

Biogeochemical cycle of organic matter in a subtidal benthic environment in Marian Cove, King George Island, Antarctica

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Abstract: The flux and composition of settling particles were measured in a subtidal benthic environment of Marian Cove, King George Island, from February 1998–January 2000. The total mass flux ranged between 2.47 g m⁻² d⁻¹ (August and September 1998) and 21.97 g m⁻² d⁻¹ (February 1999), and showed distinct seasonal variation: high in the summer and low in winter. Lithogenic particles constituted 70–95% of the total particles, while biogenic particles represented only 10%, except in spring when biogenic particles made up more than 30%. The fluxes of organic carbon, biogenic silica, nitrogen, and organic phosphorus all peaked in spring rather than in summer, with ranges of 4.4–34.0, 1.2–23.5, 0.48–5.56, and 0.01–0.15 mmol m⁻² d⁻¹, respectively. Fluxes of metals (Al, Ti, Cu, Cd, and Pb) showed temporal variability, similar to that of the total mass flux, but each metal had different enrichment factor (EF) values. The EF value of Cu correlated positively with fluxes in lithogenic components, while the EF value of Cd correlated with biogenic particle fluxes. The Cu flux is mainly related to substantial inflows of melt water laden with Cu-enriched lithogenic particles. The Cd flux is probably associated with organic matter deposition following phytoplankton blooms in the water column.

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Key words: biogenic particle, lithogenic particle, metal flux, particle flux, Southern Ocean

Introduction

The Southern Ocean is of special interest because of its role in atmospheric carbon dioxide sequestration and its consequent importance in the global ocean carbon cycle and climate change (Knox & McElroy 1984, Sarmiento *et al.* 1998, Nelson *et al.* 2002, Schlitzer 2002, Takahashi *et al.* 2002, Tréguer & Pondaven 2002). Studies of vertical flux and biogeochemical cycling of elements in the Southern Ocean, especially carbon and organic matter, are critical for improving our understanding of these global processes. Many researchers have conducted sediment trap studies around the Southern Ocean to investigate particle flux composition and variability (Wefer *et al.* 1988, Dunbar *et al.* 1989, Karl *et al.* 1991, Wefer & Fischer 1991, Shiimoto & Ishii 1995, Collier *et al.* 2000, Honjo *et al.* 2000, Langone *et al.* 2000, Anadón *et al.* 2002, Fischer *et al.* 2002, Palanques *et al.* 2002, Accornero *et al.* 2003, Kim *et al.* 2004).

By contrast, few studies have investigated the dynamics of particles in near-shore coastal environments (Cripps & Clarke 1998, Isla *et al.* 2001). The coastal and polar front zones have relatively high productivity and fluxes relative to the rest of the Southern Ocean, despite their relatively small area (Wefer & Fischer 1991). These regions occupy only 10% of the Southern Ocean's surface area, yet about 40% of the ocean's organic carbon is synthesized there. Dense summer phytoplankton blooms occur in near-shore Antarctic environments, and the relatively short residence

time of particulate matter in the water column implies that much of this material reaches the sea floor intact, i.e. it is an effective biological pump of carbon dioxide.

King George Island is in the western Antarctic and is the largest of the South Shetland Islands. Marian Cove (3.5 km

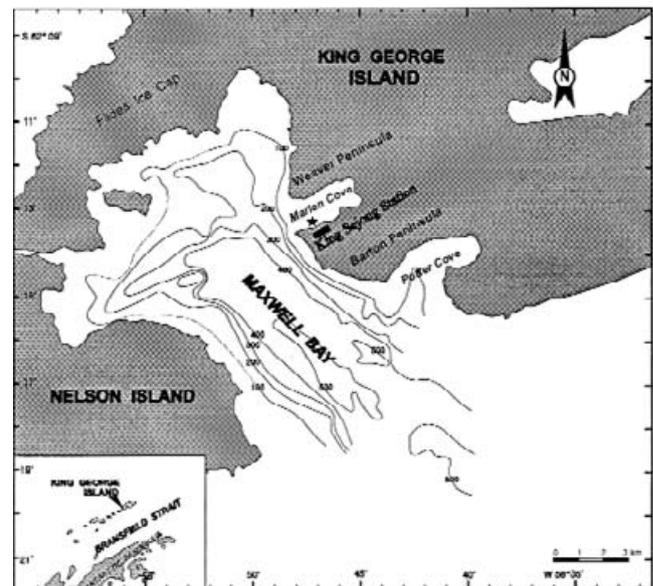


Fig. 1. Location of the study site: Marian Cove, King George Island, Antarctica. The star indicates the deployment site for the sediment traps during 1998–2000.

Table I. Fluxes and composition of biogeochemical components in settling particles at Marian Cove, King George Island (continued opposite).

