Faculty of Science and Engineering

School of Geography, Earth and Environmental Sciences

2023-07-03

## Phytoplankton responses to dust addition in the FeMn co-limited eastern Pacific sub-Antarctic differ by source region

## Wyatt, N

https://pearl.plymouth.ac.uk/handle/10026.1/20969

10.1073/pnas.2220111120 Proceedings of the National Academy of Sciences National Academy of Sciences

All content in PEARL is protected by copyright law. Author manuscripts are made available in accordance with publisher policies. Please cite only the published version using the details provided on the item record or document. In the absence of an open licence (e.g. Creative Commons), permissions for further reuse of content should be sought from the publisher or author.



Figure 1. Biogeochemical setting and spatiotemporal development of Fe and Mn (co-)limitation. (A) Annual mean dust deposition (g m<sup>-2</sup> y<sup>-1</sup>) in and around the Southern Ocean (24) alongside (B) December 2019 mean sea surface temperature and (C) chlorophyll-*a* concentration for the study region (red trapezoid in 1A; Modis AQUA at 4 km resolution). (D-I) Hovmöller diagrams (time against latitude) showing in situ biogeochemical progression during the DY111 cruise for sea surface chlorophyll-*a* (D), silicate (E), dMn (F), dFe (G), Mn<sub>Fe</sub>\* (H),  $F_{\nu}/F_m$  (I). (J-K) Summarized experimental responses (larger volume experiments after 6-days) to nutrient addition as indicated by changes in  $F_{\nu}/F_m$  (J) and chlorophyll-*a* (K). Symbol colors indicate the identity and type of limitation, see Figs. S1-S3 (43). Locations of the larger type experiments are labelled in J, see Fig. S6 for all experimental times / locations.



Figure 2. Example responses of phytoplankton ecophysiology to nutrient and dust additions. (A-B, E-F) Apparent photochemical efficiency of PSII ( $F_v/F_m$ ) and (C-D, G-H) chlorophyll-*a* response to nutrient and dust amendment in Ex-L5 at OOI (A-D) and Ex-L7 at TN (E-H), respectively. For clarity only a subset of the nutrient and dust additions are shown in the time series A, C, E, G, with the day 6 data for all treatments included in B, D, F, H. Symbols for all panels are indicated in C. Large open circles in A, C, E, G indicate initial values. Means ( $\pm$  1 standard deviation) are indicated in all panels, with individual data points also provided (small symbols) for B, D, F, H. Statistically indistinguishable means evaluated across all treatments in full factorial manner are labelled with the same letter (analysis of variance (ANOVA) followed by Bonferroni post-hoc means comparison test  $P \le 0.05$ ).



Figure 3. Change in apparent photochemical efficiency of PSII ( $\Delta F_{\nu}/F_m$ ) and net growth rates ( $\mu$ ) in response to nutrient and dust amendment across all experiments. Delta notation ( $\Delta$ ) indicates change relative to the values in control bottles. Data shown here correspond to the mean responses (*n*=2-3) from all treatments across all bioassay experiments.



Figure 4. **Patagonian dust dissolution**. Mean ( $\pm 1$  standard deviation) of dissolved (0.2 µm) trace metal concentrations per unit mass added resulting from leaching of glaciogenic (SMD13-3, PMG) and non-glaciogenic (CAR19) Patagonian dusts into ambient Southern Ocean seawater. Colored circles represent experimental duplicates.

Table S1.	<b>Trace metal</b>	intercali	bration	data.
-----------	--------------------	-----------	---------	-------

	SAFe m	neasured	SAFe co	onsensus	Detection limit	RSD
	(nmol L <sup>-1</sup> )		(nmo	ol L <sup>-1</sup> )	(nmol L <sup>-1</sup> )	(%)
	S	D2	S	D2		
Iron	0.093±0.012	1.164±0.068	0.096±0.008	0.959±0.024	0.035	<13
Manganese	0.768±0.062	0.365±0.017	0.812±0.062	0.360±0.051	0.051	<8
Zinc	0.067±0.012	7.272±0.391	0.071±0.010	7.634±0.257	0.036	<18

Accuracy of the analytical method was validated by repeat quantification of dissolved Fe, Mn, and Zn in SAFe reference seawater. Detection limits were calculated as  $3x1\sigma$  of the lowest concentration reference sample and Relative Standard Deviation (RSD) from the mean (n=3) and  $1\sigma$  of the lowest concentration reference sample.

