{CO}_2$ differences. Further data demonstrated that uptake rates in the
242 presence of the siderophore azotochelin were not affected by variations in pH and $p\text{CO}_2$.
243 Statistically significant differences in Fe uptake rates were only observed by Shi et al. when
244 the full experimental pH range was considered (pH 8.4 to 7.8), with uptake rates reported to
245 be up to 20% lower at the lowest pH compared to the highest, leading the authors to suggest
246 the possibility of increased Fe stress of phytoplankton populations in some ocean areas as a
247 result of acidification.⁵⁰ There are clearly challenges in performing experiments over the
248 moderately small pH range predicted to occur to year 2100 (e.g. a fall of 0.35 pH units from
249 pH 8.1 for RCP 8.5). However, such experiments are needed, including on natural seawater
250 samples, to fully evaluate these effects.

251

252 Fig. 3 shows the trends for selected Cu complexes. The small increase in the free ion
253 concentration is not reflected in the organic speciation, due to increased competition at
254 organic binding sites from protons. Inorganic complexes are dominated by (bi)carbonate
255 species and changes are driven by decreases in carbonate complexes together with an
256 increase in the bicarbonate speciation resulting from the increase in the proton
257 concentration. The prediction of higher Cu free ion is consistent with the estimates of Millero
258 and co-workers,¹⁴ who calculated increases in free Cu of between 40 and 190% over the pH
259 range 8.1 to 7.4 for a range of marine sites where speciation had been measured.
260 Cyanobacterial reproduction rates have been shown to be negatively affected in the
261 presence of copper free ion concentrations above pM levels,⁵¹ levels that are exceeded by
262 2100 in all RCP scenarios except RCP 2.5. However, with predicted organic complexation of
263 copper also being reduced, further experimental investigation is required to elucidate the
264 effects on organisms.

265

266 Data from the RCP 2.5, 4.5 and 6.0 scenarios (Tables 1 and 2) demonstrate that effects on
267 chemical speciation are less pronounced the lower the emissions scenario, although
268 changes to Al are still significant for the lowest emissions scenario. Conversely, longer scale
269 projections of Caldiera and Wickett,⁵ based on an earlier IPCC emission projection, IS92a,⁵²
270 show atmospheric CO₂ peaking at 1900 ppm around the year 2300, with an associated fall in
271 pH of 0.77 units in the surface ocean, sustained for several centuries. Thus, speciation
272 changes could potentially be greater further into the future depending upon anthropogenic
273 carbon emissions.

274

275 Organism sensitivity to acidification in the open oceans may be greater than in coastal
276 environments due to low deviations in the concentrations of DOC.³⁸ Gledhill et al.¹⁷ found
277 that that for Fe and Cu in estuarine environments the concentration of DOC is more critical
278 to chemical speciation relative to changes invoked by ocean acidification, and this is

279 consistent with evidence of the protective effect of dissolved organic carbon on metal
280 toxicity.⁵³

281

282 In order to directly evaluate the effect of ocean acidification of the speciation of trace metals
283 we excluded the consideration of changes in solubility of solid phase metals species, such
284 as Fe oxides. Payten et al.⁵⁴ measured the release of metals from a desert dust addition to
285 filtered seawater. They observed metal release in the sequence
286 Al>Zn>Fe>Ni,Cu,Pb>>Cd>Co. Thus, colloidal and dust derived metal in the surface ocean,
287 and higher solubility of acid reactive minerals, may result in higher absolute concentrations
288 that may additionally have secondary effects on binding of other metals. Gledhill et al.¹⁷
289 modelled the effects of ocean acidification including both the solubility and speciation of
290 estuarine Fe(III). Their results indicated a decrease in iron binding by organic matter at lower
291 pH (7.41 compared to 8.18) and a 3 fold increase in inorganic iron concentration. This
292 contrasts with the modelling results of Hirose,¹⁶ who concluded that acidification would
293 increase the concentration of organically bound iron, largely driven by increased solubility of
294 iron oxides. Understanding of the behaviour of trace metals in response to elevated $p\text{CO}_2$
295 and lower pH can also be informative in the application of these elements to past climate
296 reconstruction and understanding of the paleo-record.

