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Supplement of

Proteomic and biogeochemical perspectives on cyanobacteria nutrient acquisition – Part 2: quantitative contributions of cyanobacterial alkaline phosphatases to bulk enzymatic rates in the subtropical North Atlantic

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The below Tables S1 and S4 serve to supplement the methodology and results sections of the main manuscript and are referred to as such in the main text. In addition, and as referenced in the main text, the full data sets of quantified proteins and environmental data used in this study, are compiled in Tables S5 and S6, respectively.

The below Figures S1 through S6 serve to supplement the results sections of the main manuscript.

Supplementary Tables

Table S1 Results of the two-tailed t-tests, comparing protein concentrations and environmental data between the unamended Control and metal amendments after the 48 h incubation period.

t-statistic, *p*-value (df)		PhoA *Syn.*	PhoX *Syn.*	PstS *Syn.*	PhoA *Pro.*	PhoX *Pro.*	PstS *Pro.*	APA	Chl-*a*	*Syn.* cells	*Pro.* cells		DOP	DIP	DIN
Station 2	Control:Zn	**-28.1, 0.00 (2)**	0.64, 0.59 (2)	-1.85, 021 (2)	0.25, 0.82 (2)	2.37, 0.14 (2)	1.21, 0.35 (2)	0.66, 058 (2)	-1.41, 0.29 (2)	1.72, 0.23 (2)	-0.09, 0.94 (2)		4.51, 0.14 (1)	-0.01, 0.99 (2)	1.65, 0.24 (2)
	Control:Co	**-8.28, 0.01 (2)**	-0.98, 0.43 (2)	-1.54, 0.26 (2)	-0.45, 0.70 (2)	-1.95, 0.19 (2)	-0.40, 0.73 (2)	1.20, 0.35 (2)	-0.45, 0.70 (2)	3.26, 0.08 (2)	0.10, 0.93 (2)		5.63, 0.11 (1)	-0.46, 0.69 (2)	0.81, 0.50 (2)
	Control:Fe	-1.06, 0.40 (2)	0.80, 0.51 (2)	-0.72, 0.55 (2)	0.27, 0.81 (2)	-0.05, 0.96 (2)	0.34, 0.77 (2)	-0.55, 0.64 (2)	-1.00, 0.42 (2)	**5.42, 0.03 (2)**	-1.92, 0.19 (2)		0.61, 0.65 (1)	-0.13, 0.91 (2)	1.16, 0.37 (2)
Station 3	Control:Zn	0.29, 0.80 (2)	1.58, 0.25 (2)	1.45, 0.28 (2)	1.67, 0.24 (2)	0.58, 062 (2)	1.91, 0.20 (2)	3.08, 0.09 (2)	-3.00, 0.10 (2)	0.06, 0.96 (2)	0.06, 0.96 (2)		0.80, 0.57 (1)	-0.44, 0.70 (2)	-0.22, 0.84 (2)
	Control:Co	0.66, 0.58 (2)	-0.77, 0.52 (2)	-0.25, 0.82 (2)	0.23, 0.84 (2)	0.13, 0.91 (2)	0.09, 0.94 (2)	2.96, 0.10 (2)	-3.00, 0.10 (2)	1.69, 0.23 (2)	0.42, 0.71 (2)		n/a	-0.17, 0.88 (2)	-0.47, 0.69 (2)
	Control:Fe	0.86, 0.48 (2)	3.30, 0.08 (2)	0.90, 0.46 (2)	1.69, 0.23 (2)	0.25, 0.82 (2)	0.88, 0.47 (2)	1.60, 0.25 (2)	0.33, 0.77 (2)	0.03, 0.98 (2)	-0.27, 0.81 (2)		1.43, 0.39 (1)	-0.28, 0.81 (2)	0.31, 0.78 (2)
Station 4	Control:Zn	-0.72, 0.54 (2)	-0.10, 0.93 (2)	0.39, 0.73 (2)	-1.64, 0.24 (2)	-0.10, 0.93 (2)	-0.53, 0.65 (2)	-0.51, 0.66 (2)	-0.45, 0.70 (2)	n/a	n/a		-2.28, 0.15 (2)	2.53, 0.13 (2)	-2.75, 0.11 (2)
	Control:Co	-0.86, 0.48 (2)	-2.29, 0.15 (2)	-2.53, 0.13 (2)	-1.25, 0.34 (2)	-1.30, 0.32 (2)	-1.03, 0.41 (2)	-0.62, 0.60 (2)	-0.45, 0.70 (2)	n/a	n/a		-2.59, 0.12 (2)	**-6.30, 0.02 (2)**	0.03, 0.98 (2)
	Control:Fe	-0.20, 0.86 (2)	-0.06, 0.95 (2)	-0.82, 0.50 (2)	0.32, 0.78 (2)	-0.02, 0.98 (2)	0.40, 0.73 (2)	0.33, 0.78 (2)	-1.41, 0.29 (2)	n/a	n/a		-1.74, 0.22 (2)	0.05, 0.96 (2)	1.73, 0.23 (2)
Station 7	Control:Zn	-0.02, 0.98 (4)	2.11, 0.10 (4)	1.38, 0.24 (4)	0.21, 0.84 (4)	-1.12, 0.33 (4)	0.39, 0.72 (4)	-1.97, 0.12 (4)	0.00, 1.00 (4)	0.96, 0.44 (2)	1.95, 0.19 (2)		0.41, 0.71 (4)	0.57, 0.60 (4)	0.40, 0.71 (4)
	Control:Co	2.08, 0.11 (4)	1.59, 0.19 (4)	**2.91, 0.04 (4)**	1.44, 0.22 (4)	-2.67, 0.06 (4)	2.77, 0.05 (4)	-0.74, 0.50 (4)	1.07, 0.35 (4)	3.55, 0.07 (1)	1.16, 0.36 (1)		0.51, 0.64 (4)	0.84, 0.45 (4)	-0.73, 0.51 (4)
	Control:Fe	0.87, 0.45 (3)	3.70, 0.03 (3)	2.08, 0.13 (3)	0.44, 0.69 (3)	**-4.69, 0.02 (3)**	0.28, 0.80 (3)	-1.33, 0.28 (3)	-0.43, 0.70 (3)	-1.71, 0.34 (2)	-0.10, 0.94 (2)		-1.80, 0.17 (3)	1.03, 0.38 (3)	1.04, 0.38 (3)

