

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

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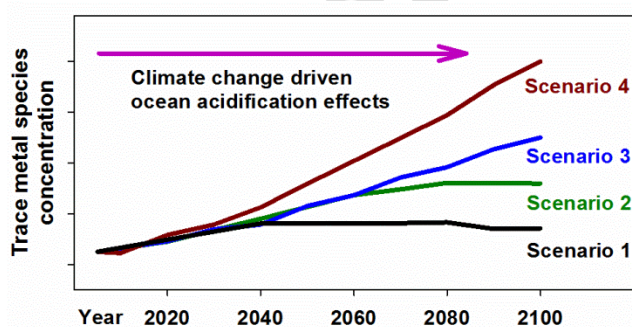
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19 **Abstract**

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

33

34 **Introduction**

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

40

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

45 changes may also have secondary and tertiary effects on ocean biogeochemistry in terms of
46 organic matter fluxes and cycling through the water column and on ocean oxygen minima
47 zones.⁸ Increasing $p\text{CO}_2$ results in an increase in the total concentration of dissolved
48 carbonate species. Resulting changes are a decrease in pH and $[\text{CO}_3^{2-}]$ and an increase in
49 $[\text{HCO}_3^-]$ (Fig. 1 shows these projected changes for a scenario where atmospheric carbon
50 emissions peak after the year 2100).

51

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

65

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

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

84

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

94

95 **Methods**

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

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

103

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

110

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

118

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

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

129

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

140

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

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

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

169

170 **Results and Discussion**

171 The chemical speciation behaviour of the ten metals of interest in surface seawater can be
172 broken down into three distinct groups with respect to chemical speciation. 1) Strongly
173 ($>85\%$) associated with organic complexes (Fe, Cu, Hg). 2) Weakly (0.5-1%) associated with
174 organic complexes together with significant complexation with (bi)carbonate (Mn, Ni, Zn,

175 Pb). 3) low organic complexation (<0.1%), plus hydroxide dominated (Al), or carbonate
176 dominated (Co), or chloride speciation dominated (Cd). Table 1 details the fraction of organic
177 complexation and most prevalent inorganic species for each of these metals, for the year
178 2005 and for each RCP scenario, the year 2100.

179

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

198

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

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

214

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

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

232

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

254

255 Fig. 3 shows the trends for selected Cu complexes. The small increase in the free ion
256 concentration is not reflected in the organic speciation, due to increased competition at
257 organic binding sites from protons. Inorganic complexes are dominated by (bi)carbonate
258 species and changes are driven by decreases in carbonate complexes together with an
259 increase in the bicarbonate speciation resulting from the increase in the proton
260 concentration. The prediction of higher Cu free ion is consistent with the estimates of Millero
261 and co-workers,¹⁴ who calculated increases in free Cu of between 40 and 190% over the pH
262 range 8.1 to 7.4 for a range of marine sites where speciation had been measured.
263 Cyanobacterial reproduction rates have been shown to be negatively affected in the
264 presence of copper free ion concentrations above pM levels,⁵¹ levels that are exceeded by
265 2100 in all RCP scenarios except RCP 2.5. However, with predicted organic complexation of
266 copper also being reduced, further experimental investigation is required to elucidate the
267 effects on organisms.

268

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

277

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

282 consistent with evidence of the protective effect of dissolved organic carbon on metal
283 toxicity.⁵³

284

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

300

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

308 include trace metal MHCO_3^+ species in calculations.^{14, 56, 57} Fig. 4 shows the trends in the
309 complexation of Ni, which is only weakly complexed by organic matter. There is a decrease
310 in the concentration of the carbonate complex that is mirrored by an almost equal increase in
311 bicarbonate complexation. This transition of complexation between carbonate species is also
312 evident in predictions for Mn, Co, Cu, Zn and Pb (Table 1, Fig. 3). Millero et al.,¹⁴ using the
313 pH and $p\text{CO}_2$ data of Caldeira and Wickett,⁵ predicted a decrease in inorganic Cu carbonate
314 complexation from 85 to 76%, Ni from 30 to 16% and Pb from 59 to 40% over the period
315 2000 to 2100, where bicarbonate complexation was not included in the calculations.