297

298 **Thermodynamic constant selection.** Database selection can have significant effects on
299 the outcome of model predictions. Here we use the WHAM default database, which is based
300 upon several literature compilations.³² For carbonate species the database includes the
301 following complexes for the divalent metals included in this study (M, excluding Hg), MCO_3
302 and MHCO_3^+ , all metals; and $\text{M}(\text{CO}_3)_2^{2-}$, Cu, Cd and Pb. Despite MgHCO_3^+ , CaHCO_3^+ and
303 NaHCO_3^0 being important components of the pool of carbonate species in seawater,⁵⁵
304 previous investigations into the effects of pH variation or $p\text{CO}_2$ induced changes do not

305 include trace metal MHCO_3^+ species in calculations.^{14, 56, 57} Fig. 4 shows the trends in the
306 complexation of Ni, which is only weakly complexed by organic matter. There is a decrease
307 in the concentration of the carbonate complex that is mirrored by an almost equal increase in
308 bicarbonate complexation. This transition of complexation between carbonate species is also
309 evident in predictions for Mn, Co, Cu, Zn and Pb (Table 1, Fig. 3). Millero et al.,¹⁴ using the
310 pH and $p\text{CO}_2$ data of Caldeira and Wickett,⁵ predicted a decrease in inorganic Cu carbonate
311 complexation from 85 to 76%, Ni from 30 to 16% and Pb from 59 to 40% over the period
312 2000 to 2100, where bicarbonate complexation was not included in the calculations.

313

314 *Handling of carbonate complexation.* For the modelling presented here we use CO2SYS to
315 calculate the concentrations of carbonate species. Values for $[\text{CO}_3^{2-}]$ calculated using the
316 default constants of WHAM/Model VII were ~9% of the CO2SYS calculated values. Thus,
317 using the default model parameters yields calculated metal carbonate and bicarbonate
318 complex concentrations typically 9 to 38% of those calculated from the CO2SYS scenario.
319 Exceptions are Pb where the values are ~77%, and polycarbonate metals species
320 ($\text{M}(\text{CO}_3)_2^{2-}$), which are ~1% (7% for Pb) of the values calculated using CO2SYS. Decreased
321 competition from lower carbonate ligand concentrations results in higher calculated values
322 for free ion concentrations. For Al, Ca, Mn, Fe, Cu, Cd and Hg, the values are 100-150%; for
323 Co, Ni and Zn values are 220-440%; and for Pb the values is 870% of the values calculated
324 using CO2SYS for carbonate speciation. The most significant variations in predicted organic
325 matter binding occur for Ni, Zn and Pb, where the concentrations are larger by factors of
326 four, two and eight respectively.

327

328 These differences in calculated speciation highlight the variations obtained using different
329 thermodynamic constants and indicate that further work is required in optimising databases

330 for accurate predictions. These improvements also need to include the measurement of
331 trace metal interactions with isolated marine DOM.

332

333 **Effects of competition.** WHAM/Model VII allows for competition between metals and
334 protons and among different metals. Modelling each metal in the absence of other metals
335 can reveal the extent of competitive effects. A previous study examined competition effects
336 when comparing model prediction with speciation measurements of 330 data for Fe and 53
337 for Cu.³⁵ This work found that Fe speciation predictions are most sensitive to the
338 presence/absence of Cu, and vice versa. In the present study, in the absence of competing
339 metals more Fe is present as organic complexes (>99.93% for all years and RCPs) and the
340 free ion concentrations are typically 6% of the values in the presence of competing metals.
341 However, the trend of increasing free ion over time is similar in magnitude to when other
342 metals are included (i.e., the absolute concentration is lower but the trend on a logarithmic
343 scale is similar in magnitude). For Cu, organic complex concentrations are ~6% greater in
344 the absence of competing metals and free ion concentrations are ~54% of the values in the
345 presence of competing metals. Hirose¹⁶ modelled the effect of pH (range 7.5 to 8.5) on the
346 speciation of marine copper with specific chelating ligands and found no change over the pH
347 range. However, this did not include the effects of iron competition that will likely be manifest
348 in natural systems. For metals that tend to exhibit weaker organic matter complexation, the
349 changes are more subtle, with small increases in the extent of organic matter complexation
350 (generally less than +1% of the total metal) and very small changes in free ion
351 concentrations (up to a 6% reduction compared to in the presence of competing metals).

