

Supplementary material

Strong seasonality in the cadmium and phosphate cycling at the subtropical convergence, south-eastern New Zealand

R. D. Frew^{A,E}, T. Adu^A, M. Gault-Ringold^A, A. Hamidian^{A,B}, K. I. Currie^C, E. Armstrong^A and K. A. Hunter^D

^ADepartment of Chemistry, University of Otago, PO Box 56, Union Street, Dunedin, 9056, New Zealand.

^BDepartment of Environment, Faculty of Natural Resources, University of Tehran, 16 Azar Street, Karaj, 31587-77878, Iran.

^CNational Institute for Water and Atmospheric Research (NIWA), Union Street, Dunedin, 9056, New Zealand.

^DDeceased. Formerly at Department of Chemistry, University of Otago, Dunedin, 9056, New Zealand.

^ECorresponding author. Email: rfreew@chemistry.otago.ac.nz

Table S1. Trace-metal concentrations obtained from solvent extraction followed by inductively coupled plasma–mass spectrometry (ICP-MS) for reference materials used during this study

The two international reference materials used were: SAFe (S-473, D1-555) and NASS-5. The data of Ellwood (2008) measurements of SAFe surface CRM (S1 403) are included for comparison. Three samples of each were analysed to verify the methodology employed. NV, there was no certified value reported for that analyte. Cd, cadmium concentration. Zn, zinc concentration. Fe, iron concentration. Co, cobalt concentration. Obtained data are those obtained in this work: the result is the mean of three measurements and the uncertainty is the standard error. Accepted data are the internationally accepted concentration data. SAFe accepted value was obtained from <http://es.ucsc.edu/~kbruland/GeotradesSaFe/kwbGeotradesSaFe.html> (accessed 26 September 2019)

Reference material	Cd (pM)		Zn (nM)		Fe (nM)		Co (pM)	
	Obtained	Accepted	Obtained	Accepted	Obtained	Accepted	Obtained	Accepted
SAFe Surface S 473	5.2 ± 1.2	1-6	0.081 ± 0.015	0.068 ± 0.014	0.095 ± 0.018	0.094 ± 0.008	2.8 ± 0.8	2.7 ± 1.3
SAFe Surface (S1 403) ^A	6± 2	NV	0.09±0.02	NV	0.10±0.03	NV	5 ± 6	NV
SAFe Deep (D1 555)	996 ± 7	1027 ± 55	7.16 ± 0.10	7.22 ± 0.62	0.65 ± 0.04	0.65 ± 0.10	27.9 ± 0.9	26.9 ± 4.7
NASS-5 Surface (µg L ⁻¹)	0.024 ± 0.001	0.023 ± 0.003	0.112 ± 0.001	0.102 ± 0.039	0.172 ± 0.040	0.207± 0.039	0.010 ± 0.0001	0.011 ± 0.003

^AData from (Ellwood 2008).

Table S2. Geochemical data collected from the Otago Munida transect, July 2007 to March 2010

Chlorophyll-*a* samples were collected only at the outermost station for each of SC and SA (SC1, station SC1 is modified with neritic water; ns, no sample; con, sample contamination). Date, the date of sample collection. Station, station identifier (cf. Fig. 1). PO₄³⁻, phosphate concentration (μM; cf. Fig. 2, 5, 6). NO₃⁻, nitrate concentration (μM; Fig. 2). Si(OH)₄, silicate concentration (μM; cf. Fig. 2, 7). DCd, dissolved-cadmium concentration (nM) for a filtered sample (0.4-μm pore; cf. Fig. 4–7). TCd, the total cadmium concentration (nM) determined by acid solubilisation (1 mL qHNO₃ L⁻¹) of an unfiltered sample. PCd, particulate cadmium concentration (nM) where particles were collected on acid-cleaned polycarbonate filters digested in nitric acid (HNO₃; cf. Fig. 7). DZn, dissolved zinc concentration (nM) for a filtered sample (0.4-μm pore; cf. Fig. 4, 7). DFe, dissolved iron concentration (nM) for a filtered sample (0.4-μm pore; cf. Fig. 4). DCo, dissolved cobalt concentration (nM) for a filtered sample (0.4-μm pore; cf. Fig. 4). PON, particulate organic nitrogen (μg L⁻¹) where particles were collected on GF/F filters, treated with acid to remove carbonate and analysed by Dumas combustion (cf. Fig. 3). POC, particulate organic carbon (μg L⁻¹) where particles were collected on GF/F filters, treated with acid to remove carbonate and analysed by Dumas combustion (cf. Fig. 3). Chl-*a*, the chlorophyll-*a* concentration (μg L⁻¹) (cf. Fig. 3, 7)

