Supplement of Biogeosciences, 17, 757–770, 2020
https://doi.org/10.5194/bg-17-757-2020-supplement

Biogeosciences Open Access EGU

Supplement of

Particulate trace metal dynamics in response to increased CO_2 and iron availability in a coastal mesocosm experiment

M. Rosario Lorenzo et al.

Correspondence to: María Segovia (segovia@uma.es) and María T. Maldonado (mmaldonado@eoas.ubc.ca)

Supplemental Table S1. Instrumental conditions of ICP-MS and measurement parameters used during determination of trace elements concentrations.

Instrument conditions		
Instrument type	ELEMENT XR	
Torch	Fassel type	
Spray chamber	Glass cyclonic spray chamber	
Nebuliser	ESI microflow ST nebuliser (self-aspirating)	
Cones	Standard Ni sampler and skimmer	
RF Power (W)	1120	
Cooling gas flow rate (L min^{-1})	16	
Auxiliary gas flow rate (L min^{-1})	0.9	
Sample gas flow rate (L min^{-1})	1.2	
Sample matrix	1% nitric acid	
Method acquisition parameters		
Scan type	E-scan	
Spectral resolution	Low (nominal m/Δm~300)	Medium (nominal m/Δm~3000)
Isotopes of interes	^{95}Mo ^{98}Mo ^{111}Cd ^{114}Cd ^{206}Pb ^{208}Pb	^{27}Al ^{31}P ^{47}Ti ^{49}Ti ^{55}Mn ^{56}Fe ^{59}Co ^{63}Cu ^{65}Cu ^{66}Zn ^{68}Zn
Internal standard	^{115}In	^{115}In
Mass window (%)	40	125
Samples/peak	10	20
Samples time (ms)	10	10
Runs	3	3
Passes	10	10

Supplemental Table S2. The concentration of particulate metals (nM) (without oxalate wash) in seawater in the different mesocosm treatments (LC: ambient CO_2; HC: increased CO_2 (900 µatm); -DFB: no DFB addition; +DFB: with a 70 nM DFB addition) during the development of a bloom of *Emiliania huxleyi* (especially in treatment LC+DFB). Data are means of measurements in 3 independent mesocosms (n = 3) except for LC−DFB where n = 2. Error bars indicate SD. Data is plotted in Figure 1. Note that the concentrations of Co, Pb and Cd were much lower than the rest of the metals, so their values were multiplied by either (10) or (100) in the table (e.g. Co, Cd, and Pb concentrations on d12 in LC-DFB were 0.01, 0.0028 and 0.025 nmol L^{-1}, respectively).