352

353 In some areas of the oceans, nutrient metal concentrations can be markedly lower than the
354 values used in our modelling, including Fe (e.g., up to 10 times lower⁴⁹). We ran an
355 additional model simulation using a value of 20 pmol L⁻¹ for Fe (7.7% of the mean value
356 used for the primary modelling) whilst keeping all other values equal. The resulting changes

357 to Cu speciation closely mirrored those predictions in the absence of other metals as
358 discussed above. For Fe the organically bound fraction is 99.94% for the year 2005 and
359 99.98% for year 2100 RCP 8.5. The Fe free ion concentrations are lower than would be
360 predicted solely by the lower total metal concentration. This is a reflection of higher relative
361 occupancy of organic binding sites under conditions of lower total Fe. Trends in free ion
362 concentrations, from a lower baseline, are of a similar magnitude to the primary modelling.
363 The ocean acidification effect on relative biological availability is likely to be similar to that for
364 the higher metal scenario.

365

366 The present study shows that changes to trace metal speciation as a result of acidification of
367 the open oceans are generally modest. Changes may have significance for the biological
368 availability of metals given the close adaptation of marine microorganisms to their
369 environment, for example the requirement of Cu for Fe utilisation. However, the magnitude
370 of any effects will be constrained by future anthropogenic CO₂ emissions. Effects are also
371 likely to differ depending upon location, as those in Fe depleted areas are likely to differ from
372 other areas. Careful consideration of selection of thermodynamic data is necessary in order
373 to achieve robust, accurate outcomes, ideally verified by measurements.

374

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379

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535

536 **Tables**

537 Table 1. Distributions of dominant inorganic species and the organic speciation of trace
 538 metals (percent of total metal). Data are shown for the 2005 'baseline' year and for 2100 for
 539 the four RCP scenarios.

RCP/Year	2005		2100		
	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-x) (7x10 ⁻⁶ %)	HgCl _x ^(2-x) (8x10 ⁻⁶ %)	HgCl _x ^(2-x) (10 ⁻⁵ %)	HgCl _x ^(2-x) (10 ⁻⁵ %)	HgCl _x ^(2-x) (2x10 ⁻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%

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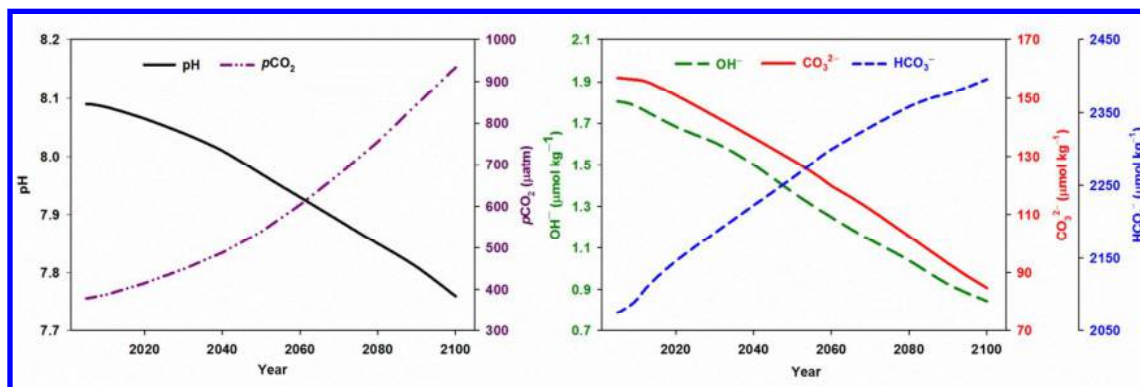
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542 Table 2. WHAM/Model VII calculated metal free ion and organically bound concentrations
 543 (moles per gram of organic matter) for the years 2005 and 2100 for the four RCP scenarios,
 544 including the percentage change from the 2005 baseline (nc 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%)