Date	Station	PO ₄ ³⁻ (μM)	NO ₃ ⁻ (μM)	Si(OH) ₄ (μM)	DCd (nM)	TCd (nM)	PCd (nM)	DZn (nM)	DFe (nM)	DCo (nM)	PON (μg L ⁻¹)	POC (μg L ⁻¹)	Chl- <i>a</i> (μg L ⁻¹)
Jul-2007	SC1	1.05			0.030								
	SC2	1.07			0.180								
	SC3	1.16			0.120								
	SC4	1.05			0.110								
	SA5	1.27			0.140								
	SA6	0.99			0.170								
	SA7	1.38			0.160								
	SA8	0.86			0.140								
Nov-2007	SC1	0.91			0.080								
	SC2	0.8			0.110								
	SC3	0.91			0.220								
	SC4	1.11			0.110								
	SA5	0.96			0.170								
	SA6	1.07			0.180								
	SA7	0.84			0.170								
	SA8	0.92			0.130								
Jan-2008	SC1	0.51			0.060								

Date	Station	PO ₄ ³⁻ (µM)	NO ₃ ⁻ (µM)	Si(OH) ₄ (µM)	DCd (nM)	TCd (nM)	PCd (nM)	DZn (nM)	DFe (nM)	DCo (nM)	PON (µg L ⁻¹)	POC (µg L ⁻¹)	Chl-a (µg L ⁻¹)
Apr-2008	SC2	0.55			0.030								
	SC3	0.76			0.030								
	SC4	0.69			0.020								
	SA5	0.76			0.020								
	SA6	0.78			0.010								
	SA7	0.57			0.010								
	SA8	0.75			0.010								
	SC1	0.37			0.060								
	SC2	0.55			0.060								
	SC3	0.56			0.050								
May-2008	SC4	0.82			0.030								
	SA5	0.83			0.040								
	SA6	0.87			0.040								
	SA7	0.89			0.030								
	SA8	0.85			0.030								
	SC1	0.64			0.100								
	SC2	0.9			0.100								
	SC3	1			0.100								
	SC4	1.03			0.140								
	SA5	1.15			0.110								
25-Mar-2009	SA6	1.04			0.110								
	SA7	0.91			0.090								
	SA8	0.99			0.130								
	SC1	0.23	0.71	1.32	0.034	0.120	0.086	0.52	2.70	0.089			
	SC2	0.29	1.29	0.96	0.021	0.107	0.085	0.07	1.48	0.037			
	SC3	0.55	6.57	0.43	0.014	0.091	0.077	0.03	0.10	0.005			
	SC4	0.65	7.35	0.28	0.011	0.022	0.010	0.00	0.05	0.007			0.29
	SA5	0.65	7.57	0.25	0.012	0.028	0.016	0.07	con	0.006			
	SA6	0.68	10.21	0.50	0.010	0.019	0.009	con	con	0.007			
	SA7	0.87	12.85	1.00	0.019	0.052	0.032	0.01	0.08	0.007			
14-Jul-2009	SA8	0.81	10.14	0.89	0.043	0.065	0.022	0.03	0.12	0.012			0.39
	SC1	0.65	6.43	3.06	0.077	0.090	0.013	0.19	2.53	0.069	12.4	62.4	
	SC2	0.84	11.07	2.28	0.087	0.116	0.029	0.07	1.30	0.037	10.9	49.3	
	SC3	0.94	12.28	2.39	0.109	0.122	0.013	0.08	0.60	0.024	8.6	43.6	
	SC4	0.84	10.57	2.28	0.107	0.114	0.006	0.07	0.53	0.027	6.7	37.2	0.16
	SA5	0.84	11.78	2.31	0.123	0.124	0.001	0.03	0.14	0.019	8.5	37.5	
	SA6	1.00	14.14	2.14	ns	0.120	ns	ns	ns	ns	4.3	20.3	
	SA7	1.10	13.85	1.78	0.137	0.139	0.002	0.08	0.15	0.020	5.2	24.8	