Table S2 Significant differences in protein concentrations between the unamended Control and the metal-amended treatments, based on the t-test results and the two-fold criterion test (see details in section on 'Statistics'). For environmental parameters, the significance is based solely on the t-test results of Table S1. Significant = 1; non-significant = 0.

Significance: Two-fold criterion, t-test		PhoA *Syn.*	PhoX *Syn.*	PstS *Syn.*	PhoA *Pro.*	PhoX *Pro.*	PstS *Pro.*	APA	Chl-*a*	*Syn.* cells	*Pro.* cells	DOP	DIP	DIN
Station 2	Control:Zn	**1,1**	0,0	0,0	0,0	0,0	0,0	0	0	0	0	0	0	0
	Control:Co	**1,1**	0,0	0,0	0,0	0,0	0,0	0	0	0	0	0	0	0
	Control:Fe	0,0	0,0	0,0	0,0	0,0	0,0	0	0	**1**	0	0	0	0
Station 3	Control:Zn	0,0	0,0	0,0	0,0	0,0	0,0	0	0	0	0	0	0	0
	Control:Co	0,0	0,0	0,0	0,0	0,0	0,0	0	0	0	0	n/a	0	0
	Control:Fe	0,0	0,0	0,0	0,0	0,0	0,0	0	0	0	0	0	0	0
Station 4	Control:Zn	0,0	0,0	0,0	0,0	0,0	0,0	0	0	n/a	n/a	0	0	0
	Control:Co	0,0	0,0	0,0	0,0	**1,0**	0,0	0	0	n/a	n/a	0	**1**	0
	Control:Fe	0,0	0,0	0,0	0,0	0,0	0,0	0	0	n/a	n/a	0	0	0
Station 7	Control:Zn	0,0	0,0	0,0	0,0	0,0	0,0	0	0	0	0	0	0	0
	Control:Co	0,0	0,0	**0,1**	0,0	0,0	0,0	0	0	0	0	0	0	0
	Control:Fe	0,0	0,0	0,0	0,0	**1,1**	0,0	0	0	0	0	0	0	0

Table S3 Details on the measured and assumed variables for the model calculations in section 'Towards a quantitative marine metalloproteome' of the main manuscript, specifically for the metal allocation to PhoA in Synechococcus in the Control treatment at 54 °W.

Variable	Unit	Value	Source	Further details
Number of metal ion co-factors		4	Assumed; after [1]	Based on the *E. coli* homologue, full metalation comprises four Zn^{2+} per dimer.
Synechococcus PhoA peptide concentration in seawater	fmol L^{-1}	6.69 ± 1.46 (RSD = 0.22)	Measured; this study	Using the mean (± 1sd) concentration of peptide HYIAVALER (by HPLC-MS/MS) in the two Control replicates at Station 2 after 48 h.
Synechococcus PhoA protein concentration in seawater	fmol L^{-1}	3.35 ± 0.73 (RSD = 0.22)	Measured; this study	Using the concentration from the row above, but accounting for the dimeric structure that is assumed based on the *E. coli* PhoA homologue[1].
Synechococcus abundance	cells ml^{-1}	3,931 ± 131 (RSD = 0.033)	Measured; this study	Using the mean (± 1sd) concentration of cell abundance (by flow cytometry) in the two Control replicates at Station 2 after 48 h.
Fraction of *Synechococcus* strain WH8102 (clade III)	%	67 ± 2.8 (RSD = 0.042)	Assumed; after[2]	Calculated from the mean (± 1sd) fraction of clade III (representative of WH8102) to total *Synechococcus* abundance in two samples at 10m at BATS in July 2012. Other literature data outside relevant depth range, season and/or vicinity to our Station 2, but within the (sub)tropical North Atlantic vary between 0 and 83 %[3–5].
Cellular Zn content in *Synechococcus*	atoms $cell^{-1}$	$463 \pm 104 \cdot 10^3$ (RSD = 0.26)	Measured; this study	Using the mean (± 1sd) Zn content of five *Synechococcus* cells (by synchotron x-ray fluorescence[6]) sampled prior to the bioassays (i.e. no metal addition) at Station 2. This Zn content is at the higher end of previously analysed *Synechococcus* cells from a phosphorus-stressed anticyclonic eddy near BATS (66,000 to 684,000 atoms $cell^{-1}$ between surface and DCM)[7], and higher than values reported elsewhere[8,9].
Cellular Co content in *Synechococcus*	atoms $cell^{-1}$	low: $8.10 \cdot 10^3$ high: $198 \cdot 10^3$	Measured; this study	Measured in the same way and in the same samples as for Zn in the row above. However, the cellular Co content was undetectable in three out of the five cells and ranged over orders of magnitude (see column to the left) for the remaining two. Hence, these likely present an upper threshold. They are also lower than previously measured 'autotrophic picoplankton cells' from the subtropical North Atlantic with a cellular Co content of 1,380 atoms $cell^{-1}$ [9] (converted using their Co:P ratio of 0.15 mmol mol^{-1} and 15.2 amol P $cell^{-1}$ from[10]) and lower than the minimal growth requirements of *Synechococcus bacillaris* of 792 Co atoms $cell^{-1}$ [11] (converted using their Co:C ratio of 0.12 µmol mol^{-1} and 11 fmol C $cell^{-1}$ from [10]). Considering these scales, only the lower Co content was used in the model calculations in the main text.