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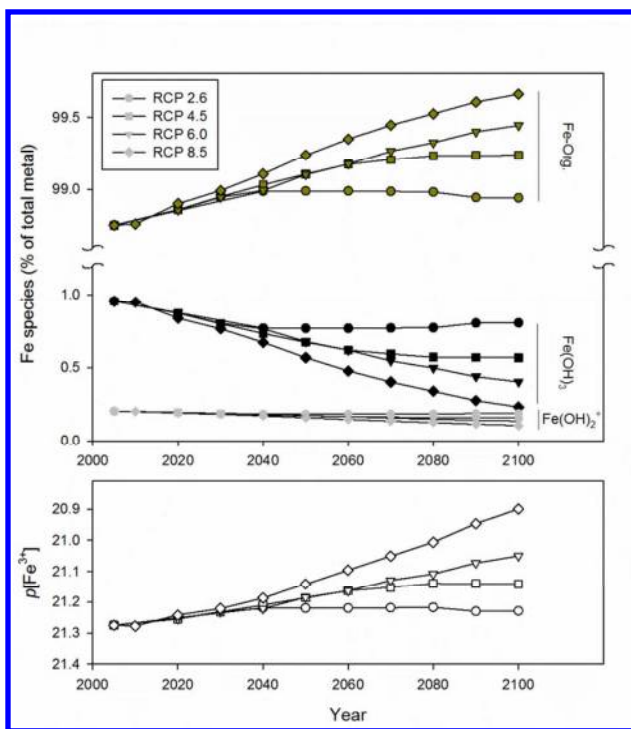
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547 **Figures**

548

549 Figure 1. Trends in pH, $p\text{CO}_2$ and associated chemical species under RCP 8.5. The left
550 panel shows pH and $p\text{CO}_2$ data as reported by IPCC.¹ The right panel shown the
551 corresponding changes to OH^- , bicarbonate and carbonate concentrations calculated using
552 CO2SYS³⁷ with a temperature of 10°C and salinity of 35 (see Methods section for the
553 selection of stability constants).

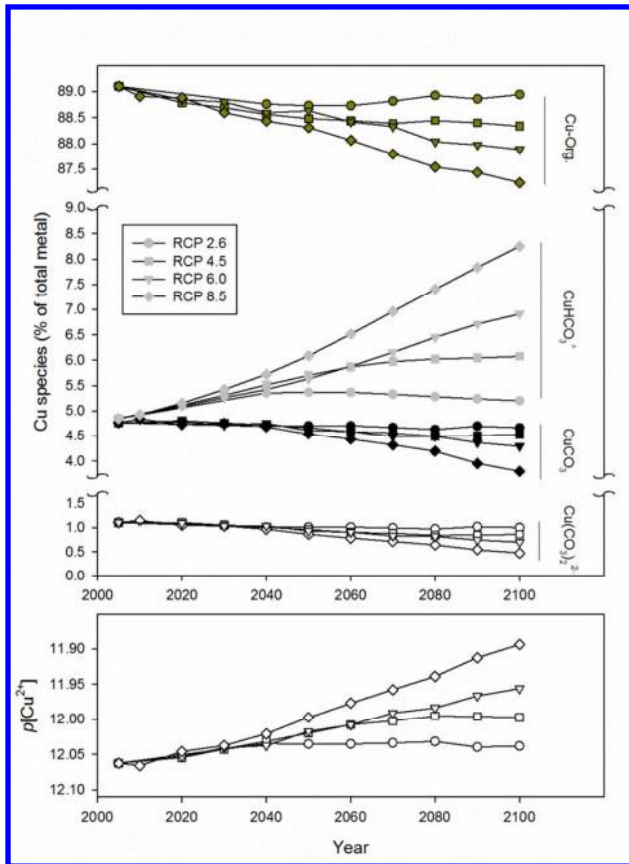
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556 Figure 2. Trends in the speciation of Fe(III) until year 2100 under the four RCP scenarios as
 557 predicted by WHAM/Model VII. The top panel shows the three most prevalent iron species
 558 with the bottom panel showing the free ion concentration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