Start date /duration in days	Trap species	TMF (g m ⁻² d ⁻¹)/(avg.)		OC (%)/(mmol m ⁻² d ⁻¹)		IC (%)/(mmol m ⁻² d ⁻¹)		TN (%)/(mmol m ⁻² d ⁻¹)		OP (%)/(mmol m ⁻² d ⁻¹)	
02/28/98	A	14.32		0.843	10.06	0.481	5.74	0.104	1.07	0.011	0.051
30	B	12.59	13.46	1.011	10.61	0.493	5.17	0.123	1.10	0.010	0.040
03/30/98	A*										
30	B	18.94	18.94	0.780	12.32	0.209	3.30	0.079	1.07	0.008	0.049
04/29/98	A	9.60		1.376	11.01	0.464	3.72	0.168	1.15	0.015	0.046
30	B	11.05	10.33	0.800	7.37	0.412	3.79	0.091	0.72	0.006	0.023
05/29/98	A*										
34	B	11.17	11.17	0.704	6.56	0.540	5.02	0.069	0.55	0.007	0.026
07/02/98	A	5.27		1.175	5.16	0.560	2.46	0.117	0.44	0.010	0.017
28	B	6.21	5.74	0.905	4.68	0.503	2.60	0.115	0.51	0.010	0.020
07/30/98	A	2.68		2.355	5.27	0.488	1.09	0.388	0.74	0.023	0.020
71	B	2.27	2.47	2.104	3.97	0.276	0.52	0.225	0.36	0.017	0.013
10/09/98	A	3.98		5.936	19.69	0.407	1.35	0.735	2.09	0.039	0.051
31	B	2.89	3.44	3.629	8.75	0.385	0.93	0.540	1.12	0.029	0.027
11/09/98	A	6.71		3.503	19.59	0.252	1.41	0.466	2.24	0.038	0.083
30	B	4.69	5.70	4.238	16.57	0.313	1.22	0.692	2.32	0.030	0.046
12/09/98	A	5.75		1.463	7.01	0.320	1.53	0.201	0.83	0.023	0.043
33	B	7.88	6.81	1.395	9.16	0.274	1.80	0.198	1.11	0.018	0.045
01/11/99	A	22.86		0.825	15.72	0.195	3.71	0.122	1.99	0.010	0.075
29	B	13.81	18.33	0.793	9.12	0.242	2.79	0.108	1.06	0.009	0.040
02/09/99	A*										
27	B	23.69	23.69	0.578	11.42	0.304	6.00	0.103	1.75	0.005	0.037
03/08/99	A	21.55		0.761	13.68	0.242	4.35	0.117	1.80	0.009	0.062
31	B	16.44	19.00	0.678	9.29	0.219	3.00	0.092	1.07	0.007	0.039
04/08/99	A	13.16		0.787	8.63	0.280	3.07	0.112	1.05	0.008	0.036
32	B*		13.16								
05/10/99	A	9.06		1.076	8.12	0.237	1.79	0.171	1.11	0.011	0.032
31	B	8.30	8.68	0.897	6.21	0.266	1.84	0.142	0.84	0.008	0.023
06/10/99	A	8.97		1.022	7.63	0.315	2.36	0.148	0.95	0.003	0.010
29	B	9.32	9.14	1.028	7.98	0.202	1.57	0.156	1.04	0.012	0.036
07/09/99	A	10.93		0.739	6.73	0.347	3.16	0.101	0.79	0.006	0.019
34	B	10.63	10.78	0.721	6.38	0.219	1.94	0.109	0.83	0.005	0.016
08/12/99	A	9.06		0.840	6.34	0.435	3.28	0.125	0.81	0.006	0.019
35	B	9.43	9.25	0.822	6.46	0.266	2.09	0.108	0.73	0.006	0.020
09/16/99	A	5.20		1.120	4.85	0.283	1.23	0.182	0.67	0.013	0.022
41	B	3.49	4.34	1.331	3.87	0.199	0.58	0.200	0.50	0.013	0.014
10/27/99	A	6.44		1.175	6.30	0.254	1.36	0.170	0.78	0.015	0.030
21	B	8.54	7.49	1.207	8.59	0.124	0.88	0.186	1.13	0.006	0.016
11/17/99	A*										
16	B	11.05	11.05	3.694	34.01	0.242	2.23	0.705	5.56	0.042	0.150
12/03/99	A	8.07		2.147	14.43	0.245	1.65	0.383	2.21	0.039	0.101
28	B	12.19	10.13	1.053	10.70	0.189	1.92	0.177	1.54	0.011	0.043
12/31/99	A	16.43		0.985	13.48	0.185	2.54	0.166	1.94	0.009	0.047
22	B	19.50	17.96	1.007	16.37	0.148	2.40	0.177	2.47	0.027	0.172

* = no sample

long and 1.2 km wide) is an inlet of Maxwell Bay on King George Island with a mean water depth of < 100 m (Fig. 1). There is a submarine sill at about 40 m depth between the cove and the bay, across which the surface water of Maxwell Bay is transported (Mullins & Priddle 1987). The bottom sediments consist of poorly sorted silty sand and mud, with a considerable component of ice-rafted debris. Dense populations of the Antarctic lamellibranch *Laternula elliptica* occurred both subtidally and intertidally (Chung *et al.* 1998), while low primary productivity (0.04–0.56 g C m⁻² d⁻¹) and organic carbon contents in the water column

were reported in 1989 and 1994 (Kim *et al.* 1998). Ahn (1993) and Kang (1998) have suggested that the summer phytoplankton production levels and organic content of the water column are not sufficient to support all the benthic organisms, and that other supplementary food sources are necessary. Therefore, to understand the bio-geochemical cycle and mass balance of organic matter in a subtidal, benthic, near-shore, Antarctic environment, we investigated year-round settling particle dynamics in Marian Cove. We also discuss the main factor(s) controlling the seasonality of the particle flux and composition in this environment.

Table 1. (continued) Fluxes and composition of biogeochemical components in settling particles at Marian Cove, King George Island.

Start date /duration in days	Trap species	Bio-Si		Al		Ti		Cu		Cd		Pb	
		(%)/(mmol m ⁻² d ⁻¹)	(ppm)/(μmol m ⁻² d ⁻¹)										
02/28/98	A	1.32	6.73	10.24	54.35	0.47	1.41	89	20.06	0.32	0.040	79.4	5.49
30	B	1.04	4.68	10.13	47.27	0.47	1.24	97	19.15	0.30	0.033	36.4	2.21
03/30/98	A*												
30	B	0.82	5.52	10.66	74.88	0.50	1.99	106	31.61	0.38	0.064	40.5	3.70
04/29/98	A	0.85	2.91	9.69	34.49	0.50	0.99	104	15.78	0.29	0.024	42.8	1.98
30	B	0.88	3.46	9.98	40.85	0.50	1.15	104	18.12	0.22	0.022	41.4	2.21
05/29/98	A*												
34	B	0.70	2.79	9.48	39.23	0.48	1.13	109	19.24	0.16	0.016	37.3	2.01
07/02/98	A	0.92	1.74	9.39	18.35	0.49	0.54	98	8.15	0.30	0.014	29.3	0.75
28	B	0.88	1.94	9.45	21.73	0.50	0.64	96	9.39	0.29	0.016	26.9	0.81
07/30/98	A	0.97	0.93	9.28	9.23	0.49	0.28	106	4.46	0.29	0.007	39.5	0.51
71	B	1.77	1.43	9.61	8.07	0.51	0.24	96	3.43	0.39	0.008	64.3	0.70
10/09/98	A	11.31	16.08	7.46	11.00	0.34	0.28	73	4.59	0.55	0.019	47.5	0.91
31	B	2.35	2.42	8.16	8.75	0.38	0.23	84	3.81	0.39	0.010	27.9	0.39
11/09/98	A	9.18	22.00	9.03	22.46	0.46	0.65	97	10.23	0.30	0.018	19.2	0.62
30	B	5.91	9.90	9.15	15.92	0.45	0.44	97	7.20	0.29	0.012	17.7	0.40
12/09/98	A	2.83	5.82	7.92	16.89	0.44	0.52	110	9.95	0.27	0.014	25.1	0.70
33	B	4.26	11.98	7.52	21.96	0.41	0.67	104	12.95	0.23	0.016	19.3	0.73
01/11/99	A	2.22	18.11	8.95	75.79	0.45	2.17	126	45.31	0.31	0.062	29.2	3.22
29	B	2.43	11.98	8.61	44.06	0.44	1.26	128	27.82	0.23	0.028	22.8	1.52
02/09/99	A*												
27	B	1.37	11.61	9.08	79.76	0.45	2.25	142	52.87	0.39	0.081	22.3	2.54
03/08/99	A	3.09	23.77	8.52	68.09	0.45	2.04	131	44.52	0.32	0.061	22.7	2.36
31	B	1.73	10.13	8.72	53.13	0.46	1.58	137	35.34	0.30	0.043	21.3	1.69
04/08/99	A	2.19	10.30	8.54	41.66	0.46	1.25	130	26.83	0.29	0.035	23.6	1.50
32	B*												
05/10/99	A	1.43	4.62	8.99	30.19	0.45	0.85	110	15.66	0.16	0.013	33.0	1.44
31	B	1.06	3.16	9.31	28.66	0.45	0.78	106	13.91	0.13	0.010	26.7	1.07
06/10/99	A	1.25	4.00	8.97	29.80	0.47	0.89	107	15.14	0.12	0.010	24.2	1.05
29	B	0.85	2.81	8.86	30.60	0.45	0.88	97	14.23	0.09	0.008	16.5	0.74
07/09/99	A	0.76	2.98	8.79	35.62	0.46	1.05	97	16.67	0.14	0.013	21.0	1.11
34	B	0.72	2.72	8.81	34.70	0.46	1.02	101	16.82	0.12	0.011	16.7	0.86
08/12/99	A	0.75	2.44	8.46	28.43	0.46	0.87	81	11.50	0.10	0.008	16.4	0.72
35	B	0.86	2.89	8.16	28.53	0.45	0.88	77	11.46	0.12	0.010	18.9	0.86
09/16/99	A	2.03	3.76	8.48	16.34	0.42	0.46	78	6.40	0.13	0.006	32.0	0.80
41	B	3.13	3.90	7.03	9.09	0.37	0.27	70	3.85	0.11	0.003	28.1	0.47
10/27/99	A	3.49	8.02	8.06	19.23	0.38	0.51	83	8.42	0.13	0.008	21.9	0.68
21	B	1.99	6.07	8.20	25.97	0.42	0.74	84	11.29	0.11	0.009	26.9	1.11
11/17/99	A*												
16	B	5.96	23.50	5.84	23.93	0.27	0.62	65	11.24	0.34	0.034	17.2	0.92
12/03/99	A	6.87	19.79	7.44	22.25	0.35	0.59	88	11.23	0.35	0.025	26.9	1.05
28	B	2.86	12.47	9.10	41.11	0.42	1.07	111	21.28	0.47	0.051	19.7	1.16
12/31/99	A	1.78	10.43	9.51	57.88	0.42	1.45	117	30.33	0.18	0.026	33.2	2.63
22	B	1.93	13.45	9.63	69.61	0.42	1.71	112	34.49	0.22	0.038	23.2	2.18