	Treatment	**Al**	**Ti**	**P**	**Fe**	**Cu**	**Co** (·10)	**Zn**	**Cd** (·100)	**Mn**	**Mo**	**Pb** (·10)
d12												
	LC-DFB	9.16 (3.16)	1.30 (0.27)	131.8 (27.05)	13.5 (0.88)	0.24 (0.04)	0.10 (0.06)	3.24 (0.15)	0.28 (0.06)	0.24 (0.06)	0.08 (0.01)	0.25 (0.01)
	LC+DFB	29.2 (6.00)	3.16 (0.52)	329.3 (107.8)	14.8 (1.78)	0.30 (0.01)	0.22 (0.05)	14.81 (2.69)	0.91 (0.22)	0.54 (0.14)	0.09 (0.02)	0.56 (0.05)
	HC+DFB	11.0 (7.04)	1.23 (0.54)	120.1 (45.49)	7.29 (0.41)	0.32 (0.09)	0.07 (0.01)	3.13 (0.55)	0.26 (0.23)	0.17 (0.06)	0.04 (0.02)	0.12 (0.05)
	HC-DFB	18.1 (8.53)	1.28 (0.53)	193.7 (66.43)	11.2 (4.43)	0.29 (0.08)	0.11 (0.07)	4.48 (0.38)	0.23 (0.03)	0.29 (0.13)	0.07 (0.01)	0.85 (0.51)
d17												
	LC-DFB	27.1 (14.8)	0.27 (0.14)	171.6 (20.1)	17.1 (8.08)	0.10 (0.04)	0.07 (0.00)	2.87 (1.23)	0.45 (0.32)	0.20 (0.04)	0.08 (0.05)	0.28 (0.11)
	LC+DFB	29.2 (19.2)	4.63 (2.84)	972.8 (563)	12.2 (9.14)	1.02 (0.56)	0.68 (0.42)	62.7 (38.2)	2.38 (0.87)	2.36 (1.49)	0.37 (0.08)	0.77 (0.41)
	HC+DFB	5.94 (4.38)	0.59 (0.34)	134.1 (47.7)	1.98 (0.76)	0.13 (0.07)	0.05 (0.02)	2.53 (0.49)	0.19 (0.03)	0.14 (0.04)	0.06 (0.03)	0.14 (0.05)
	HC-DFB	35.4 (17.9)	4.11 (1.86)	372.7 (253)	9.34 (7.29)	0.50 (0.06)	0.19 (0.02)	5.88 (3.78)	0.98 (0.65)	0.56 (0.42)	0.09 (0.06)	1.42 (0.37)
d21												
	LC-DFB	19.2 (1.01)	2.95 (0.06)	341.9 (20.1)	5.83 (1.81)	0.48 (0.02)	0.35 (0.03)	15.5 (0.97)	1.13 (0.26)	0.66 (0.06)	0.10 (0.02)	2.07 (0.26)
	LC+DFB	9.18 (5.35)	1.53 (0.55)	380.9 (45.3)	2.52 (0.35)	0.44 (0.06)	0.37 (0.07)	26.2 (2.96)	1.41 (0.25)	0.88 (0.09)	0.20 (0.05)	1.23 (0.75)
	HC+DFB	2.64 (1.58)	0.49 (0.40)	95.9 (12.5)	0.53 (0.32)	0.15 (0.06)	0.09 (0.04)	3.24 (1.96)	0.30 (0.16)	0.14 (0.05)	0.05 (0.01)	0.19 (0.05)
	HC-DFB	8.22 (2.05)	0.87 (0.20)	134.7 (22.1)	3.19 (1.21)	0.26 (0.05)	0.12 (0.02)	3.47 (0.97)	0.27 (0.13)	0.22 (0.08)	0.08 (0.03)	0.58 (0.18)

Supplemental Table S3. The concentration of particulate metals (nM), with oxalate wash, in seawater in the different mesocosm treatments; (LC: ambient CO_2; HC: increased CO_2 (900 µatm); -DFB: no DFB addition; +DFB: with a 70 nM DFB addition) during the development of a bloom of *Emiliania huxleyi* (especially in treatment LC+DFB). Data are means of measurements in 3 independent mesocosms (n = 3) except for LC−DFB where n = 2. Error bars indicate SD. Note that the concentrations of Co, Pb and Cd were much lower than the rest of the metals, so their values were multiplied by either (10) or (100) in the table (e.g. Co, Cd, and Pb concentrations on d12 in LC-DFB were 0.007, 0.0009 and 0.01 nmol L^{-1}, respectively). The percentage (%) indicates the mean quantity of metal remaining after the oxalate wash. Statistically significant differences are indicated with asterisk (* if p <0.05; ** if p <0.01 and *** if p<0.001; ns: not significant).

