

Supplementary Information for: Carbonate chemistry of an in situ free-ocean CO₂ enrichment experiment (antFOCE) in comparison to short term variation in Antarctic coastal waters

J.S Stark, N.P. Roden, G. Johnstone, M. Milnes, J. Black, S. Whiteside, W. Kirkwood, K. Newbery, S. Stark, E. van Ooijen, B. Tilbrook, E.T. Peltzer, K. Berry, D. Roberts

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Supplementary Table S1: Summary of weekly mean carbonate chemistry conditions in antFOCE experiment showing pH_{tot}, aragonite saturation state and fugacity of fCO₂. Data are shown for the acclimatization period (19 December 2014 – 2 January 2015) and experimental period (2 January 2015 – 27 February 2015), with the total number of downtime days (system stoppages) for each corresponding week and period at the bottom of each column. Ambient seawater data are from experiment site. s.d. = standard deviation. Offset shows the difference between the ambient and control chambers, and acidified and control chambers.

	Acclimatization period			Experimental period								Mean
	Week 1	Week 2	Mean	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	
mean pH _{tot} (\pm 1 s.d.)												
Ambient seawater	8.054 ± 0.005	8.049 ± 0.009	8.052 ± 0.008	8.043 ± 0.008	8.053 ± 0.006	8.065 ± 0.011	8.084 ± 0.010	8.091 ± 0.007	8.101 ± 0.015	8.102 ± 0.008	8.108 ± 0.008	8.081 ± 0.025
Control chambers	7.997 ± 0.019	8.005 ± 0.037	8.001 ± 0.029	8.036 ± 0.032	8.023 ± 0.041	8.055 ± 0.031	8.067 ± 0.026	8.082 ± 0.030	8.099 ± 0.033	8.099 ± 0.035	8.100 ± 0.032	8.068 ± 0.044
Offset _{cont-amb}	-0.059 ± 0.020	-0.049 ± 0.037	-0.054 ± 0.030	-0.006 ± 0.035	-0.029 ± 0.040	-0.010 ± 0.031	-0.015 ± 0.028	-0.009 ± 0.031	-0.003 ± 0.032	-0.004 ± 0.032	-0.009 ± 0.030	-0.011 ± 0.034
Experiment chamber (A)	7.978 ± 0.060	7.948 ± 0.057	7.964 ± 0.060	7.749 ± 0.110	7.645 ± 0.091	7.660 ± 0.050	7.682 ± 0.102	7.683 ± 0.063	7.705 ± 0.062	7.701 ± 0.081	7.700 ± 0.072	7.687 ± 0.085