* = no sample

Materials and methods

Two near-bottom sediment traps were deployed within 10 m of each other at a water depth of 30 m, 150 m away from the pier of the King Sejong Korean Antarctic Research Station (62°13'S, 58°47'W) at King George Island (Fig. 1). The traps were in position from 28 February 1998–21 January 2000, a total of 694 days. We used traps similar to those described by Shim *et al.* (1997): a stainless steel tripod supported the trap body (consisting of a 100 cm long PVC pipe, 7 cm in diameter) and a polyethylene sample bottle (2 l volume). The sample bottle was replaced nearly every

month on a SCUBA dive, which we conducted in summer, and the members of the overwintering teams of the 11th (1998/99) and 12th (1999/2000) Korea Antarctic Research Program performed in other seasons. It was impossible to approach the trap site and replace the bottles when strong thick ice formed in Marian Cove in August and September 1998, and the bottles were not replaced for 71 days at that time. In addition, in November 1999, we replaced the bottle after just 16 days in order to detect the spring bloom. No preservatives were added to the sample bottles before deployment and consequently, the downward

flux of organic materials was probably underestimated. However, it has been reported that commonly used preservatives containing formalin, azide ions (sodium azide), and mercuric ions (mercury chloride) can cause contamination or errors in measuring inorganic particle concentrations, owing to their ability to chelate metals (Knauer *et al.* 1984, Hedges *et al.* 1993). In any case, the loss of organic material was probably minimal, due to the unusually short deployment duration. Retrieved samples were stored immediately in a freezer (-20°C) and kept until laboratory analyses. The measured values of biogeochemical components of the two traps (A and B) are listed in Table I; they were averaged to estimate the total mass flux and the composition and fluxes of each component for descriptions and figures.

Frozen samples were melted at room temperature. After removing recognizable swimmers by hand, the samples were centrifuged, decanted, and desalted by washing with distilled water. The washed sediment was freeze-dried and placed in a constant humidity chamber for at least 24 h before weighing. The total mass flux (TMF), expressed as $\text{g m}^{-2} \text{d}^{-1}$, was calculated from the sample dry weight, the collection trap area, and the sampling interval. The total and organic carbon, total nitrogen, biogenic silica, and total and inorganic phosphorus levels were quantified for each sample. The total carbon and nitrogen levels were determined using a Carlo Erba CHNS analyser. After removing the inorganic carbon by treatment with 8% H_2SO_3 , the organic carbon component was also determined using the Carlo Erba CHNS analyser (Van Iperen & Helder 1985, Verardo *et al.* 1990). The inorganic carbon level was calculated from the difference between the total and organic carbon concentrations. Biogenic silica (BSi) was extracted by time series dissolution with 0.5 N NaOH at 85°C for 5 h, a procedure modified from Mortlock & Froelich (1989) and Müller & Schneider (1993). An aliquot of each sample was taken for analysis after every hour, and the relative silica concentrations were extrapolated back to time zero, to correct for the silica originating from coexisting clay minerals (DeMaster 1991). Total and inorganic phosphorus were extracted in 1 N HCl for 14–18 h (Aspila *et al.* 1976).

The organic phosphorus content was calculated from the difference between the total phosphorus extracted from ignited samples (500°C for 2 h) and the inorganic phosphorus extracted from fresh samples. The biogenic particle flux was assumed to be equivalent to the total of opal flux, carbonate flux, and $2\times$ organic carbon flux. The lithogenic flux was calculated from the difference between the total mass flux and biogenic particle fluxes, according to Fischer & Wefer (1996):

$$\text{lithogenic flux} = \text{total mass flux} - (\text{opal flux} + \text{carbonate flux} + 2 \times \text{C}_{\text{org}} \text{ flux}).$$

The concentrations of Al, Fe, and Ti were measured with an ICP-AES (Shimadzu model ICPS-1000III), and Cd, Cu, and Pb concentrations were determined with an ICP-MS (VG model PQ3 STE) following overnight digestion at $100\text{--}150^{\circ}\text{C}$ with HNO_3 , HClO_4 , and HF (Kitano & Fujiyoshi 1980).