316

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

330

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

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

335

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

355

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

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

368

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

377

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382

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538

539 **Tables**

540 Table 1. Distributions of dominant inorganic species and the organic speciation of trace
 541 metals (percent of total metal). Data are shown for the 2005 'baseline' year and for 2100 for
 542 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%) MnCl ⁺ (24%) MnCO ₃ (13%) MnHCO ₃ ⁺ (10%) MnSO ₄ (6%)	Mn ²⁺ (46%) MnCl ⁺ (24%) MnCO ₃ (12%) MnHCO ₃ ⁺ (11%) MnSO ₄ (7%)	Mn ²⁺ (46%) MnCl ⁺ (24%) MnHCO ₃ ⁺ (11%) MnCO ₃ (11%) MnSO ₄ (7%)	Mn ²⁺ (47%) MnCl ⁺ (24%) MnHCO ₃ ⁺ (12%) MnCO ₃ (10%) MnSO ₄ (7%)	Mn ²⁺ (48%) MnCl ⁺ (25%) MnHCO ₃ ⁺ (13%) MnCO ₃ (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) ₂ ⁻ (0.20%)	Fe(OH) ₃ (0.80%) Fe(OH) ₂ ⁻ (0.19%)	Fe(OH) ₃ (0.57%) Fe(OH) ₂ ⁻ (0.16%)	Fe(OH) ₃ (0.40%) Fe(OH) ₂ ⁻ (0.14%)	Fe(OH) ₃ (0.23%) Fe(OH) ₂ ⁻ (0.11%)
Fe(III) – Org.	98.8%	98.9%	99.2%	99.4%	99.7%
Co – Inorg.	CoCO ₃ (46%) CoHCO ₃ ⁺ (31%) Co ²⁺ (15%)	CoCO ₃ (44%) CoHCO ₃ ⁺ (32%) Co ²⁺ (16%)	CoCO ₃ (40%) CoHCO ₃ ⁺ (36%) Co ²⁺ (16%)	CoHCO ₃ ⁺ (39%) CoCO ₃ (36%) Co ²⁺ (17%)	CoHCO ₃ ⁺ (43%) CoCO ₃ (30%) Co ²⁺ (19%)
Co – Org.	0.021%	0.021%	0.022%	0.022%	0.023%
Ni – Inorg.	NiCO ₃ (53%) NiHCO ₃ ⁺ (31%) Ni ²⁺ (10%)	NiCO ₃ (51%) NiHCO ₃ ⁺ (33%) Ni ²⁺ (10%)	NiCO ₃ (47%) NiHCO ₃ ⁺ (36%) Ni ²⁺ (11%)	NiCO ₃ (43%) NiHCO ₃ ⁺ (40%) Ni ²⁺ (11%)	NiHCO ₃ ⁺ (45%) NiCO ₃ (36%) Ni ²⁺ (13%)
Ni – Org.	0.8%	0.9%	0.9%	0.9%	0.9%
Cu – Inorg.	CuHCO ₃ ⁺ (4.8%) CuCO ₃ (4.8%)	CuHCO ₃ ⁺ (5.2%) CuCO ₃ (4.7%)	CuHCO ₃ ⁺ (6.1%) CuCO ₃ (4.5%)	CuHCO ₃ ⁺ (6.9%) CuCO ₃ (4.3%)	CuHCO ₃ ⁺ (8.3%) CuCO ₃ (3.8%)
Cu – Org.	89.1%	88.9%	88.3%	87.9%	87.2%
Zn – Inorg.	ZnHCO ₃ ⁺ (43%) Zn ²⁺ (27%) ZnCO ₃ (14%) ZnCl ⁺ (8%) ZnSO ₄ (6%)	ZnHCO ₃ ⁺ (44%) Zn ²⁺ (27%) ZnCO ₃ (13%) ZnCl ⁺ (8%) ZnSO ₄ (6%)	ZnHCO ₃ ⁺ (47%) Zn ²⁺ (26%) ZnCO ₃ (11%) ZnCl ⁺ (8%) ZnSO ₄ (6%)	ZnHCO ₃ ⁺ (48%) Zn ²⁺ (27%) ZnCO ₃ (10%) ZnCl ⁺ (8%) ZnSO ₄ (6%)	ZnHCO ₃ ⁺ (50%) Zn ²⁺ (27%) ZnCl ⁺ (8%) ZnCO ₃ (7%) ZnSO ₄ (6%)
Zn – Org.	0.75%	0.74%	0.72%	0.70%	0.67%
Cd – Inorg.	CdCl ⁺ (53%) CdCl ₂ (40%) Cd ²⁺ (4%)	CdCl ⁺ (53%) CdCl ₂ (40%) Cd ²⁺ (4%)	CdCl ⁺ (53%) CdCl ₂ (40%) Cd ²⁺ (4%)	CdCl ⁺ (53%) CdCl ₂ (40%) Cd ²⁺ (4%)	CdCl ⁺ (53%) CdCl ₂ (40%) 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%) Pb(CO ₃) ₂ ²⁻ (23%)	PbCO ₃ (73%) Pb(CO ₃) ₂ ²⁻ (21%)	PbCO ₃ (74%) Pb(CO ₃) ₂ ²⁻ (19%)	PbCO ₃ (76%) Pb(CO ₃) ₂ ²⁻ (17%)	PbCO ₃ (77%) Pb(CO ₃) ₂ ²⁻ (13%)
Pb – Org.	0.72%	0.75%	0.80%	0.87%	1.03%