Table S4 Details on the measured and assumed variables for the model calculations in section 'Towards a quantitative marine metalloproteome' of the main manuscript, specifically for the protein-abundance based hydrolysis rates of Synechococcus PhoA in the Control treatment at 54 °W.

Variable	Unit	Value/range	Source	Details
Molecular weight of *Synechococcus* PhoA	g mol^{-1} (Da)	$126.12 \cdot 10^3$	Calculated	Calculated using the amino acid sequence of full protein (see footnote*).
Synechococcus PhoA protein concentration in seawater	ng L^{-1}	0.845 ± 0.178 (RSD = 0.21)	Measured; this study	Converted from the mean (± 1sd) protein concentration in fmol L^{-1} (see third row in Table S3) and the molecular protein weight in the above row.
Molecular weight of *Prochlorococcus* PhoA	g mol^{-1} (Da)	$165.28 \cdot 10^3$	Calculated	Calculated using the amino acid sequence of full protein (see footnote**).
Prochlorococcus PhoA protein concentration in seawater	ng L^{-1}	5.67 ± 1.70 (RSD = 0.30)	Measured; this study	Converted from the mean (± 1sd) protein concentration in fmol L^{-1} of the *Prochlorococcus* PhoA and the molecular protein weight in the above row.
DOP concentration	nmol L^{-1}	135	Measured; this study	Using the mean (± 1sd) concentration of DOP (as DOP = TDP – DIP) in the Control treatment at Station 2 after 48 h (only one replicate available).
Phosphoester fraction	%	80	Assumed; after [12]	Using the mean fraction of phosphoesters to the DOP pool measured in some near-by Gulf Stream samples[12], which is also close toestimate of 75 % for a variety of samples from the oligotrophic ocean[13].
Available substrate concentration	nmol L^{-1}	108	Calculated	Calculated from the DOP concentration and phosphoester fraction in the two rows above. It is important to note that this is the standing stock of the substrate in the seawater during the bioassays, not necessarily the substrate availability *near* or *in* the cell, where the enzyme is thought to be active. At this point, a more accurate approximation of the substrate availability is not available, but we do acknowledge that the current one is a likely underestimation.
APA	nmol L^{-1} h^{-1}	3.25 ± 0.23 (RSD = 0.071)	Measured; this study	Using the mean (± 1sd) rate of APA (by MUF-P assay) in the two Control replicates at Station 2 after 48 h.
Periplasmic outwards fraction	%	20 to 80	Assumed; various studies	It was shown that MUF-P does not cross the inner membrane[14], meaning that the MUF-P assay can only detect extracellular and periplasmic hydrolysis rates (i.e. periplasmic-outwards). Therefore, the total APA in our samples is estimated from the measured APA in the row above, while accounting for the fraction of marine alkaline phosphatases that is not captured by the MUF-P assay. Marine bacterial alkaline phosphatases were predicted to be between ~80 and 50 % periplasmic-outwards[15], while field-based estimates of extracellular-only APA (i.e. by filtration with <0.2 µm) ranged between 21 to 80 % in the North Atlantic[16–19]. For the calculation and the associated figure in the main text, a higher periplasmic-outwards fraction translates to a lower 'correction' on the measured APA, and hence higher a contribution of *Synechococcus* PhoA to total APA.

V_{max} for Zn-dependent PhoA	µmol min^{-1} mg^{-1}	28, 7.0, 43, 28.6, 26.7, 17, 21.5, 28	Assumed; after [20]	Using enzyme kinetics of purified *E. coli* PhoA under optimal metal co-factor occupation (i.e. two Zn^{2+} and 2 Ca^{2+}). The large range of discrete V_{max} values results from testing a variety of different phosphoester substrates and is within values reported by others [1,21–23].
K_m for Zn-dependent PhoA	µmol L^{-1}	2.7, 7.3, 1.0, 6.1, 6.1, 6.1, 7.7, 14.7	Assumed; after [20]	Same as row above, but for K_m.
V_{max} for Co-dependent PhoA	µmol min^{-1} mg^{-1}	2.86, 1.10. 2.86, 2.70, 2.86, 2.46, 2.60, 2.80	Assumed; after [20]	Using enzyme kinetics of purified *E. coli* PhoA, where Zn^{2+} co-factors were substituted by Co^{2+}, which resulted in reduced enzyme efficiency. The large range of discrete V_{max} values results from testing a variety of different phosphoester substrates.
K_m for Co-dependent PhoA	µmol L^{-1}	0.73, 1.30, 3.32, 1.70, 1.85, 2.20, 2.40, 1.82	Assumed; after [20]	Same as row above, but for K_m.