Offset _{exp-cont} chamber (A)	-0.020 ± 0.058	-0.059 ± 0.067	-0.038 ± 0.065	-0.290 ± 0.113	-0.381 ± 0.057	-0.395 ± 0.028	-0.391 ± 0.074	-0.402 ± 0.025	-0.392 ± 0.054	-0.405 ± 0.034	-0.402 ± 0.042	-0.383 ± 0.066
Experiment chamber (B)	7.981 ± 0.053	7.945 ± 0.051	7.964 ± 0.055	7.752 ± 0.105	7.654 ± 0.088	7.655 ± 0.050	7.688 ± 0.097	7.682 ± 0.051	7.701 ± 0.051	7.701 ± 0.073	7.697 ± 0.060	7.688 ± 0.078
Offset _{exp-cont} chamber (B)	-0.017 ± 0.053	-0.059 ± 0.056	-0.036 ± 0.058	-0.285 ± 0.109	-0.370 ± 0.056	-0.400 ± 0.027	-0.382 ± 0.076	-0.400 ± 0.026	-0.399 ± 0.032	-0.401 ± 0.041	-0.404 ± 0.033	-0.382 ± 0.065
mean aragonite saturation state (Ω_{ar}) (\pm 1 s.d.)												
Ambient seawater	1.36 ± 0.01	1.36 ± 0.02	1.36 ± 0.02	1.35 ± 0.02	1.38 ± 0.02	1.42 ± 0.04	1.46 ± 0.04	1.43 ± 0.02	1.44 ± 0.03	1.44 ± 0.02	1.46 ± 0.03	1.42 ± 0.05
Control chambers	1.21 ± 0.05	1.24 ± 0.10	1.22 ± 0.08	1.33 ± 0.09	1.30 ± 0.11	1.39 ± 0.09	1.39 ± 0.07	1.40 ± 0.09	1.43 ± 0.09	1.43 ± 0.10	1.44 ± 0.10	1.39 ± 0.11
Offset _{cont-amb}	-0.16 ± 0.05	-0.13 ± 0.10	-0.15 ± 0.08	-0.02 ± 0.10	-0.08 ± 0.11	-0.03 ± 0.09	-0.04 ± 0.08	-0.03 ± 0.09	-0.01 ± 0.09	-0.01 ± 0.10	-0.03 ± 0.09	-0.03 ± 0.10
Experiment chamber (A)	1.17 ± 0.14	1.10 ± 0.13	1.14 ± 0.14	0.74 ± 0.19	0.58 ± 0.15	0.60 ± 0.07	0.62 ± 0.18	0.60 ± 0.11	0.62 ± 0.11	0.62 ± 0.15	0.62 ± 0.14	0.62 ± 0.15
Offset _{exp-cont} chamber (A)	-0.04 ± 0.13	-0.14 ± 0.16	-0.09 ± 0.15	-0.60 ± 0.21	-0.72 ± 0.09	-0.79 ± 0.05	-0.78 ± 0.14	-0.81 ± 0.05	-0.80 ± 0.11	-0.82 ± 0.07	-0.82 ± 0.10	-0.77 ± 0.13
Experiment chamber (B)	1.17 ± 0.11	1.09 ± 0.12	1.14 ± 0.12	0.75 ± 0.18	0.60 ± 0.14	0.59 ± 0.07	0.63 ± 0.19	0.60 ± 0.08	0.61 ± 0.09	0.62 ± 0.13	0.61 ± 0.11	0.62 ± 0.13
Offset _{exp-cont} chamber (B)	-0.04 ± 0.10	-0.14 ± 0.13	-0.08 ± 0.13	-0.59 ± 0.2	-0.70 ± 0.09	-0.80 ± 0.05	-0.77 ± 0.14	-0.81 ± 0.05	-0.82 ± 0.05	-0.82 ± 0.08	-0.83 ± 0.09	-0.77 ± 0.13
mean fugacity of carbon dioxide (f CO ₂) (μatm) (\pm 1 s.d.)												