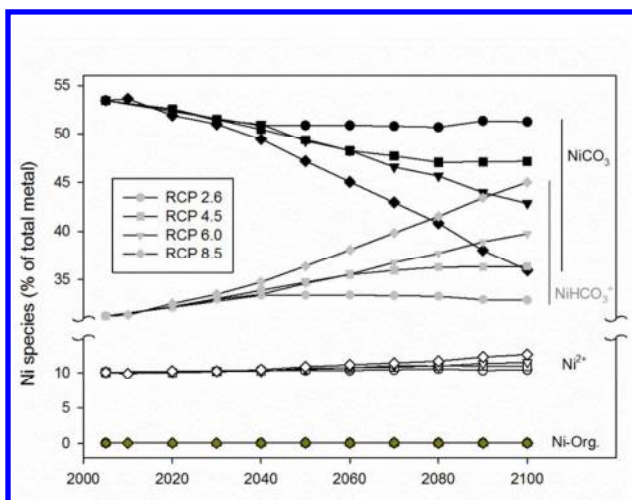
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560

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

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565

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

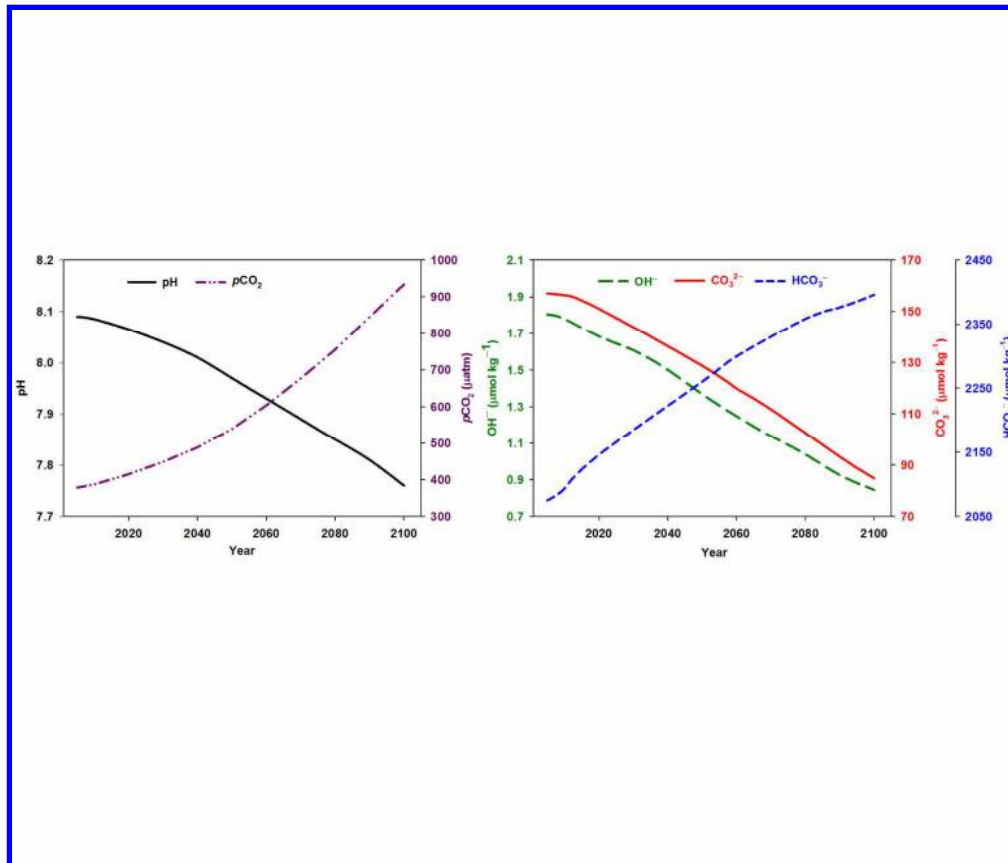


Figure 1. Trends in pH, $p\text{CO}_2$ and associated chemical species under RCP 8.5. The left panel shows pH and $p\text{CO}_2$ data as reported by IPCC.¹ The right panel shows the corresponding changes to OH^- , bicarbonate and carbonate concentrations calculated using CO2SYS³⁷ with a temperature of 10°C and salinity of 35 (see Methods section for the selection of stability constants).