* >tr|Q7U3N9|Q7U3N9_SYNPX Putative alkaline phosphatase OS=Synechococcus sp. (strain WH8102) OX=84588 GN=SYNW2391 PE=4 SV=1
MARISDSIISPLQSVSPGGAEKVDWYAPTKTAFVITGEYTDDKGGQVVAIDYSNGYGKGT
AIDEYYFEGDVSDVRVSSQGLIAASVFDKVTREGTVQFLDFTKESGFTSLGSVEVGYQPD
QLAFTKNGKKLVTANEGEPLMFYGSDETSQNPRGSISIINIANDLTKSKVNTLYFTKSNK
YYEKRGVRLYGPEMDSNSKFGEYDIEPEYVGITGNNTALVALQENNALARVNLKKEKITG
VFGLGYKDWSGIPFDTTDKDDGYNPTVKEGVTSARMPDGIDTFQIKLGGKKQILFISPNE
GDGRVRPDDVNFEAPADGVYSWGTNSTGAEIESFTDPLTLTDEIYIYDKAGVGNSGDIED
VEEGDEFFITQKYGVSSDDEFWSDEVRAKDLEDFGDVSKYDSQIIGEGRMKTLADQNDPV
TGGLVGFGGRGFSIHANDGSVIYDSGNLTEEIAAELGYYPDNRSDDKGTEPETVEYFSFG
KKKNKRHYIAVALERCFNNGDEDRLGTIVPIFEVVDLEAADNDERVKHVATLQSPESLSP
EGLLFVNDTNTSGHMFVTNEVSRTLDTYAISQADLA

** >tr|A0A0A2AKF8|A0A0A2AKF8_PROMR Alkaline phosphatasee OS=Prochlorococcus marinus str. MIT 9314 OX=167548 GN=EU98_0531 PE=4 SV=1
MKKTLAAASFSALLAIVASSTSSGFANWNTKYWANEKNFNRISSFNVSDNLPKGSKSTTK
TSSEVVTASEDGKTLIYTDSDLGVVGLVDISDPAKPKALGVVELEAEPTGIAALGNNAYI

GSNTSESYTNPSGALVQYNLETRKAVKECDLGGQPDSVFVSPDGTFLAVAIENERDEEYK
NGFIPQIDDNGIQINPAGYVSLVKLNKRGKIQCNSIKKVDLTGLSEIAPFDPEPEFVAIN
DLGETVVSLQENNHLAVIDKDGNVISHFSAGVVKQMAGMDTKKDGAHKFKSKLKNVRREP
DGLTWIDNDHFATANEGDYKHIDPNQAKRGGSRSWTIFKKDGTVVYEDANRLERAIAQIG
HFQDGRAGKKGVEPESVTYSKINGTPYLFVGAERAGIVAVYDITELNQPLLTQLLPSGIG
PEGFVAIPERGLIASANEKDYNKKEPGLSSHVTIYQLQDAPASYPHLTNENGLEFVSWGA
ISGMVAGDDGKIYAVNDGTFKTQPRIYVIDPSSSPALLERAIDIKLDGKTALFMDQEGIT
TDGNGGFYISTEGIKKKLDEHPPAIYHVSSDGEILEKITPPPSYLNYAKNPGFEGITRNG
DILYIAQQKPWGDDTFNTTKILSYNLKTKQWGAVNYQLDRIKKGGVGISELTYHDGALYV
IERDSFYGKKAKLKAIYKVDLDDVIFEGLQTNIPPRLYPLVEKELVTDLKPVMQSTGGFI
LEKVEGLAITSEGQAWISTDNDGTGKKSTGETLFLNIGKI

Table S5 Data set for quantitated proteins used in the main manuscript, shown as seawater concentrations of the individual replicates of each treatment after the 48 h-incubation period.

Treatment		PhoA *Syn.* (fmol L^{-1})		PhoX *Syn.* (fmol L^{-1})		PstS *Syn.* (fmol L^{-1})		PhoA *Pro.* (fmol L^{-1})		PhoX *Pro.* (fmol L^{-1})		PstS *Pro.* (fmol L^{-1})	
Station 2	Control	7.7	5.7	25.5	16.8	1.9	0.7	54.5	35.4	17.9	15.1	473.5	330.7
	+ Zn	37.4	38.1	16.2	20.0	3.9	2.3	27.5	54.1	9.0	12.8	161.7	353.7
	+ Co	42.4	51.9	23.4	29.3	10.7	3.3	61.6	40.9	50.1	27.5	633.0	311.0
	+ Fe	7.9	45.2	6.6	21.7	0.4	7.1	11.7	63.3	8.7	25.	80.5	554.7
Station 3	Control	30.0	13.3	16.6	13.4	3.6	0.9	54.7	41.0	23.3	8.3	470.3	246.9
	+ Zn	6.9	28.4	4.8	12.3	0.3	0.4	17.7	37.7	4.9	16.0	132.5	155.0
	+ Co	22.1	5.7	42.3	11.5	2.1	3.1	62.3	24.0	14.1	15.6	467.9	218.6
	+ Fe	19.2	5.7	9.9	8.8	0.4	1.5	37.7	19.8	14.0	13.8	205.3	298.5
Station 4	Control	10.1	5.7	12.9	5.6	0.3	0.5	39.9	21.7	6.4	6.6	261.5	112.9
	+ Zn	23.2	5.7	7.0	12.4	0.03	0.6	43.2	50.7	0.5	13.9	219.3	234.2
	+ Co	38.7	5.7	18.1	17.4	1.4	0.9	96.3	38.7	85.0	16.6	611.2	207.4
	+ Fe	7.8	8.8	7.5	11.6	0.4	1.0	33.8	20.6	12.0	1.2	222.7	66.5
Station 7	Control	42.5	21.3	19.2	17.8	16.4	13.5	2.7	4.8	3.6	4.4	3.2	2.0	10.7	6.0	7.9	168.9	133.8	115.1
	+ Zn	5.7	12.1	66.6	3.3	12.2	12.0	0.4	1.4	4.1	0.5	1.1	6.7	3.5	17.5	53.4	13.4	99.2	229.2
	+ Co	7.7	17.7	5.7	11.4	15.4	12.8	1.3	1.5	2.3	1.6	2.6	2.0	23.2	15.9	12.7	92.9	93.9	99.1
	+ Fe	12.0	-	24.6	10.2	-	9.2	2.3	-	1.8	2.7	-	3.0	20.6	-	16.9	103.8	-	158.6

Table S6 Data set for the environmental data used in the main manuscript, shown as seawater concentrations of the individual replicates of each treatment (where applicable) after the 48 h-incubation period.