	Treatment	**Al**	**Ti**	**P**	**Fe**	**Cu**	**Co** (·10)	**Zn**	**Cd** (·100)	**Mn**	**Mo**	**Pb** (·10)
d12												
	LC-DFB	11.6 (2.8)	1.32 (0.34)	117 (3.27)	12.52 (0.78)	0.16 (0.03)	0.07 (0.00)	1.92 (0.86)	0.09 (0.06)	0.15 (0.02)	0.02 (0.00)	0.10 (0.00)
	LC+DFB	28.3 (12)	4.49 (1.91)	258 (46.1)	14.67 (3.35)	0.23 (0.08)	0.19 (0.00)	7.16 (1.29)	0.51 (0.14)	0.41 (0.06)	0.03 (0.01)	0.20 (0.11)
	HC+DFB	15.9 (2.3)	2.52 (0.66)	139 (14.2)	8.05 (1.08)	0.22 (0.06)	0.09 (0.01)	2.39 (0.93)	0.20 (0.09)	0.21 (0.07)	0.03 (0.01)	0.11 (0.06)
	HC-DFB	11.6 (8.8)	1.66 (0.68)	178 (66.3)	9.79 (3.75)	0.19 (0.08)	0.08 (0.03)	2.84 (0.52)	0.22 (0.06)	0.28 (0.08)	0.02 (0.01)	0.19 (0.08)
d17												
	LC-DFB	6.42 (2.9)	0.85 (0.35)	97 (41.6)	1.23 (0.56)	0.11 (0.07)	0.09 (0.05)	2.86 (1.45)	0.26 (0.09)	0.18 (0.07)	0.03 (0.00)	0.09 (0.05)
	LC+DFB	7.53 (4.7)	1.85 (0.63)	245 (136)	1.28 (0.68)	0.24 (0.11)	0.22 (0.08)	12.1 (3.78)	1.20 (0.69)	0.54 (0.29)	0.05 (0.03)	0.18 (0.09)
	HC+DFB	4.48 (0.2)	1.29 (0.01)	131 (5.31)	1.55 (0.19)	0.14 (0.01)	0.07 (0.00)	3.03 (0.90)	0.21 (0.06)	0.14 (0.02)	0.03 (0.00)	0.10 (0.05)
	HC-DFB	12.8 (2.7)	1.98 (0.74)	233 (162)	5.31 (0.99)	0.29 (0.11)	0.18 (0.06)	5.03 (3.06)	0.35 (0.13)	0.43 (0.33)	0.06 (0.01)	0.24 (0.02)
d21												
	LC-DFB	13.9 (3.2)	1.54 (0.48)	257 (20.9)	3.76 (0.75)	0.29 (0.06)	0.26 (0.01)	8.59 (0.69)	0.74 (0.31)	0.35 (0.04)	0.05 (0.02)	0.21 (0.08)
	LC+DFB	4.36 (0.4)	1.01 (0.41)	253 (47.6)	2.04 (0.63)	0.23 (0.02)	0.20 (0.01)	14.3 (1.32)	0.67 (0.09)	0.43 (0.05)	0.05 (0.01)	0.09 (0.02)
	HC+DFB	2.49 (0.9)	0.62 (0.17)	79 (19.6)	0.33 (0.07)	0.11 (0.02)	0.07 (0.03)	2.36 (1.38)	0.09 (0.06)	0.09 (0.03)	0.01 (0.00)	0.03 (0.01)
	HC-DFB	2.56 (1.2)	0.98 (0.30)	74 (20.7)	1.03 (0.18)	0.12 (0.03)	0.05 (0.01)	1.01 (0.35)	0.05 (0.02)	0.07 (0.01)	0.02 (0.00)	0.13 (0.01)
%		ns	ns	80*	75*	60*	70*	55**	45***	55**	35***	30***

Supplemental Table S4. The percentage of lithogenic and biogenic component in our calculated, expected particulate metal concentrations as described in section 4.2 in the discussion. The calculated, expected particulate metal concentrations are also compared with the measured particulate metal concentrations, and are reported as % accounted for. For these calculations we used the means for each day and treatment reported in Table S2, and the Me : P of Marine Plankton$_{Field}$ and crustal Me : Al reported in Table 2.