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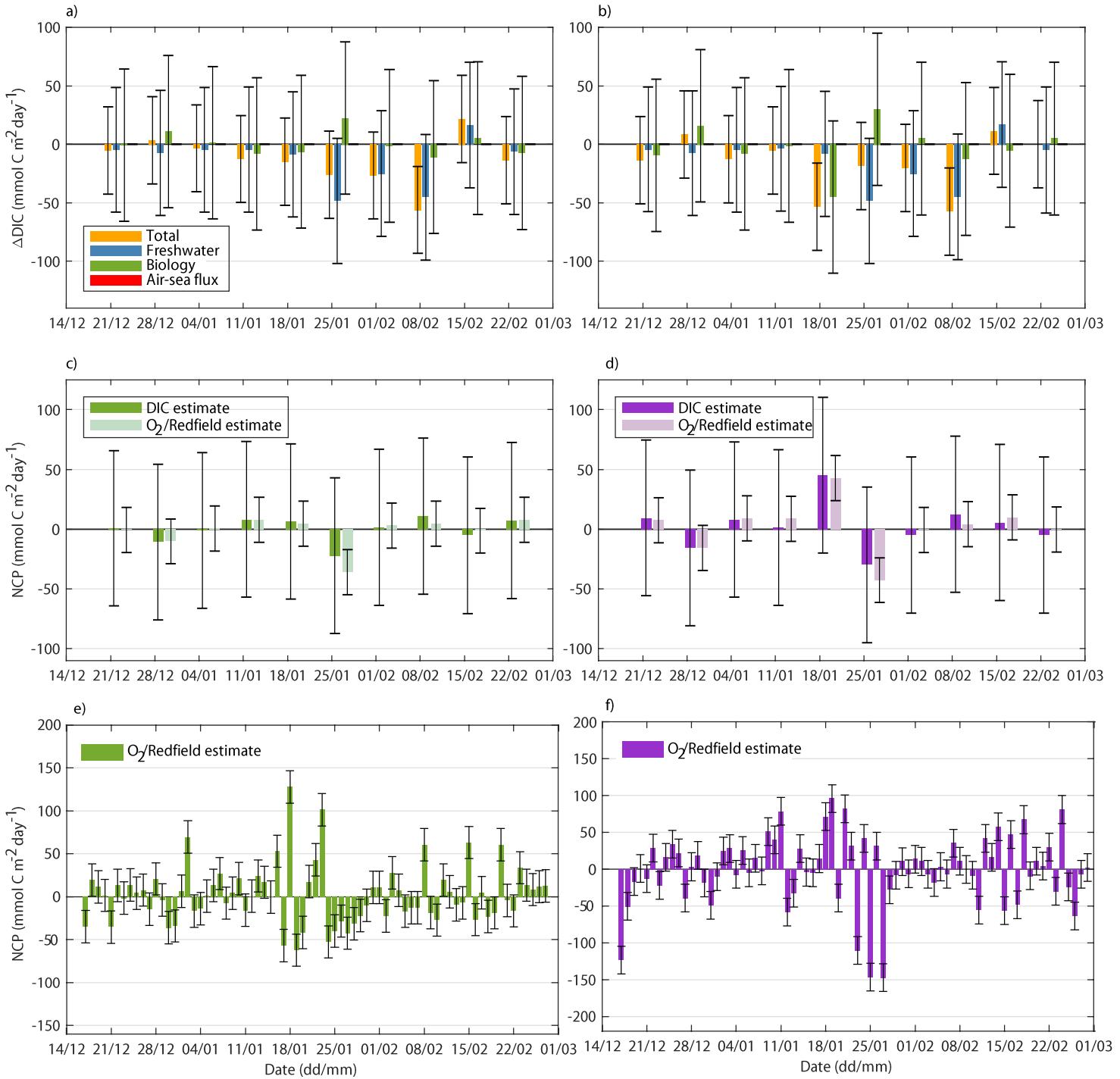
Ambient seawater	368 ± 4	374 ± 9	371 ± 8	379 ± 7	370 ± 6	359 ± 10	340 ± 9	329 ± 6	319 ± 13	318 ± 7	314 ± 7	341 ± 25
Control chambers	425 ± 20	419 ± 37	422 ± 29	387 ± 31	400 ± 39	369 ± 29	354 ± 23	338 ± 26	321 ± 28	321 ± 28	321 ± 26	354 ± 42
Offset _{cont-amb}	59 ± 20	49 ± 38	55 ± 30	7 ± 34	30 ± 39	10 ± 29	13 ± 24	8 ± 26	3 ± 26	4 ± 26	8 ± 24	11 ± 31
Experiment chamber (A)				$810 \pm$	$1028 \pm$	$979 \pm$	$938 \pm$	$908 \pm$	$855 \pm$	$868 \pm$	$868 \pm$	$914 \pm$
	450 ± 75	485 ± 69	466 ± 74	203	189	110	155	112	106	129	111	159
Offset _{exp-cont} chamber (A)				$428 \pm$	$631 \pm$		$589 \pm$					$564 \pm$
	26 ± 74	69 ± 80	46 ± 79	202	149	610 ± 85	127	575 ± 74	530 ± 93	556 ± 79	550 ± 75	130
Experiment chamber (B)				$801 \pm$	$1003 \pm$	$990 \pm$	$919 \pm$			$865 \pm$	$872 \pm$	$911 \pm$
	446 ± 84	487 ± 62	465 ± 77	191	179	112	153	908 ± 97	861 ± 92	121	100	150
Offset _{exp-cont} chamber (B)				$417 \pm$	$605 \pm$		$569 \pm$					$559 \pm$
	23 ± 87	67 ± 66	43 ± 81	190	141	622 ± 86	128	571 ± 69	541 ± 66	549 ± 86	553 ± 67	124
Downtime (total days)	4.15	4.4	8.55	2.26	0.44	0.22	2.03	1.49	1.1	2.32	2.33	12.19