543

544

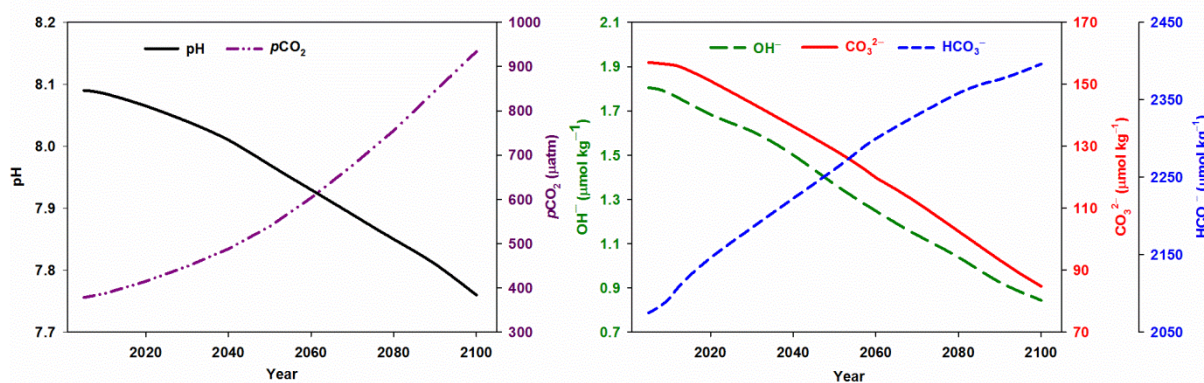
545 Table 2. WHAM/Model VII calculated metal free ion and organically bound concentrations
 546 (moles per gram of organic matter) for the years 2005 and 2100 for the four RCP scenarios,
 547 including the percentage change from the 2005 baseline (nc denotes no change).