	Mn	**Fe**	**Co**	**Cu**	**Zn**	**Cd**	**Mo**
% Lithogenic	35 ± 12	78 ± 10	6 ± 3	5 ± 2	1 ± 1	6 ± 3	2 ± 1
% Biogenic	65 ± 12	22 ± 10	94 ± 3	95 ± 2	99 ± 1	94 ± 3	98 ± 1
% Accounted for	71 ± 27	115 ± 60	255 ± 94	36 ± 16	8 ± 4	721 ± 274	6 ± 2

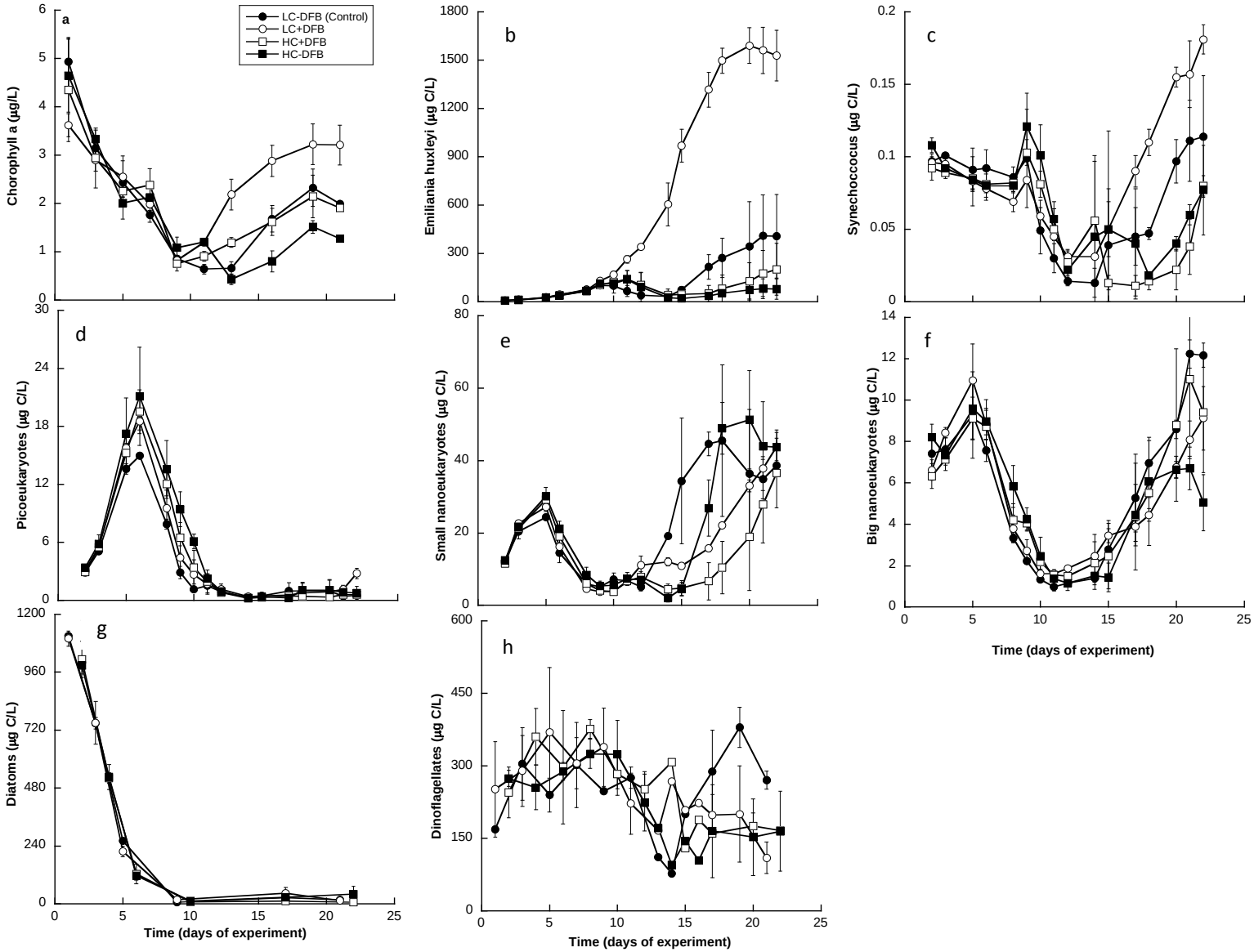


Fig. S1. Temporal development of chlorophyll a (µg L^{-1}) and phytoplankton biomass (µg C L^{-1}) in the mesocosms exposed to different treatments (LC: ambient CO2; HC: increased CO2 (900 µatm); -DFB: no DFB addition; +DFB: with a 70 nM DFB addition). (a) Chlorophyll a, (b) *Emiliania huxleyi* (5−10 µm), (c) *Synechococcus sp.* (0.6−2 µm), (d) picoeukaryotes (0.1−2 µm), (e) small nanoeukaryotes (prasinophytes, small haptophytes, 2−7 µm), (f) large nanoeukaryotes (small single-celled diatoms and flagellated forms, 6−20 µm), (g) diatoms (chain-forming Skeletonema sp. 20−> 500 µm), (h) dinoflagellates (20−200 µm). Figure reproduced with permission from Segovia et al. Mar. Ecol. Prog. Ser. 2017 .