Cripps & Clarke (1998) have demonstrated that there are many practical difficulties associated with the use of sediment traps in shallow near-shore Antarctic marine environments; these include damage by ice, contamination by resuspended bottom sediments, and artifacts introduced by lateral transport and the placement of traps within the euphotic zone. The type of sediment trap used in our study, and its near-bottom location, meant that there were concerns about the possibility of sample contamination by resuspended bottom material. In this situation, turbulent mixing in the water column could eventually result in overestimation of flux. Unfortunately, it was impossible to obtain water column turbulence data at the trap site that might have been used as an indirect indicator of resuspension rates for bottom sediments. Instead, we have used wind speed data (available from the meteorological laboratory at King Sejong station) as an indicator of bottom sediment resuspension. However, there was no significant correlation between monthly average lithogenic particle flux and wind speed (Shim *et al.* 2002). Throughout the year, the wind speed ranged from $7\text{--}10 \text{ m sec}^{-1}$ with little significant seasonal change (MOMAF 1999, 2000). Divers reported that the trap site was calm, with no evidence of wind- or current-mediated particle resuspension, even in

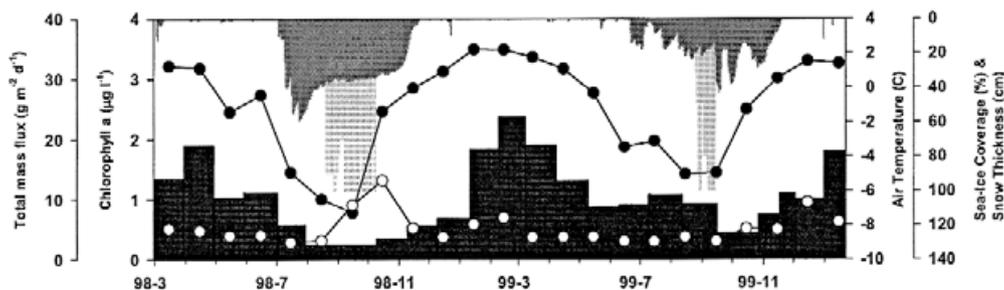


Fig. 2. Temporal variations in TMF ($\text{g m}^{-2} \text{d}^{-1}$, bar), monthly mean air temperature ($^{\circ}\text{C}$, black circled line), monthly mean Chl *a* concentration ($\mu\text{g l}^{-1}$, white circled line), sea ice coverage (%), and snow thickness (cm, dark grey) around King Sejong station. Air temperature, Chl *a* concentration, sea ice coverage and snow thickness were deduced and modified from MOMAF (1999, 2000).

Table II. Seasonal averaged fluxes of biogenic and lithogenic components in settling particles at Marian Cove, King George Island.

Season	TMF (g m ⁻² d ⁻¹)		OC (mmol m ⁻² d ⁻¹)		IC (mmol m ⁻² d ⁻¹)		Bio-Si (mmol m ⁻² d ⁻¹)		TN (mmol m ⁻² d ⁻¹)		OP (mmol m ⁻² d ⁻¹)		Litho. (g m ⁻² d ⁻¹)	
	1998	1999	1998	1999	1998	1999	1998	1999	1998	1999	1998	1999	1998	1999
Autumn	14.17	15.02	10.53	9.50	4.19	3.24	4.76	11.19	1.02	1.23	0.043	0.039	13.37	14.16
Winter	6.49	9.72	5.39	6.98	2.80	2.31	1.94	3.10	0.53	0.88	0.020	0.017	6.03	9.23
Spring	3.55	6.89	11.00	9.67	1.04	1.46	7.34	7.18	1.31	1.42	0.035	0.038	2.97	6.31
Summer	14.06	14.25	11.19	14.99	3.08	2.18	12.16	14.65	1.45	2.25	0.049	0.096	13.15	13.12
Annual flux (g m ⁻² yr ⁻¹)	3789		42.5		11.2		76.7		6.2		0.45		3351	

rough weather conditions. Some independent measures have suggested that background rates of resuspension are probably low at this site, despite the shallow near-shore location and, therefore, the effect on our samples may be negligible.

Results

Total mass flux and environmental setting

The total mass flux (TMF) in the subtidal benthic environment of Marian Cove ranged from 2.47 g m⁻² d⁻¹ (August and September 1998) to 23.69 g m⁻² d⁻¹ (February 1999), and averaged 10.26 g m⁻² d⁻¹ over the entire study period (Fig. 2, Table I). TMF decreased after April 1998, reaching minimum values in August and September, and then began to increase in October, reaching maximum values in February 1999. In 1999, TMFs were somewhat higher throughout the year than those in 1998, especially in winter and spring (Table II). From August to November 1999, TMFs were double (7.65 g m⁻² d⁻¹) those of the same period in 1998 (3.28 g m⁻² d⁻¹), and the duration of the low particle flux period was shorter in 1999 than in 1998.

Marian Cove is south of the Antarctic Polar Front, but is free of sea ice throughout most of the year, although it is covered with ice in winter. There was substantial interannual variation in the distribution of winter sea ice, from strong one-year ice, which covered all of Marian Cove and Maxwell Bay in 1998, to slight pancake ice, which was frequently broken apart by wind in 1999. Sea ice covered Marian Cove for about 50 days in 1998 (MOMAF 1999, Fig. 2). In 1999, sea ice did not fully cover Marian Cove; it was frequently broken up by wind and was gone after about 20 days (MOMAF 2000, Fig. 2). Like the ice on the sea surface, the snow thickness on the land around King Sejong station in 1998 was also about double that in 1999 (MOMAF 1999, 2000, Fig. 2). In 1998, the average snow thickness from July to October was about 37 cm, vs 20 cm in 1999. Snow thickness peaked at 63 cm on 24–25 July 1998. Air temperatures were lower in 1998 than in 1999 (MOMAF 1999, 2000, Fig. 2). For example, the average temperatures over the three months from August to October were -5.0°C in 1998 and -3.7°C in 1999. The winter of 1998 was colder than that of 1999, resulting in strong ice conditions on the sea surface and thick accumulations of snow on land. We speculate that the strong ice and heavy

snow conditions in the winter of 1998 prevented particle input to the water column and decreased the source area of lithogenic particles, resulting in the relatively low particle fluxes observed.

Monthly average Chl *a* concentrations ranged from 0.28–1.32 µg l⁻¹, with higher values occurring in spring and summer (MOMAF 1999, 2000, Fig. 2). In 1998/99, the Chl *a* concentration peaked in October (1.32 µg l⁻¹), whereas in 1999/2000, it peaked in December (0.95 µg l⁻¹). According to Kang *et al.* (2000, 2002), the timing and scale of the spring bloom are highly variable in Marian Cove. The annual mean total Chl *a* concentrations in 1998 and 1999 were 0.65 and 0.47 µg l⁻¹, respectively, much lower than the

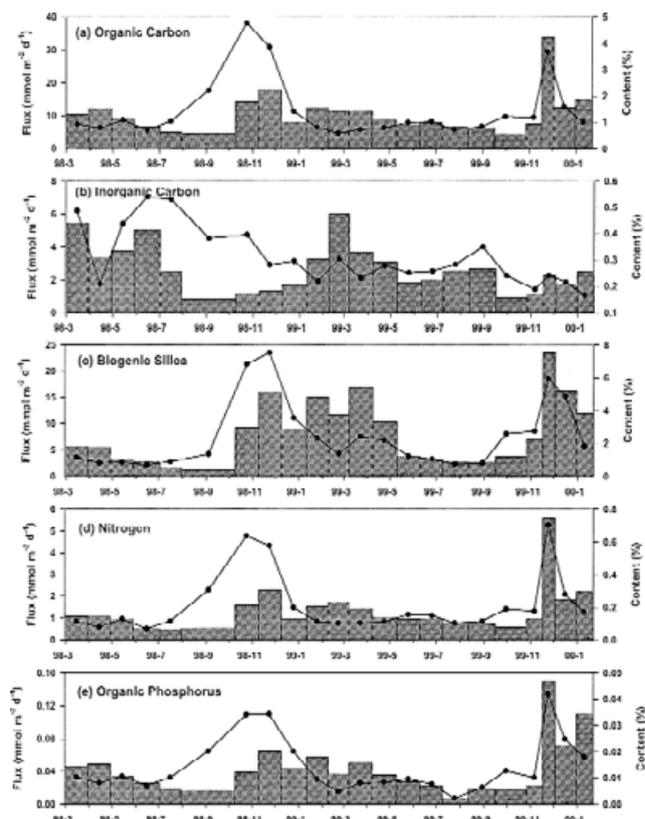


Fig. 3. Temporal variations in the flux (mmol m⁻² d⁻¹, bar) and contents (% , connected points) of **a.** particulate organic carbon, **b.** inorganic carbon, **c.** biogenic silica, **d.** total nitrogen, and **e.** organic phosphorus.