Treatment		APA (nM h^{-1})			Chl-*a* (µg L^{-1})			*Syn.* cells (cells ml^{-1})			*Pro.* cells (cells ml^{-1})			DIP (nM)			DOP (nM)			DIN (nM)		
Station 2	Control	3.41	3.08		0.070	0.080		3838	4023		55816	54151		5.4	4.2		135			3.7	7.4	
	+ Zn	2.97	3.24		0.090	0.080		3680	3801		55282	54843		5.7	3.93		82	94		1.11	3.08	
	+ Co	2.96	3.1		0.070	0.090		3203	3504		47575	61071		5.43	4.8		86	95		2.34	5.06	
	+ Fe	3.77	3.12		0.080	0.080		3181	3344		57450	62222		5.64	4.2		99	134		2.59	3.95	
Station 3	Control	3.66	3.43		0.080	0.080		2829	5328		116715	54862		1.54	3.09		117			1.42	4.2	
	+ Zn	3.12	3.21		0.100	0.090		2740	5194		113715	52767		3.16	2.27		98	114		3.12	3.12	
	+ Co	3.05	3.21		0.090	0.100		2036	1888		47758	91752		2.71	2.2		111			0.28	10.1	
	+ Fe	3.18	3.4		0.060	0.090		2912	5135		64679	131180		3.09	2.06		85	103		1.25	3.29	
Station 4	Control	3.68	5.19		0.100	0.110		-			-			1.5	1.6		93	112		3.6	3.74	
	+ Zn	5.94	4.13		0.120	0.100		-			-			1.41	1.44		126	121		4.31	5.03	
	+ Co	4.38	5.76		0.100	0.120		-			-			2.41	2.19		126	126		1.44	5.75	
	+ Fe	4.38	3.98		0.120	0.110		-			-			1.82	1.25		133	116		0.72	2.88	
Station 7	Control	2.68	2.21	2.93	0.100	0.180	0.130	-	1955	1832	-	261931	199483	2.9	6.42	3.63	162	155	149	2.32	2.98	4.47
	+ Zn	3.05	3.02	3	0.130	0.140	0.140	-	1666	1883	-	154382	177475	3.79	3.9	3.4	181	104	154	2.98	3.81	1.99
	+ Co	2.38	2.95	3.2	0.050	0.120	0.130	1682	1663	-	207527	167529	-	3.48	3.59	3.17	189	93	143	1.66	18.87	1.82
	+ Fe	2.81	27.05	3.25	0.140	1.120	0.160	-	4286	2076	-	500388	236133	2.67	23.19	3.09	165	195	214	2.32	10.6	2.48

Table S7 Michaelis-Menten kinetics data (K_m and V_{max}) of APA in the each treatment of the bioassays after the 48 h-incubation period. No data is available for Station 4.

Treatment		K_m (nM)	V_{max} (nM h^{-1})
Station 2	Control	125 ± 22	3.32 ± 0.10
	+ Zn	76 ± 72	4.23 ± 0.27
	+ Co	39 ± 28	3.24 ± 0.14
	+ Fe	138 ± 56	4.95 ± 0.25
Station 3	Control	222 ± 125	5.25 ± 0.54
	+ Zn	124 ± 112	4.02 ± 0.40
	+ Co	181 ± 22	4.46 ± 0.09
	+ Fe	131 ± 14	3.47 ± 0.08
Station 7	Control	340 ± 141	5.02 ± 0.51
	+ Zn	314 ± 112	5.59 ± 0.47
	+ Co	318 ± 166	3.89 ± 0.72
	+ Fe	240 ± 74	4.45 ± 0.40