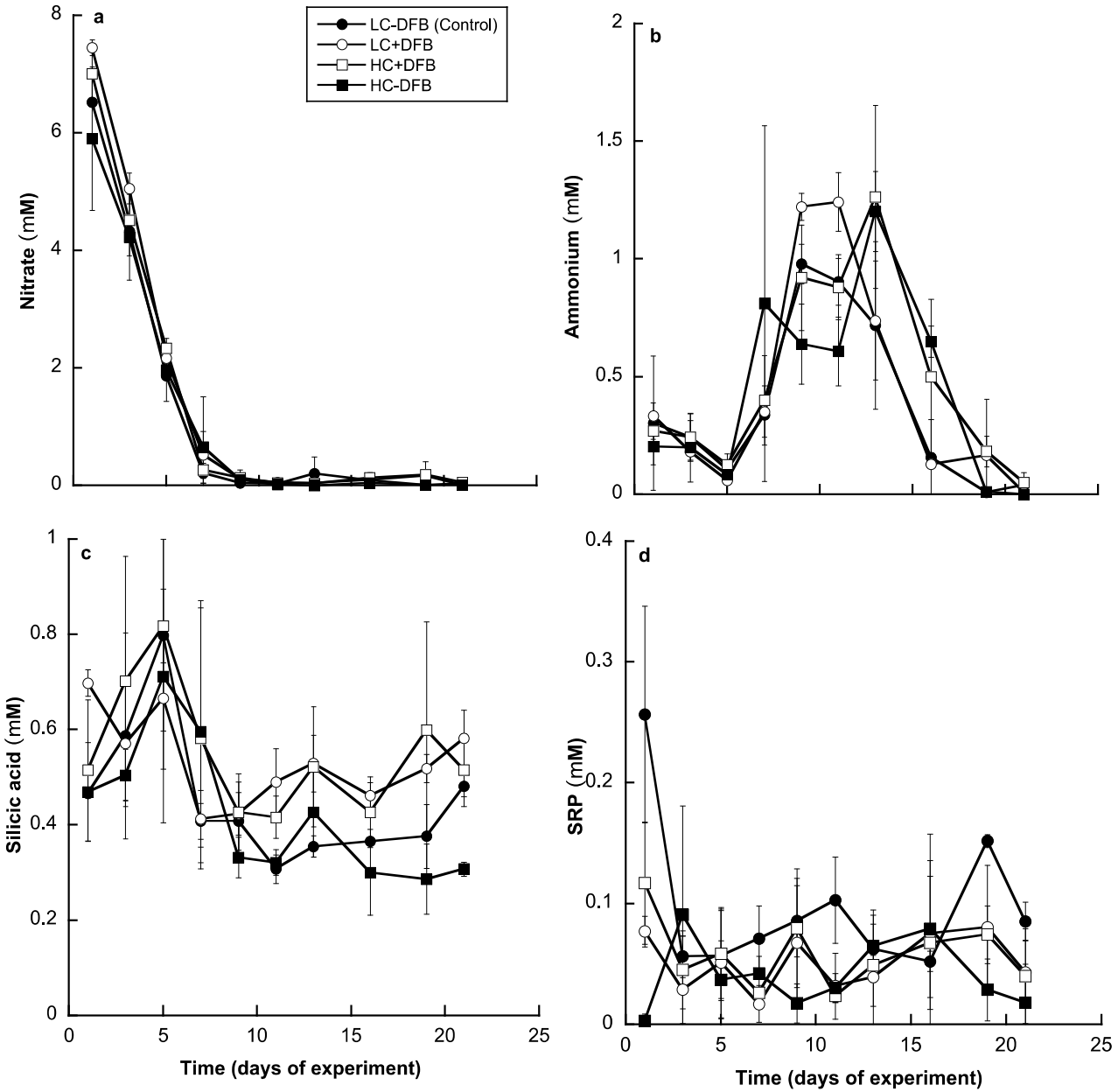
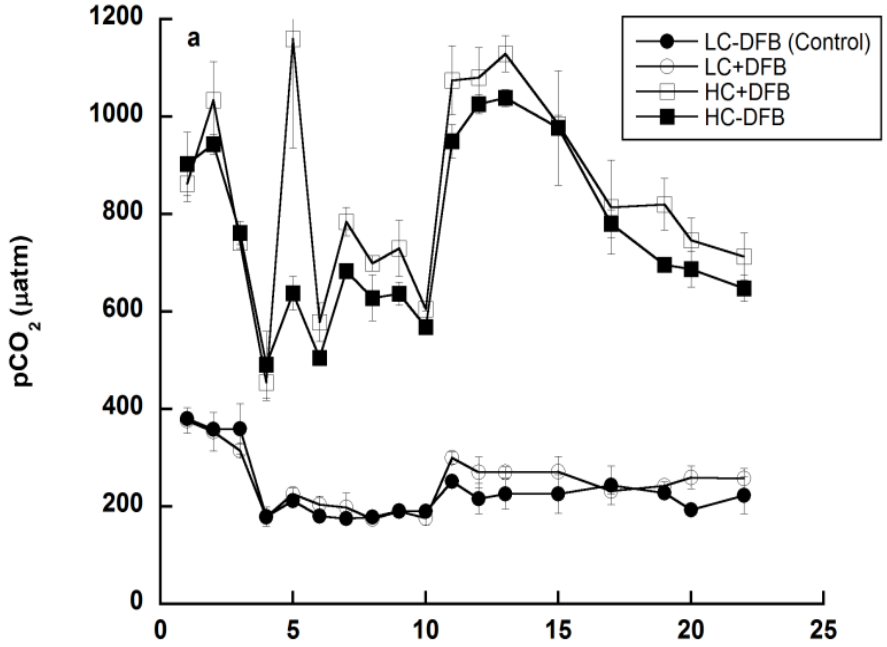