value of $1.38 \mu\text{g l}^{-1}$ recorded in 1996, when a massive biomass of microplankton occurred in November and December ($2.09\text{--}2.83 \mu\text{g l}^{-1}$). Kim *et al.* (1998) also reported that in 1994, Chl *a* ranged from negligible to $3.03 \mu\text{g l}^{-1}$ (average: $0.63 \mu\text{g l}^{-1}$), and the primary productivity correlated closely with irradiance ($r^2 = 0.85$, $P < 0.001$); neither temperature nor nutrients seem to affect the temporal variation in primary production at Marian Cove. Despite the low annual mean, monthly average Chl *a* concentrations increased rapidly during and after the sea ice melted in 1998, while in 1999 there was no clear increase associated with the melting of sea ice. This suggests that the strong sea ice conditions in 1998 resulted in a stable, favourable environment for phytoplankton growth, while the unstable ice conditions of 1999 were not favourable for phytoplankton production.

Biogenic material: composition and fluxes

The time series of fluxes and concentrations of organic carbon (OC), inorganic carbon (IC), biogenic silica (BSi), total nitrogen (TN), and organic phosphorus (OP) at Marian Cove are shown in Fig. 3, and the seasonal averaged fluxes in 1998/99 and 1999/2000 are listed in Table II. During the study period, the OC flux ranged from $4.4 \text{ mmol C m}^{-2} \text{ d}^{-1}$ (August and September 1998) to $34.0 \text{ mmol C m}^{-2} \text{ d}^{-1}$ (November 1999) (Fig. 3a). The maximum value in late November 1999 was measured during a period when sample bottles were deployed for a short duration (15 days) in order to detect the spring bloom. Although the magnitude of the peak flux in 1999 was double that in 1998 ($18.1 \text{ mmol C m}^{-2} \text{ d}^{-1}$), the monthly average values of the two Novembers were very similar, 17.0 and $19.0 \text{ mmol C m}^{-2} \text{ d}^{-1}$, respectively. In 1998, the OC flux began to increase in October and peaked in early November, whereas the OC flux values were low in October 1999, with the peak occurring in late November. The timing and magnitude of the OC flux peak was subject to interannual variability. There were peaks in OC content in spring (October 1998 and late November 1999, 4.78% and 3.69%, respectively), but the levels were consistently low during other seasons ($< 1\%$) (Fig. 3a). The particulate organic carbon (OC) flux showed a characteristic seasonal and interannual variability relative to the fluxes in TMF.

The maximum flux in particulate inorganic carbon (IC) was observed in February 1999 ($6.0 \text{ mmol C m}^{-2} \text{ d}^{-1}$), and the minimum flux occurred in August and September 1998 ($0.8 \text{ mmol C m}^{-2} \text{ d}^{-1}$), a seasonal variability pattern similar to that seen in TMF (Fig. 3b). The IC sample content was relatively stable at 0.2–0.3%, except during the autumn and early winter of 1998, when values rose to $\sim 0.5\%$ (Fig. 3b). Throughout the year, IC represented a small portion (7–30%) of the total particulate carbon (TC) content, and its seasonal variability did not parallel that of OC, indicating that calcareous phytoplankton remains did not dominate the

organic matter deposition in Marian Cove during the study period.

There was also great seasonal variation in the biogenic silica (BSi) flux. Recorded values ranged from $1.2 \text{ mmol Si m}^{-2} \text{ d}^{-1}$ (August and September 1998) to $23.5 \text{ mmol Si m}^{-2} \text{ d}^{-1}$ (November 1999), involving a 20-fold change during the year (Fig. 3c). High values were sustained until late summer, giving BSi flux a more characteristic pattern of seasonal variability than that of OC flux. In terms of sample content, the BSi values ranged from 0.7–7.5%, with spring peaks coinciding with those of the OC content (Fig. 3c). This suggests that siliceous plankton dominate the plankton communities of Marian Cove, which concurs with the finding of Ahn *et al.* (1997) that diatoms dominated the water column microalgal populations.

The temporal variation in the flux and content of particulate total nitrogen (TN) and organic phosphorus (OP) was very similar to the pattern observed for OC, i.e. with peaks in spring rather than in summer (Fig. 3d & e). The maximum fluxes observed during the study period for both TN and OP occurred in late November 1999 ($5.56 \text{ mmol N m}^{-2} \text{ d}^{-1}$ and $0.15 \text{ mmol P m}^{-2} \text{ d}^{-1}$, respectively). There were corresponding peaks in sample content in November 1998 (0.64% N, 0.034% P) and 1999 (0.70% N, 0.042% P, Fig. 3d & e). The similarity of the timing of the peaks, for

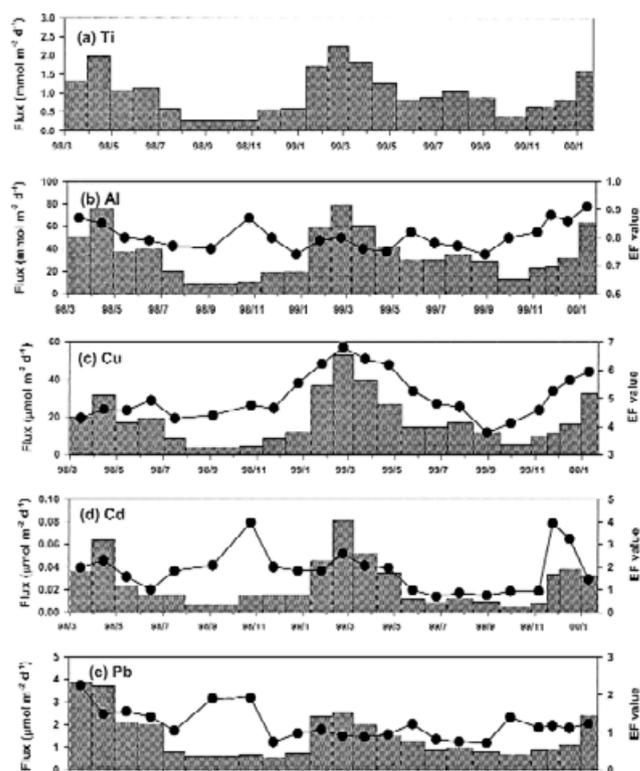


Fig. 4. Temporal variation in the flux ($\text{mmol m}^{-2} \text{ d}^{-1}$ for Al and Ti, and $\mu\text{mol m}^{-2} \text{ d}^{-1}$ for Cu, Cd and Pb, bar) and enrichment factors (connected points) of a. Ti, b. Al, c. Cu, d. Cd, and e. Pb.

both flux and content, with those of OC and BSi implies that all these components have the same origin.