Supplementary Figures

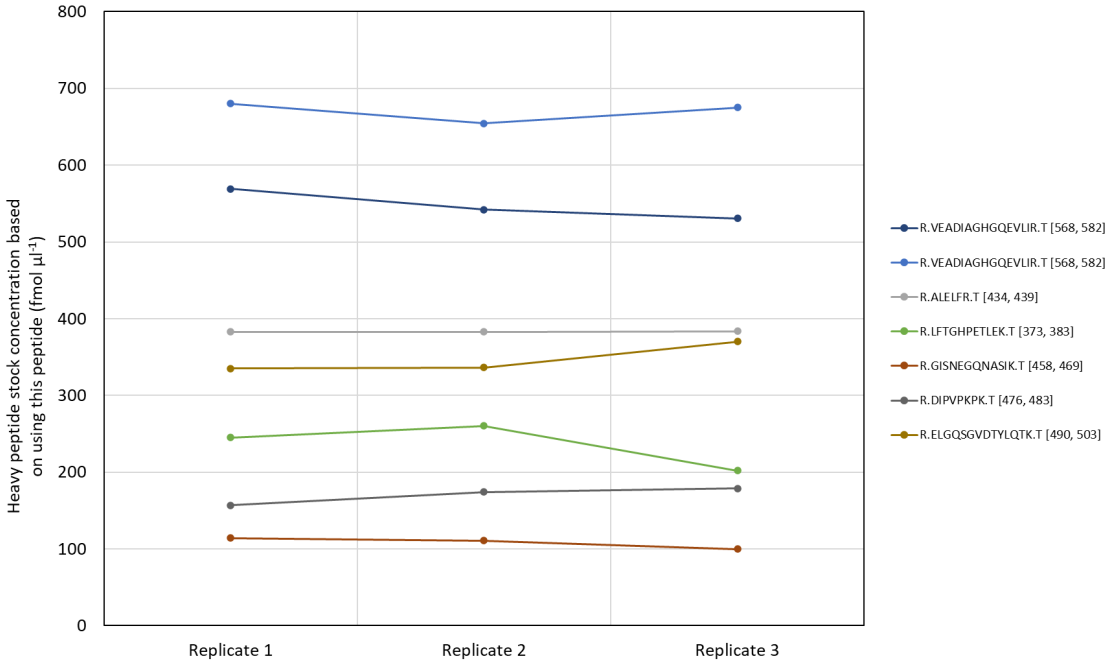

Figure S1 Results of calibration process using commercially available standard peptides, highlighting cross-peptide and cross-replicate variability.

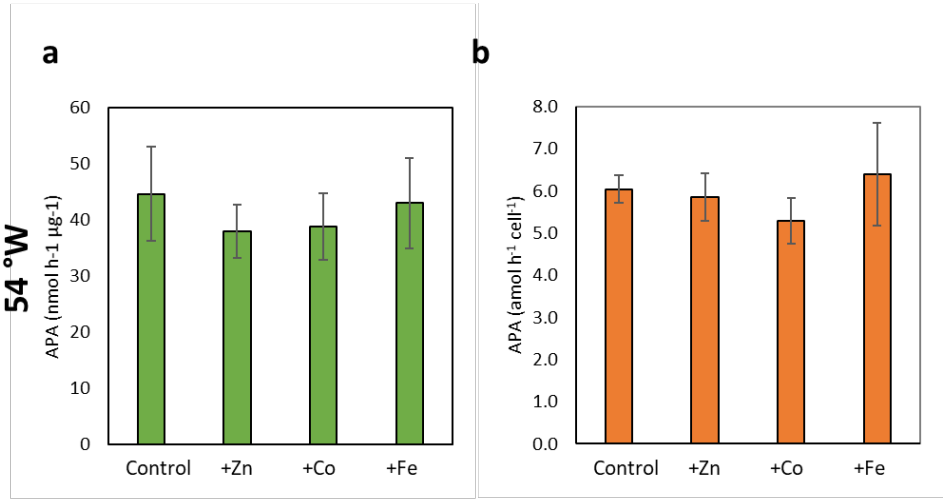

Figure S2 APA from the bioassays at 54 °W normalised to (a) Chl-a concentrations or (b) total cell counts from flow cytometric analyses (sum of Prochlorococcus, Synechococcus, picoeukaryotes, high nucleic acid bacteria, low nucleic acid bacteria).

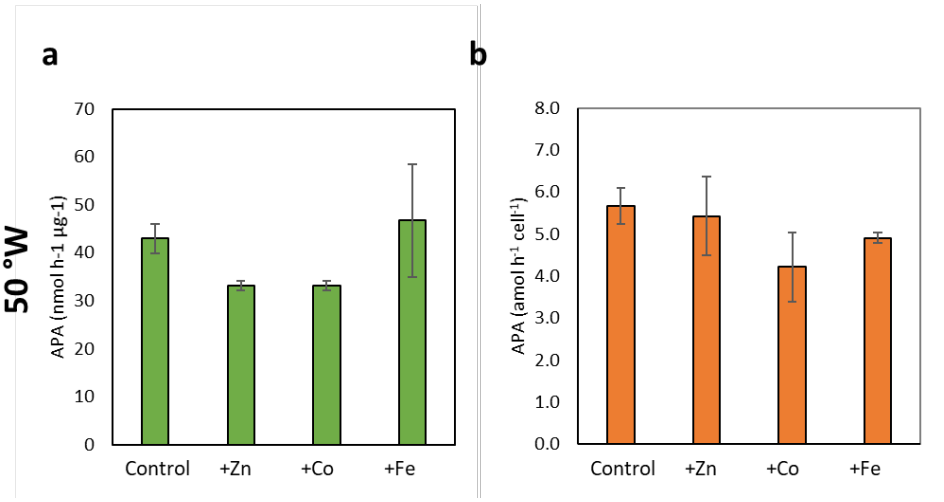

Figure S3 APA from the bioassays at 50 °W normalised to (a) Chl-a concentrations or (b) total cell counts from flow cytometric analyses (sum of Prochlorococcus, Synechococcus, picoeukaryotes, high nucleic acid bacteria, low nucleic acid bacteria).

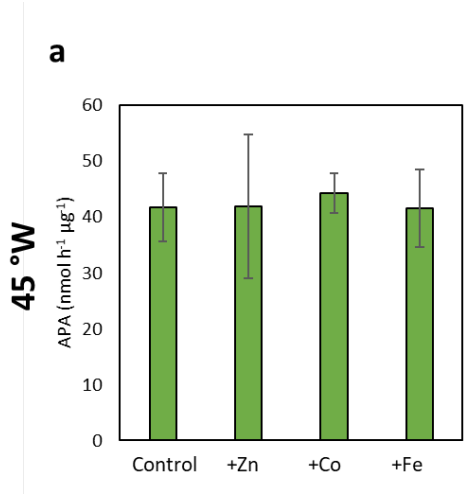

Figure S4 APA from the bioassays at 45 °W normalised to Chl-a concentrations. No flow cytometr available for this station.