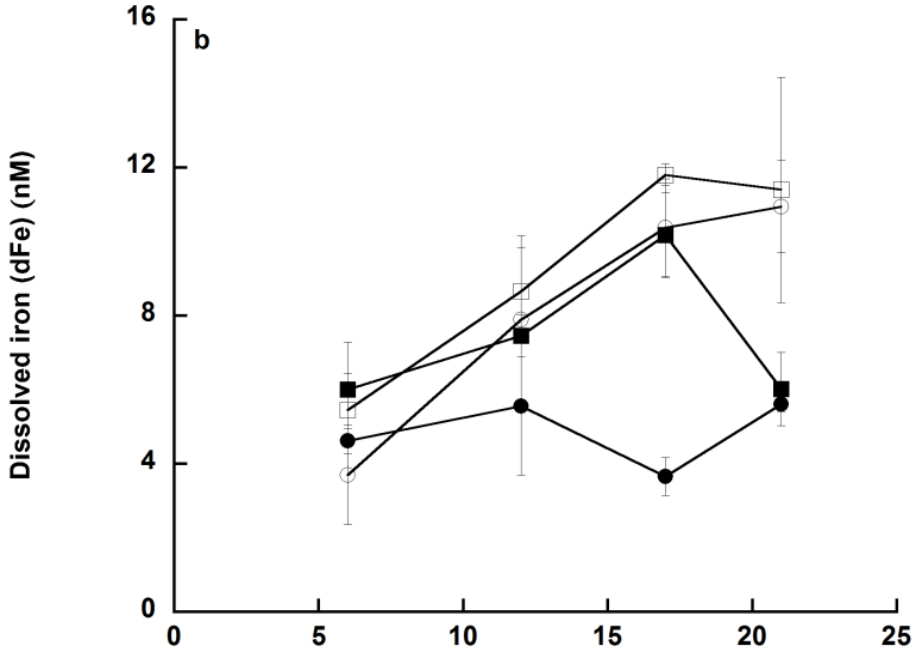