Metal: composition and fluxes

The time series for fluxes of Al, Ti, Cu, Cd, and Pb are shown in Fig. 4. The flux of the major elements of lithographic material, Al and Ti, showed clear seasonal variability, similar to the pattern observed for TMF. The values were high in summer and low in winter, with maximum observed fluxes occurring in February 1999 (74 mmol Al m⁻² d⁻¹, 2.25 mmol Ti m⁻² d⁻¹) and minimums in August and September 1998 (9 mmol Al m⁻² d⁻¹, 0.26 mmol Ti m⁻² d⁻¹, Fig. 4 a & b). Cu and Cd fluxes also showed high summer values and low winter values, ranging from 4.0 μmol Cu m⁻² d⁻¹ (August and September 1998) and 0.005 μmol Cd m⁻² d⁻¹ (September 1999) to 52.8 μmol Cu m⁻² d⁻¹ and 0.081 μmol Cd m⁻² d⁻¹ in February 1999 (Fig. 4c & d). However, Pb flux patterns were substantially different. During the study period, the maximum observed Pb flux value occurred in March 1998 at 3.85 μmol m⁻² d⁻¹, and the minimum in November 1998 at 0.51 μmol m⁻² d⁻¹ (Fig. 4e).

Of these metals, Al and Ti are the major elements of the minerals composing the earth's crust and, therefore, can be used as proxies to estimate the lithogenic fraction of settling particles. Al may be particularly useful in this context because it occurs in high and relatively constant abundance, in a variety of rock types (roughly 80 000 ppm; Turekian & Wedepohl 1961). However, Murray & Leinen (1996) and Dymond *et al.* (1997) reported that Al was additionally scavenged by biological material in the water column, resulting in high Al/Ti ratios in sediment trap samples. Therefore, we used Ti as the reference element to calculate the enrichment factor (EF_{crust}), which indicates the sample concentration of an element relative to its average concentration in the earth's crust, according to the following equation:

$$EF_{\text{crust}} = (X/M)_{\text{sample}} / (X/M)_{\text{rock, soil}}$$

where X is the concentration of the element and M is the concentration of the reference element (in our case Ti). (X/M)_{rock, soil} is the average ratio of crust rock and soil, for which we used the average values of upper continental crust suggested by Wedepohl (1995). The EF_{crust} values for Al, Cu, Cd, and Pb varied seasonally, in characteristic but element-specific ways (Fig. 4). The EF_{crust} values for Al showed a very narrow variability over time, and ranged from 0.75 to 0.91 (Fig. 4b), implying that Al in settling particles is diluted by biogenic sinking particles produced in the water column, or that Al is distributed at low concentrations in the rocks and soils around Marian Cove relative to the average upper continental crust. However, the EF_{crust} values for Cu demonstrated clear seasonal variability, with high values in summer and low values in winter. The ratio ranged from 3.93 to 6.61 (Fig. 4c), suggesting that Cu might be enriched in the rocks and soils around Marian Cove and/or scavenged massively from the water column by settling particles. The EF_{crust} values for Cd ranged between 0.8 and 3.3 (Fig. 4d), with a spring peak, sustained high values in summer, and lower values in winter. The EF_{crust} values for Pb displayed a distinct seasonal variability, high in winter and autumn and low in summer, ranging from 0.73 to 2.22 (Fig. 4e). The range and seasonality of the EF_{crust} values for each element were different and distinct, suggesting that in this area, each has a characteristic biogeochemical cycle.

Discussion

Lithogenic and biogenic particle flux

The TMF values for Marian Cove are comparable to those measured in other Antarctic coastal environments, but they are two to four orders of magnitude higher than those measured in open seas (Table III). An exponential increase in TMF is to be expected close to land, as is the observed

Table III. Total and lithogenic particle flux in Marian Cove compared with data from other areas.

Area	Water depth (m)	Trap depth (m)	Total mass flux (g m ⁻² yr ⁻¹)	Lithogenic flux		Organic carbon flux (g m ⁻² yr ⁻¹)	Source
				(g m ⁻² yr ⁻¹)	(% of total)		
Antarctic zone	2885	1031	80.6	0.12	0.15	2.2	Honjo <i>et al.</i> 2000
Antarctic zone	3015	937	27.6	0.05	0.18	1.9	Honjo <i>et al.</i> 2000
Weddell Sea	3880	863	0.4	0.004	1	0.02	Fischer <i>et al.</i> 1988
Maud Rise	5053	360	33.7	2.5	7.4	2.3	Wefer & Fischer 1991
Ross Sea	765	715	38–59	4–9.5	11–16	2.5–2.9	Dunbar <i>et al.</i> 1998
Bransfield Strait, eastern	1778	678	66	21	41	6.8	Kim <i>et al.</i> 2004
Bransfield Strait, center	1960	960	33	19	57	2.2	Kim <i>et al.</i> 2004
Bransfield Strait, western	1000	500	4	2.2	57	0.35	Palanques <i>et al.</i> 2002
Factory Cove, Signy Island**	20	10	2500–97000	2250–87300	70–95	125–4850*	Cripps & Clarke 1998
Johnson's Dock, Livingston Island***	19.5	15	23235–89073	22074–86881	95–98	125–315	Isla <i>et al.</i> 2001
Marian Cove, King George Island	30	25	3789	3351	88	42	This study

* if, AFDM:organic carbon of 2:1 (Platt & Irwin, 1973)

** ranges within a year (g m⁻² d⁻¹)

*** ranges in summer (g m⁻² d⁻¹)

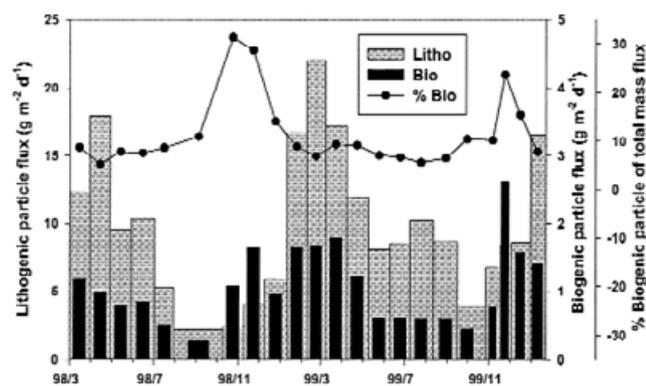


Fig. 5. Temporal variation in the flux ($\text{g m}^{-2} \text{d}^{-1}$, bar) and contents (% , connected points) of lithogenic particles and biogenic particles.