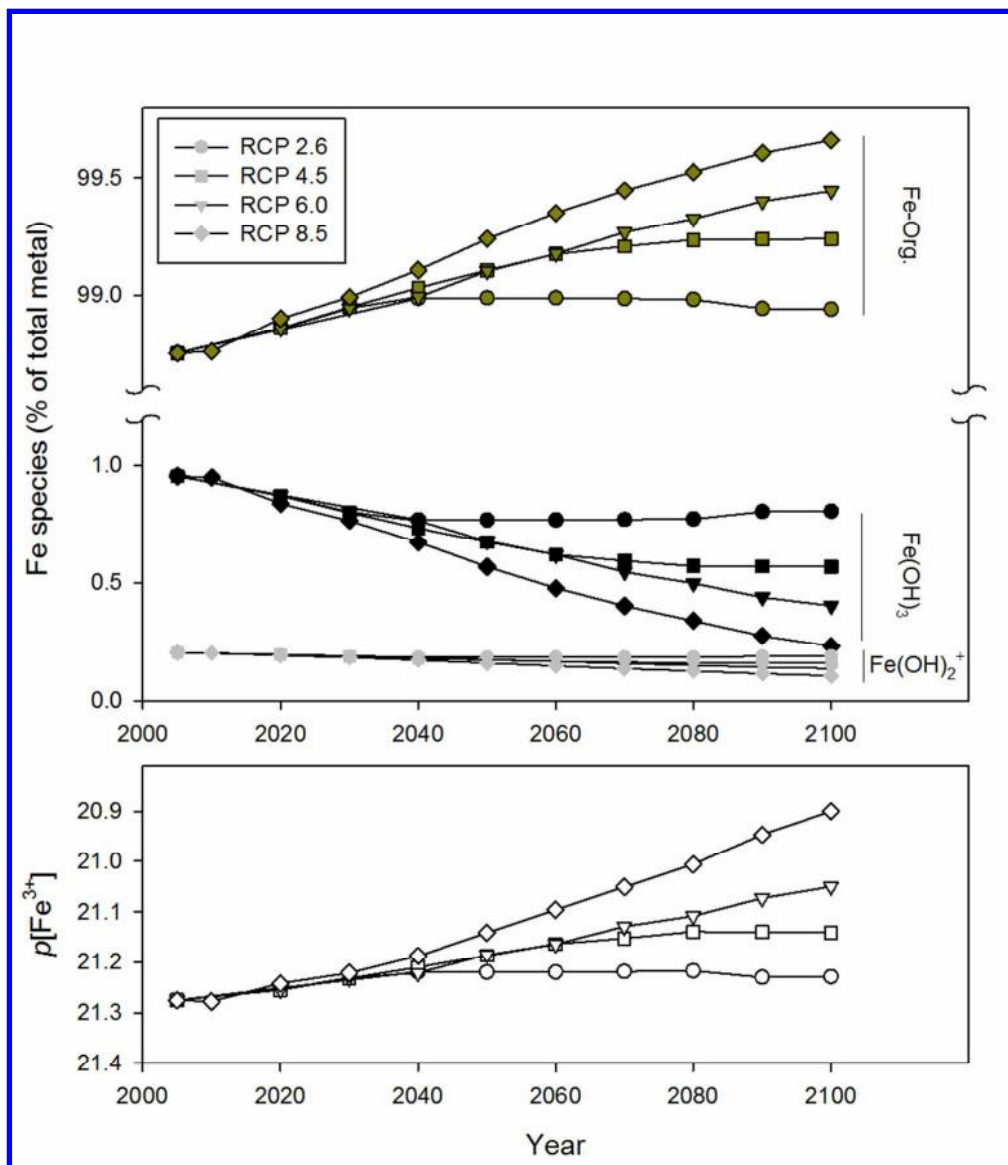


Figure 2. Trends in the speciation of Fe(III) until year 2100 under the four RCP scenarios as predicted by WHAM/Model VII. The top panel shows the three most prevalent iron species with the bottom panel showing the free ion concentration trends.