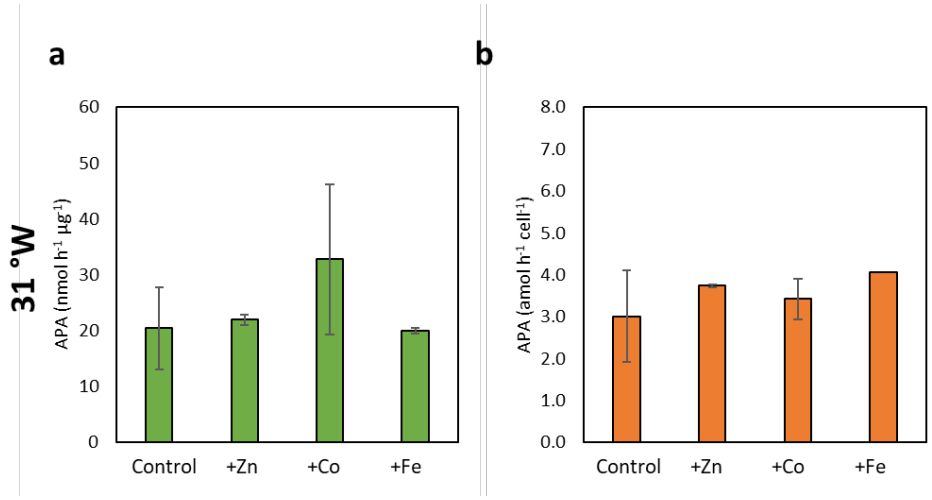

Figure S5 APA from the bioassays at 31 °W normalised to (a) Chl-a concentrations or (b) total cell counts from flow cytometric analyses (sum of Prochlorococcus, Synechococcus, picoeukaryotes, high nucleic acid bacteria, low nucleic acid bacteria).

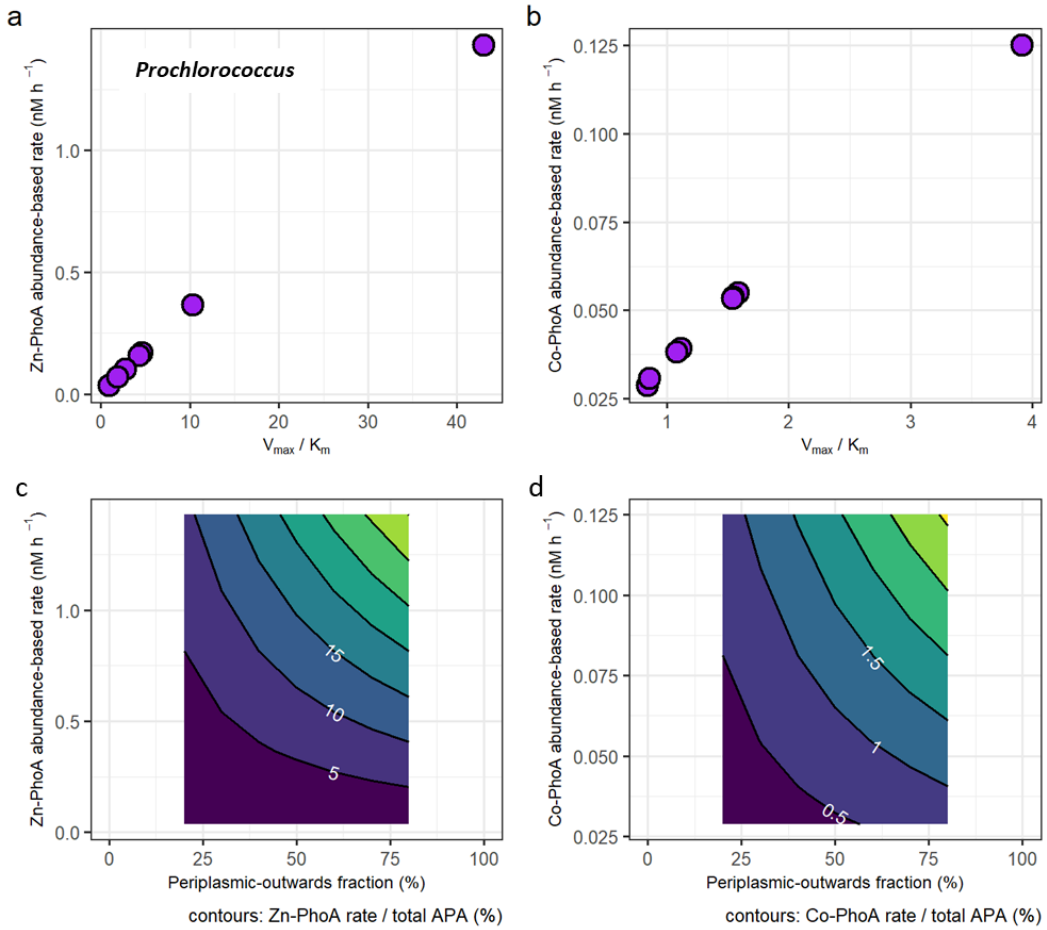

Figure S6 Same as Fig. 6 of the main manuscript but for the Prochlorococcus PhoA. (a) Protein abundance-based APA estimates of Prochlorococcus Zn-dependent PhoA as a function of different enzyme kinetic parameters V_{max} and K_m. (b) Same as (a), but with enzyme parameters for the less efficient Co-dependent PhoA. (see Table S4). (c) The fraction of the Zn-PhoA abundance-based APA from (a) over the total APA. (d) Same as (c) but using the Co-PhoA rates from (b). Note the scale difference between (a,c) and (b,d).