	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%)

548

549

550 **Figures**

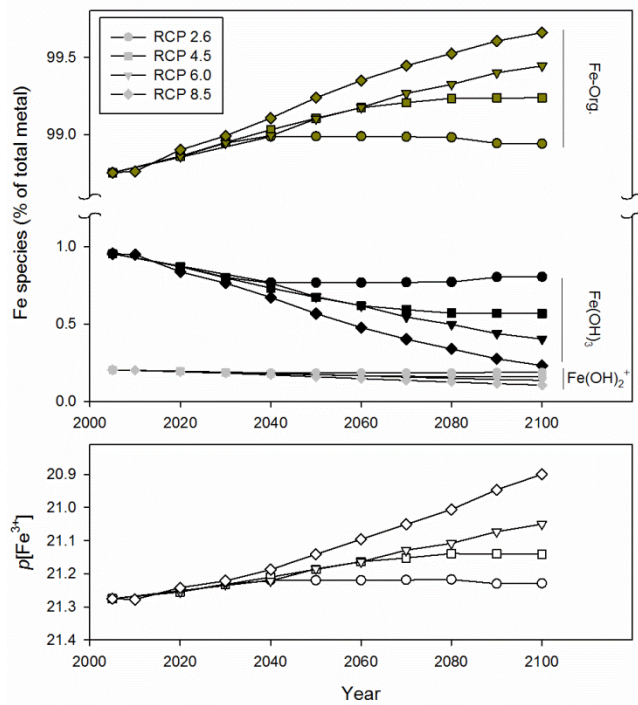


551

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

557

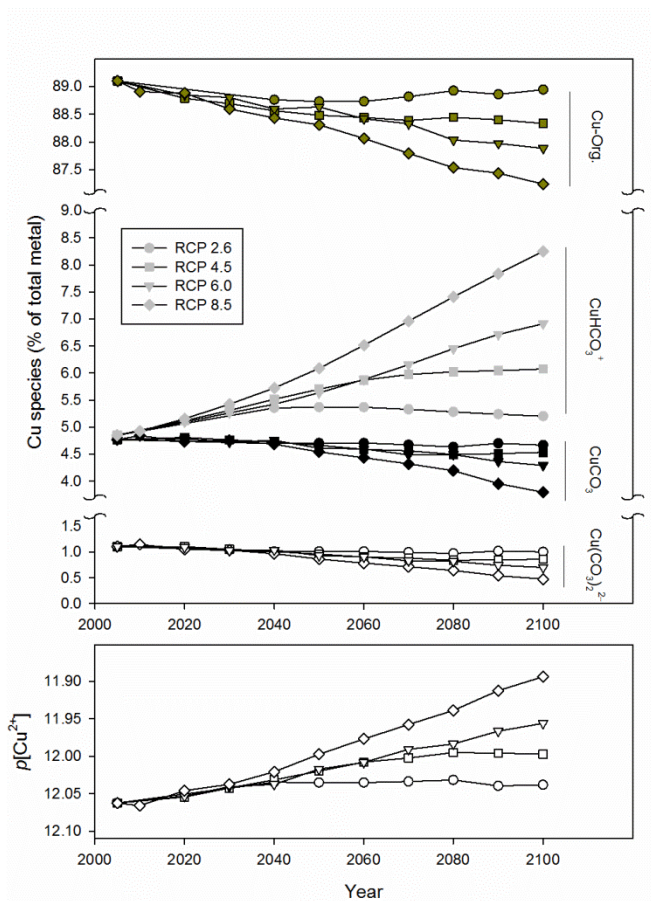
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558

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

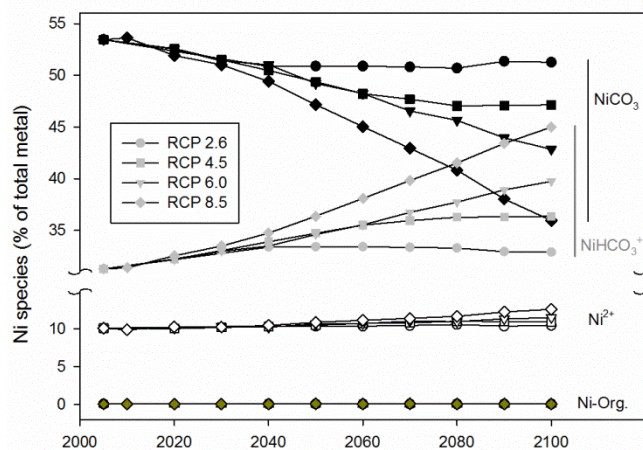
562



563

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

567



568

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

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