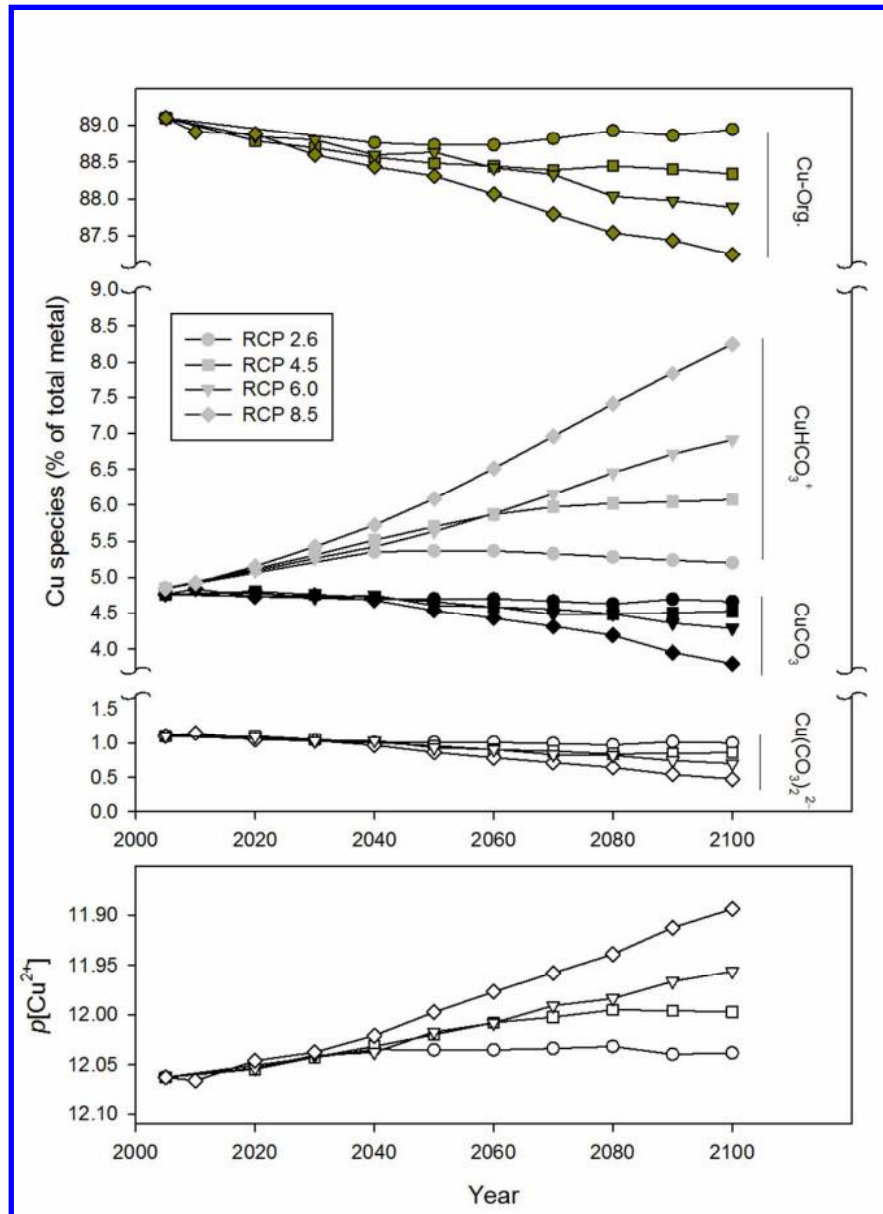


Figure 3. Trends in the speciation of Cu until year 2100 under the four RCP scenarios as predicted by WHAM/Model VII. The top panel shows the three most prevalent copper species with the bottom