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Supplementary Table S2: Summary of changes in ambient seawater conditions within O'Brien Bay, the site of the antFOCE experiment. a) daily changes and b) seasonal values between 19 December 2014 – 27 February 2015. O₂ = dissolved oxygen; DIC = calculated dissolved inorganic carbon; Ω_{ar} = saturation state of aragonite; fCO₂ = fugacity of CO₂.

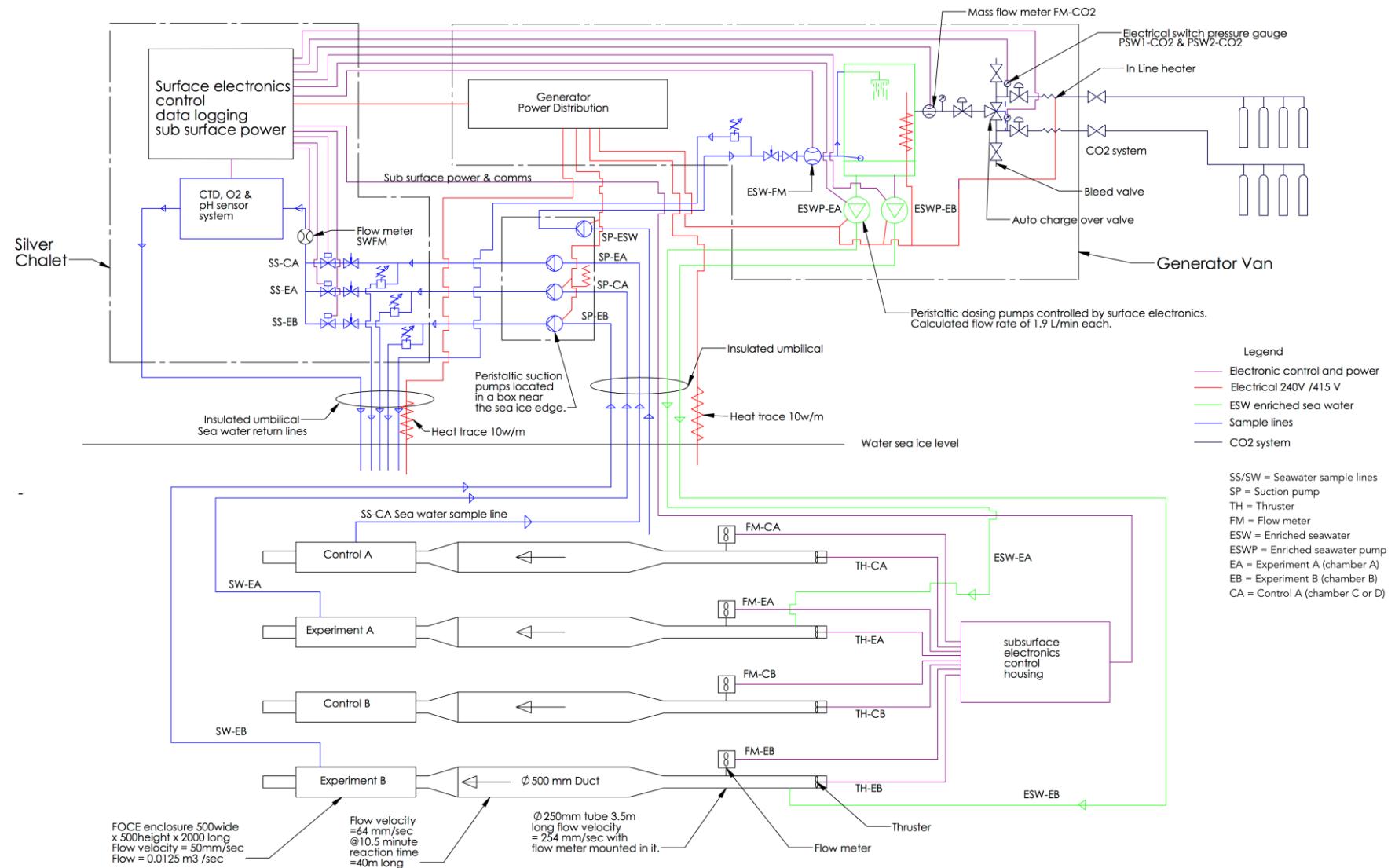
a) Daily changes	pH _{tot}	O ₂ (μmol kg ⁻¹)	DIC (μmol kg ⁻¹)	Ω _{ar}	fCO ₂ (μatm)	Salinity	Temp (°C)
Ambient (experiment site)							
Minimum range	0.008	3	3	0.02	8	0.007	0.008
Maximum range	0.049	23	22	0.16	44	0.226	0.301
Mean range (± 1 s.d.)	0.020 ± 0.008	8 ± 3	9 ± 4	0.06 ± 0.02	18 ± 7	0.050 ± 0.048	0.076 ± 0.069
Ambient (outer O'Brien Bay)							
Minimum range	0.007	4	2	0.02	6	0.004	0.012
Maximum range	0.073	33	28	0.24	52	0.221	0.343
Mean range (± 1 s.d.)	0.029 ± 0.016	13 ± 7	11 ± 6	0.09 ± 0.05	23 ± 12	0.046 ± 0.045	0.082 ± 0.067
Control chambers							
Minimum range	0.014	-	5	0.04	10	-	-
Maximum range	0.127	-	47	0.37	115	-	-
Mean range (± 1 s.d.)	0.077 ± 0.027	-	28 ± 10	0.22 ± 0.08	69 ± 25	-	-
Experimental chamber (A)							
Minimum range	0.039	-	12	0.04	43	-	-
Maximum range	0.535	-	167	1.13	891	-	-
Mean range (± 1 s.d.)	0.242 ± 0.17	-	73 ± 52	0.46 ± 0.36	390 ± 246	-	-
Experimental chamber (B)							
Minimum range	0.046	-	14	0.07	49	-	-
Maximum range	0.545	-	167	1.1	835	-	-
Mean range (± 1 s.d.)	0.231 ± 0.16	-	69 ± 49	0.43 ± 0.34	382 ± 233	-	-