Exp.	Lat.	Lon.	DIN	Phosphate	Silicate	Fe	Mn	Zn	Chl-a	$F_{\nu}/F_m$
OOI Ex-S1	-54.01	-85.34	20.318	1.374	5.113	0.037	0.222	0.448	0.486	0.284
OOI Ex-S2	-54.56	-89.14	19.950	1.340	4.535	0.035	0.214	0.346	0.377	0.260
TN Ex-S3	-57.31	-89.22	19.517	1.316	3.783	0.041	0.193	1.863*	0.762	0.221
TN Ex-S4	-57.61	-88.76	16.823	1.041	0.047	0.056	0.051	0.189	2.416	0.196
TN Ex-S5	-57.39	-90.06	17.013	1.068	0.077	0.017	0.025	0.143	1.108	0.207
Ex-S6	-58.89	-89.14	18.460	1.176	0.053	0.084	0.034	0.189	0.757	0.179
Ex-S7	-58.16	-90.62	18.317	1.162	0.143	0.029	0.025	0.160	0.763	0.172
OOI Ex-S8	-54.54	-89.13	18.600	1.195	2.220	0.040	0.122	0.161	0.461	0.145
OOI Ex-L1	-54.39	-88.53	20.220	1.364	4.843	0.096	0.169	0.267	0.377	0.189
TS Ex-L2	-59.98	-89.26	24.117	1.532	7.063	0.032	0.100	0.769	1.702	0.167
OOI Ex-L3	-54.61	-89.01	19.623	1.321	3.833	0.064	0.182	0.247	0.506	0.164
TS Ex-L4	-59.84	-89.37	21.243	1.334	1.013	0.055	0.037	0.658	2.596	0.164
OOI Ex-L5	-54.48	-89.03	19.130	1.277	3.427	0.047	0.147	0.189	0.591	0.162
TS Ex-L6	-59.91	-89.49	23.093	1.458	0.727	0.050	0.022	0.342	1.031	0.152
TN Ex-L7	-57.10	-89.12	17.143	1.100	0.097	0.020	0.026	0.088	0.796	0.142

Table S2. Experiment starting conditions.

Units: Latitude, °N; Longitude, °E; Macronutrients (DIN, phosphate, silicate),  $\mu$ mol L<sup>-1</sup>; Dissolved trace metals (Fe, Mn, Zn), nmol L<sup>-1</sup>; Chl-*a*,  $\mu$ g L<sup>-1</sup>;  $F_{\nu}/F_m$ , unitless. Macronutrient, Chl-*a* and  $F_{\nu}/F_m$  values represent an average calculated from the measurement of triplicate initial samples. Trace metal data represent the mean of triplicate measurement on the same sample. Here DIN represents nitrate + nitrite. \*Sample likely contaminated.

Dust source	Source origin	Total concentration (µmol g <sup>-1</sup> )		Fractional	mass content	Fractional solubility		
	6			(	%)	(%)		
		Fe	Mn	Fe	Mn	Fe	Mn	
SMD13-3	Glaciogenic	1793±31	64±1.0	10.01±0.17	0.350±0.005	$0.05 \pm 0.00$	7.29±0.40	
PMG	Glaciogenic	235±5	10±0.1	1.31±0.03	0.053±0.001	0.23±0.15	1.79±0.20	
CAR19	Non-glaciogenic	671±16	14±0.1	3.75±0.09	0.077±0.001	$0.05 \pm 0.01$	8.82±0.02	

Table S3. Total and soluble Fe and Mn in Patagonian dust sources.

Total concentration and mass content following total particle digestion. Fractional solubility following 2-day seawater leach into ambient Southern Ocean seawater. Concentration error represents  $1\sigma$  of repeat analysis (n=3) whilst solubility error represents  $1\sigma$  of dissolution experiment duplicates.



Figure S1. Apparent photochemical efficiency of PSII ( $F_v/F_m$ ) from larger volume experiments at 6 days. Mean values (bars) with individual data points (small symbols) are shown. Statistically indistinguishable means evaluated across all treatments in full factorial manner are labelled with the same letter (analysis of variance (ANOVA) followed by Bonferroni post-hoc means comparison test  $P \le 0.05$ ). Large round symbol colors indicate the identity and type of limitation diagnosed from the statistical responses.



Figure S2. Chlorophyll-*a* from larger volume experiments at 6 days. Mean values (bars) with individual data points (small symbols) are shown. Statistically indistinguishable means evaluated across all treatments in full factorial manner are labelled with the same letter (analysis of variance (ANOVA) followed by Bonferroni post-hoc means comparison test  $P \le 0.05$ ). Large round symbol colors indicate the identity and type of limitation diagnosed from the statistical responses.



Figure S3. Dissolved inorganic nitrogen drawdown from larger volume experiments at 6 days. Mean values (bars) with individual data points (small symbols) are shown. Statistically indistinguishable means evaluated across all treatments in full factorial manner are labelled with the same letter (analysis of variance (ANOVA) followed by Bonferroni post-hoc means comparison test  $P \le 0.05$ ). Large round symbol colors indicate the identity and type of limitation diagnosed from the statistical responses.



Figure S4. Apparent photochemical efficiency of PSII ( $F_v/F_m$ ) from smaller volume experiments. For clarity, only the partial results of the statistical testing are included. Mean values (bars) with individual data points (small symbols) are shown. Error bars represent  $\pm 1$  standard deviation. Treatments that are statistically different from controls (ANOVA followed by Bonferroni means comparison test, p < 0.05) are labelled with a red asterisk.



Figure S5. Chlorophyll-*a* from smaller volume experiments. For clarity, only the partial results of the statistical testing are included. Mean values (bars) with individual data points (small symbols) are shown. Error bars represent  $\pm 1$  standard deviation. Treatments that are

statistically different from controls (ANOVA followed by Bonferroni means comparison test, p < 0.05) are labelled with a red asterisk.



Figure S6. Time and space variability in 48 h (2-day) responses of  $\Delta F_{\nu}/F_m$  across all experiments. (A) Experiment latitudes and dates superimposed on cruise track. (B) Response of  $F_{\nu}/F_m$  to amendment with Mn. (C) Response of  $F_{\nu}/F_m$  to amendment with Fe. (D) Response of  $F_{\nu}/F_m$  to amendment with Fe and Mn. Delta notation ( $\Delta$ ) indicates change relative to the value from control bottles.