panel showing the free ion concentration trends.

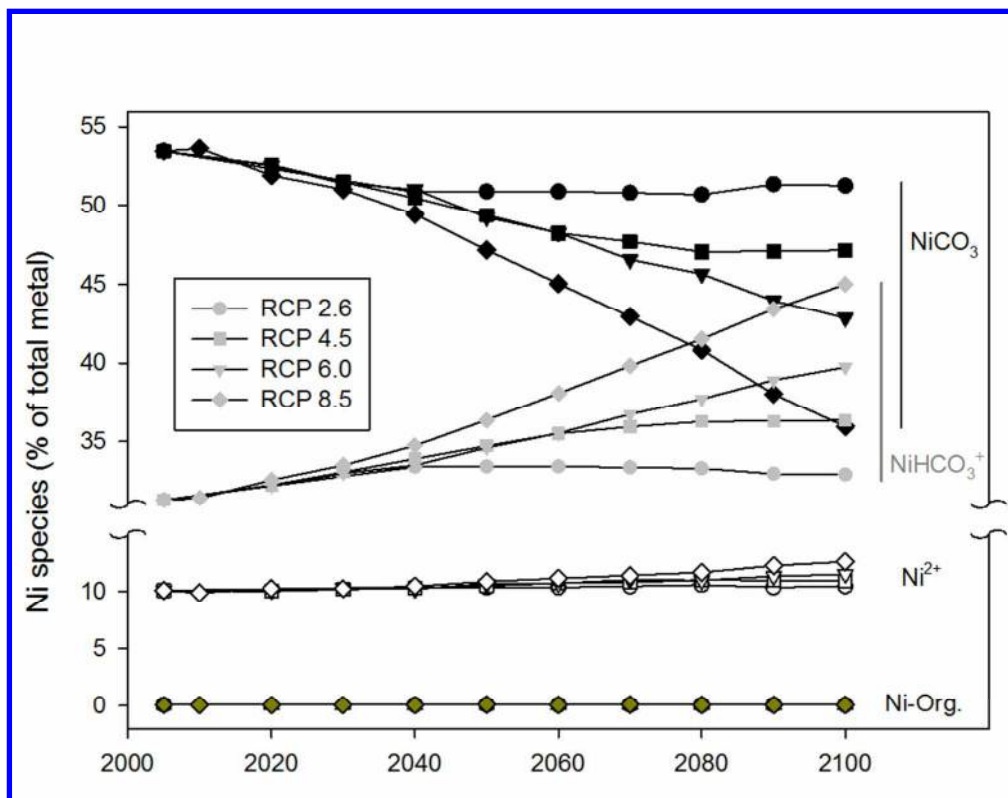


Figure 4. Trends in the modelled speciation of selected Ni species until year 2100 under the four RCP scenarios as predicted by WHAM/Model VII.