b) Seasonal values	pH _{tot}	O ₂ (μmol kg ⁻¹)	DIC (μmol kg ⁻¹)	Ω _{ar}	fCO ₂ (μatm)	Salinity	Temp (°C)
Ambient (experiment site)							
Minimum	8.025	333	2105	1.3	291	33.079	-1.479
Maximum	8.137	374	2206	1.55	397	34.257	-0.609
Range	0.112	41	100	0.25	106	1.178	0.87
Mean (± 1 s.d.)	8.075 ± 0.025	348 ± 7	2166 ± 32	1.41 ± 0.05	348 ± 26	33.785 ± 0.430	-1.120 ± 0.242
Ambient (outer O'Brien Bay)							
Minimum	8.052	335	2089	1.37	249	33.088	-1.466
Maximum	8.198	400	2196	1.79	371	34.256	-0.639
Range	0.146	65	107	0.42	122	1.168	0.827
Mean (± 1 s.d.)	8.107 ± 0.028	356 ± 11	2153 ± 32	1.51 ± 0.07	320 ± 25	33.776 ± 0.432	-1.112 ± 0.243

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Supplementary Figure S3: Daily changes in ambient seawater conditions at two sites in O'Brien Bay, Casey station, Antarctica. At the experimental site, a) the weekly mean of daily changes in DIC partitioned into total change, and changes caused by freshwater input, biological activity and air-sea flux. c) The weekly mean of daily NCP values estimated from calculated DIC and measured oxygen and e) daily NCP estimates from calculated DIC. The corresponding parameters for the outer O'Brien Bay site are shown in panels b), d) and f) respectively. Error bars represent the propagated measurement uncertainties and positive NCP values indicate net primary production.

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Supplementary Figure S4 Schematic plan of the antFOCE system components.