Figure S2. Temporal development of major nutrient concentrations within the mesocosms in the different treatments (LC: ambient CO_2 (390 µatm); HC: increased CO_2 (900 µatm); -DFB: no DFB addition; +DFB: with a 70 nM DFB addition): (a) nitrate, (b) ammonium, (c) silicic acid, (d) soluble reactive phosphate (SRP). Figure reproduced with permission from Segovia et al. Mar. Ecol. Prog. Ser. 2017 .





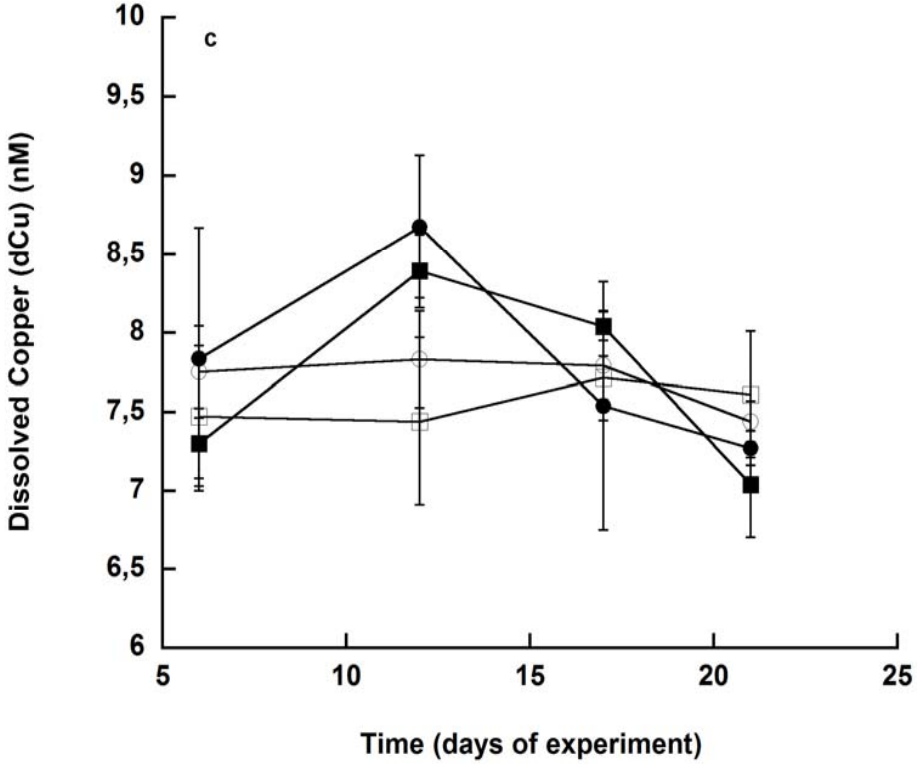


Fig. S3. Temporal development of (a) CO2 partial pressure (pCO2) , (b) dissolved iron (dFe) and (c) dissolved copper (dCu) within the mesocosms. The treatments include LC (ambient CO2, 390 µatm), HC (increased CO2, 900 µatm), -DFB (no DFB addition) and +DFB (with a 70 nM DFB addition). Symbols indicate means of measurements in 3 independent mesocosms (n = 3) except for LC−DFB where n = 2. Error bars indicate SD. Panels a) and b) reproduced with permission from Segovia et al. Mar. Ecol. Prog. Ser. 2017