Date	Station	PO_4^{3-} (μM)	NO_3^- (μM)	Si(OH)_4 (μM)	DCd (nM)	TCd (nM)	PCd (nM)	DZn (nM)	DFe (nM)	DCo (nM)	PON ($\mu\text{g L}^{-1}$)	POC ($\mu\text{g L}^{-1}$)	$\text{Chl-}a$ ($\mu\text{g L}^{-1}$)
29-Sep-2009	SA8	1.03	11.57	1.64	0.139	0.141	0.002	0.07	0.12	0.017	5.4	23.9	0.17
	SC1	ns	ns	ns	ns	ns	ns	ns	ns	ns			
	SC2	0.52	4.36	1.82	0.058	0.074	0.015	0.10	2.03	0.055			
	SC3	0.48	4.50	1.74	0.095	0.104	0.009	0.08	0.89	0.031			
	SC4	0.81	10.71	2.74	0.121	0.142	0.021	0.14	0.27	0.024			0.18
	SA5	0.97	12.28	2.63	0.135	0.135	0.000	con	0.54	0.026			
	SA6	0.90	11.71	2.74	0.136	0.151	0.014	0.11	0.30	0.024			
	SA7	1.03	12.78	2.67	0.150	0.167	0.017	0.10	0.13	0.023			
8-Dec-2009	SA8	1.07	13.99	2.35	0.128	0.149	0.021	con	0.16	0.021			
	SC1	0.16	1.21	0.25	0.029	0.051	0.022	0.07	0.59	0.026	22.4	165.5	
	SC2	0.32	1.86	0.25	0.056	0.068	0.012	0.08	0.47	0.025	30.4	210.7	
	SC3	0.36	1.07	0.25	0.066	0.109	0.043	0.09	0.38	0.021	51.3	296.3	
	SC4	0.58	5.07	0.36	0.067	0.131	0.064	0.09	0.18	0.014	40.5	238.2	2.43
	SA5	0.81	9.42	0.53	0.056	0.122	0.066	0.07	0.14	0.010	14.8	76.8	
	SA6	0.87	11.42	0.39	0.026	0.069	0.043	0.08	0.11	0.006	20.4	106.5	
	SA7	0.77	10.99	0.18	0.055	0.092	0.037	0.08	0.22	0.014	16.7	97.9	
15-Jan-2010	SA8	0.71	11.14	0.11	0.044	0.133	0.089	0.09	0.20	0.009	17.3	98.6	0.43
	SC1	0.29	0.64	1.57	0.044	0.047	0.003	0.07	4.22	0.087	35.4	181.8	
	SC2	0.16	0.14	1.17	0.021	0.054	0.033	0.04	3.62	0.055	42.0	208.7	
	SC3	0.13	0.07	1.25	0.021	0.062	0.041	0.03	3.39	0.046	37.4	192.7	
	SC4	0.45	3.93	0.57	0.024	0.060	0.036	0.02	1.59	0.017	21.0	108.8	0.69
	SA5	0.68	4.85	0.14	0.013	0.054	0.041	0.01	0.16	0.006	7.1	40.0	
	SA6	0.68	9.50	0.28	0.009	0.030	0.021	0.00	0.11	0.005	8.9	47.9	
	SA7	0.68	8.28	0.36	0.009	0.025	0.016	0.07	0.15	0.004	10.7	61.2	
5-Mar-2010	SA8	0.77	10.28	0.53	0.007	0.022	0.015	0.04	0.19	0.005	9.3	48.5	0.40
	SC1	0.32	1.14	1.39	0.024	0.055	0.031	0.04	1.99	0.047	25.9	111.3	
	SC2	0.39	3.28	0.57	0.023	0.062	0.039	0.02	0.29	0.010	23.1	111.0	
	SC3	0.65	5.50	0.71	0.028	0.071	0.044	0.04	0.17	0.010	23.0	111.3	
	SC4	0.61	4.64	0.18	0.019	0.065	0.046	0.03	0.15	0.006	22.8	113.8	0.60
	SA5	0.58	7.00	0.50	0.019	ns	ns	0.01	0.12	0.003	18.9	93.0	
	SA6	0.71	8.57	0.36	0.018	0.031	0.013	0.02	con	0.003	19.7	95.6	
	SA7	0.68	8.57	0.53	0.028	0.034	0.006	0.04	0.12	0.005	18.6	94.9	
	SA8	0.68	6.85	0.53	0.013	0.036	0.023	0.05	0.16	0.002	19.0	96.2	0.46

Reference

- Ellwood, M. J. (2008). Wintertime trace metal (Zn, Cu, Ni, Cd, Pb and Co) and nutrient distributions in the Subantarctic zone between 40–52°S; 155–160°E. *Marine Chemistry* **112**(1–2), 107–117. doi:10.1016/j.marchem.2008.07.008