Supplementary References

1. Coleman, J. E. Structure and mechanism of alkaline phosphatase. *Annu. Rev. Biophys. Biomol. Struct* **21**, 441–483 (1992).

2. Ohnemus, D. C. *et al.* Silicon content of individual cells of Synechococcus from the North Atlantic Ocean. *Marine Chemistry* **187**, 16–24 (2016).

3. Mazard, S., Ostrowski, M., Partensky, F. & Scanlan, D. J. Multi-locus sequence analysis, taxonomic resolution and biogeography of marine Synechococcus. *Environmental Microbiology* **14**, 372–386 (2012).

4. Ahlgren, N. A. & Rocap, G. Diversity and distribution of marine Synechococcus: Multiple gene phylogenies for consensus classification and development of qPCR assays for sensitive measurement of clades in the ocean. *Frontiers in Microbiology* **3**, 1–24 (2012).

5. Sohm, J. A. *et al.* Co-occurring Synechococcus ecotypes occupy four major oceanic regimes defined by temperature, macronutrients and iron. *ISME Journal* **10**, 333–345 (2016).

6. Sofen, L. E. *et al.* Metal contents of autotrophic flagellates from contrasting open-ocean ecosystems. *Limnology & Oceanography Letters* **In revision**, (2022).

7. Twining, B. S., Nuñez-Milland, D., Vogt, S., Johnson, R. S. & Sedwick, P. N. Variations in Synechococcus cell quotas of phosphorus, sulfur, manganese, iron, nickel, and zinc within mesoscale eddies in the Sargasso Sea. *Limnology and Oceanography* **55**, 492–506 (2010).

8. Barnett, J. P., Scanlan, D. J. & Blindauer, C. A. Identification of major zinc-binding proteins from a marine cyanobacterium: insight into metal uptake in oligotrophic environments. *Metallomics* **6**, 1254–1268 (2014).

9. Twining, B. S., Rauschenberg, S., Morton, P. L. & Vogt, S. Metal contents of phytoplankton and labile particulate material in the North Atlantic Ocean. *Progress in Oceanography* **137**, 261–283 (2015).

10. Bertilsson, S., Berglund, O., Karl, D. M. & Chisholm, S. W. Elemental composition of marine Prochlorococcus and Synechococcus: Implications for the ecological stoichiometry of the sea. *Limnology and Oceanography* **48**, 1721–1731 (2003).

11. Sunda, W. G. & Huntsman, S. A. Cobalt and zinc interreplacement in marine phytoplankton: Biological and geochemical implications. *Limnology and Oceanography* **40**, 1404–1417 (1995).

12. Young, C. L. & Ingall, E. D. Marine dissolved organic phosphorus composition: Insights from samples recovered using combined electrodialysis/reverse osmosis. *Aquatic Geochemistry* **16**, 563–574 (2010).

13. Kolowith, L. C., Ingall, E. D. & Benner, R. Composition and cycling of marine organic phosphorus. *Limnology and Oceanography* **46**, 309–320 (2001).

14. Martinez, J. & Azam, F. Periplasmic aminopeptidase and alkaline phosphatase activities in a marine bacterium: implications for substrate processing in the sea. *Marine Ecology Progress Series* **92**, 89–97 (1993).

15. Luo, H., Benner, R., Long, R. a & Hu, J. Subcellular localization of marine bacterial alkaline phosphatases. *Proc Natl Acad Sci U S A* **106**, 21219–21223 (2009).

16. Baltar, F. *et al.* High dissolved extracellular enzymatic activity in the deep central Atlantic ocean. *Aquatic Microbial Ecology* **58**, 287–302 (2010).

17. Davis, C. E. & Mahaffey, C. Elevated alkaline phosphatase activity in a phosphate-replete environment: Influence of sinking particles. *Limnology and Oceanography* **62**, 2389–2403 (2017).

18. Labry, C., Delmas, D. & Herbland, A. Phytoplankton and bacterial alkaline phosphatase activities in relation to phosphate and DOP availability within the Gironde plume waters (Bay of Biscay). *Journal of Experimental Marine Biology and Ecology* **318**, 213–225 (2005).

19. Vidal, M., Duarte, C. M., Agustí, S., Gasol, J. M. & Vaqué, D. Alkaline phosphatase activities in the central Atlantic Ocean indicate large areas with phosphorus deficiency. *Marine Ecology Progress Series* **262**, 43–53 (2003).

20. Lazdunski, C. & Lazdunski, M. Zn2+ and Co2+-Alkaline Phosphatases of E. coli. *European Journal of Biochemistry* **7**, 294–300 (1969).

21. Gottesman, M., Simpson, R. T. & Vallee, B. L. Kinetic Properties of Cobalt Alkaline Phosphatase. *Biochemistry* **8**, 3776–3783 (1969).

22. Krishnaswamy, M. & Kenkare, U. W. The effect of pH, temperature, and organic solvents on the kinetic parameters of Escherichia coli alkaline phosphatase. *Journal of Biological Chemistry* **245**, 3956–3963 (1970).

23. Martinez, M. B., Flickinger, M. C. & Nelsestuen, G. L. Accurate kinetic modeling of alkaline phosphatase in the Escherichia coli periplasm: Implications for enzyme properties and substrate diffusion. *Biochemistry* **35**, 1179–1186 (1996).