increase in the contribution of terrigenous particles to TMF. Along the Antarctic coast, meltwater streams transport massive amounts of terrigenous particles in summer. These particles are composed mainly of lithogenic debris with low organic content, because the terrestrial flora of the Antarctic and sub-Antarctic regions is limited to small populations of mosses and lichens. As shown in Table III, lithogenic particles constituted less than 1% of TMF in the open sea, e.g. the Antarctic Circumpolar Current region and Weddell Sea (Fischer *et al.* 1988, Honjo *et al.* 2000), and between 10% and 57% of TMF in the Ross Sea and Bransfield Strait (Dunbar *et al.* 1998, Kim *et al.* 2004, Palanques *et al.* 2002). By contrast, in coastal environments, lithogenic particles dominate TMF, representing 70–96% of TMF in near-shore locations, such as Factory Cove, Signy Island and Johnson's Dock, Livingston Island (Cripps & Clarke 1998, Isla *et al.* 2001). As in other Antarctic coastal environments, the settling particles at Marian Cove were dominated by those of lithogenic origin, which represented about 88% of TMF (Table III, Fig. 5). This implies that the main factor controlling temporal variation of TMF is the input of lithogenic particles. Cripps & Clarke (1998) reported that the peak in TMF at their site occurred in late summer, at the time of maximum meltwater flow into Factory Cove. In Admiralty Bay, King George Island, estimates of the annual inflow from meltwater streams transporting terrigenous suspended matter ranged from 200 000 to 240 000 tons (2000 tons per day; Pecherzewski 1980). Therefore, quantifying the inputs of meltwater streams into Antarctic coastal environments is essential if variability in lithogenic particle flux (as well as TMF) is to be understood. Yoon *et al.* (1994, 1998) and Yoo *et al.* (1999) have also remarked on the high rates of terrigenous sediment delivery to Marian Cove in summer by meltwater streams and icebergs. Although meltwater streams have been commonly observed around King Sejong station during summer, there are very few data regarding the meltwater volume, as it is difficult to quantify its sporadic, intermittent, and spatially random

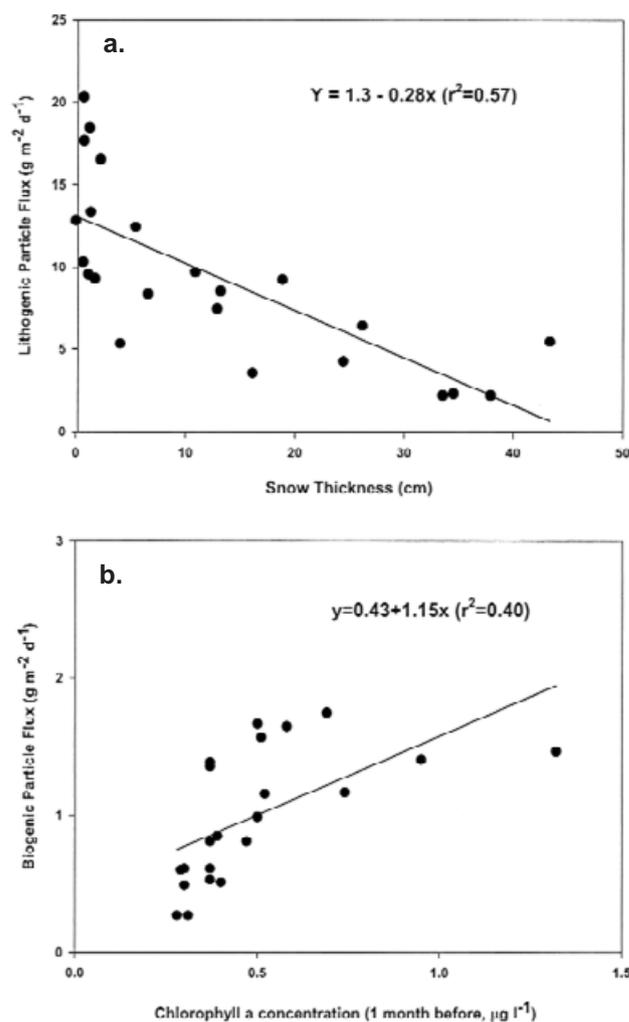


Fig. 6. Relationships **a.** between lithogenic particle flux and snow accumulation, and **b.** between biogenic particle flux and Chl *a* concentration. All values are monthly averages.

distribution.

Patterns of lithogenic particle flux parallel those of TMF, with high values in summer and low values in winter. The maximum observed flux of lithogenic particles was $20.3 \text{ g m}^{-2} \text{d}^{-1}$ in February 1999, the minimum was $2.7 \text{ g m}^{-2} \text{d}^{-1}$ in August and September 1998 and the mean value was $9.3 \text{ g m}^{-2} \text{d}^{-1}$ (Fig. 5). Similar to the temporal variability patterns observed for TMF, the lithogenic particle fluxes in 1999 were somewhat higher throughout the year than those in 1998, especially in winter and spring. From August to November 1999, lithogenic fluxes were about 2.5 times higher ($7.08 \text{ g m}^{-2} \text{d}^{-1}$) than those of the same period in 1998 ($2.80 \text{ g m}^{-2} \text{d}^{-1}$). As mentioned above, the winter of 1998 was much colder than that of 1999, with thick sea ice and heavy snow on land in the winter of 1998. Many researchers have reported that vertical particle flux in the Antarctic is strongly affected by sea ice characteristics such as duration of cover, melting time, and water column stability (in terms of preventing aeolian particle input, polynya formation, and

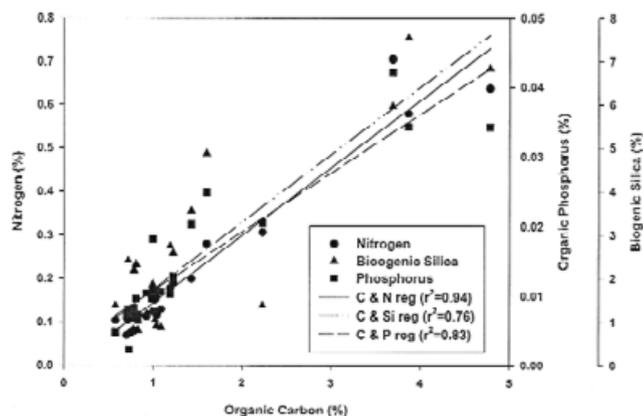


Fig. 7. Relationships between OC flux and BSi, TN and OP flux (respectively).

increases in plankton production; Smith & Nelson 1985, Fischer *et al.* 1988, Bathmann *et al.* 1991, Nedwell *et al.* 1993, Dunbar *et al.* 1998, Collier *et al.* 2000, Langone *et al.* 2000, Accornero *et al.* 2003). Like sea ice, the accumulation of snow on land has two contradictory features with regard to particle flux. On the one hand, it might prevent transport of terrestrial material to the sea. Conversely, meltwater might be important in transporting terrestrial material to the sea. Plots of the monthly averaged data for lithogenic particle flux in Marian Cove and snow thickness at King Sejong station (Fig. 6a) show a negatively linear correlation with a medium correlation coefficient ($r^2 = 0.57$). This means that when snow accumulation is high, the lithogenic flux is negligible, but when the snow melts, the flux increases greatly. This also suggests that in these coastal environments where the land surface is seasonally exposed and covered by snow, snow accumulation could be an indirect indicator of the meltwater stream input and, consequently, of the amount of lithogenic particles in coastal waters.

The biogenic particle flux ranged from $0.27 \text{ g m}^{-2} \text{ d}^{-1}$ (August and September 1998) to $2.62 \text{ g m}^{-2} \text{ d}^{-1}$ (November 1999). Biogenic particles formed a small proportion of sample content ($\sim 10\%$) throughout the year, except in October and November when values were $\sim 30\%$ (Fig. 5). In contrast to the lithogenic particle flux, the biogenic particle flux showed high values in each spring, October 1998 and November 1999. As previously mentioned, most components of biogenic particles (i.e. OC, BSi, TN and OP) showed very similar seasonal patterns. All biogenic fluxes and contents peaked in spring, with significant linear correlations in plots of OC content and TN, BSi, and OP contents ($r^2 = 0.94, 0.76, \text{ and } 0.83$ respectively; Fig. 7). Among these, OC and BSi constituted the major fraction of biogenic particle flux, ranging from 8–20% and 22–70% respectively, and represented more than 75% of the organic particles deposited during the dominant season of siliceous plankton ($2 \geq \text{BSi/POC}$). This indicates that marine biota,

particularly siliceous plankton, might be responsible for the organic fraction of the settling material. Considering the entire carbon flux in a year ($42 \text{ g C m}^{-2} \text{ yr}^{-1}$), the organic matter supply to the sea floor might be not insufficient to sustain the metabolism of benthic organisms nor unbalanced relative to remineralization of organic matter at the sediment-water interface, as claimed by Ahn (1993) and Kang (1998), respectively.

During the study period, the Chl *a* concentrations peaked in spring, at a similar time to that of the biogenic particles, and the Chl *a* temporal distribution progressed in a pattern similar to, but a little ahead of, that of the biogenic particle flux. A plot of the monthly average biogenic particle flux with the previous month's average Chl *a* concentration demonstrates a positive relationship ($r^2 = 0.4$, Fig. 6b). This suggests that there was a one month gap between production and deposition of biogenic particles in Marian Cove during the study period. In polynya of Terra Nova Bay, the time lag between production and accumulation of biogenic materials ranged from a few weeks to one month (Accornero *et al.* 2003). Cripps & Clarke (1998) also reported a lag in maximum flux of phaeopigments relative to the bloom maximum, which indicated that grazing activity delayed sedimentation of particulate material.

Biogeochemistry of metal flux

The temporal variations in Cu, Cd, and Pb fluxes were very similar to those observed for Al and Ti, the major lithogenic elements. However, the EF_{crust} values showed distinct variations for each metal, and all values were higher than 1 (Fig. 4), implying that each of these elements has a characteristic biogeochemical cycle and is enriched in the settling particles.

Many research studies have reported that copper is enriched around Marian Cove (Lee *et al.* 1990, Jwa & Lee 1992, Ahn *et al.* 1996). Terrestrial volcanic rocks at Barton and Weaver peninsulas, King George Island, are high in Cu-rich minerals and have high Cu concentrations ($>100\text{--}186 \mu\text{g g}^{-1}$, Jwa & Lee 1992). Lee *et al.* (1990) found that Cu concentrations in Marian Cove surface waters were much higher in near-shore areas ($0.35\text{--}1.21 \mu\text{g l}^{-1}$) than in offshore areas, with a trend showing a sharp decrease toward offshore waters. In addition, Antarctic clam (*Laternula elliptica*) tissues and sediment at Marian Cove had high copper concentrations relative to other coastal environments ($38 \mu\text{g g}^{-1}$ in whole soft tissue and $77 \mu\text{g g}^{-1}$ in sediments, Ahn *et al.* 1996). This has been ascribed, in part, to the input of Cu-laden melt water during summer rather than to anthropogenic pollution. Among the settling particles, the EF values of Cu were much higher throughout the year than those of other metals ($> 4x$), and values peaked in summer when meltwater streams were abundant (Fig. 4c). In addition, the EF values of Cu were highly positively correlated ($r^2 = 0.42$) with the lithogenic particle

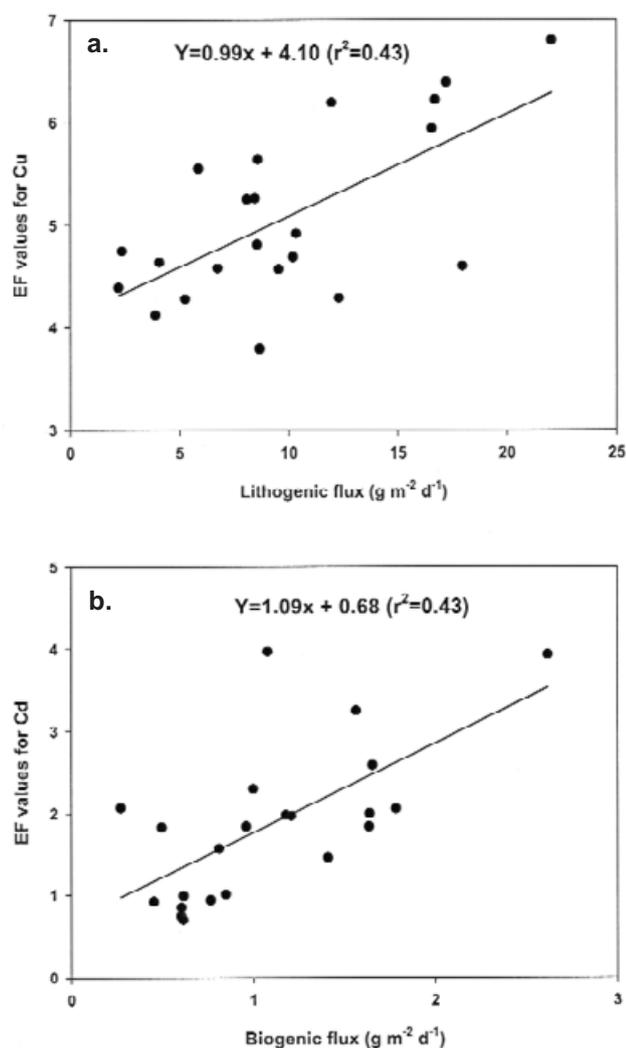


Fig. 8. Relationships between **a.** lithogenic particle flux and EF of Cu, and **b.** biogenic particle flux and EF of Cd.

flux (Fig. 8a). These findings suggest that Cu in settling particles was derived from terrestrial rocks rather than organic matter or anthropogenic pollution.

In contrast, the EF values of Cd were highly positively correlated ($r^2 = 0.43$) with the biogenic particle flux (Fig. 8b). Kang *et al.* (1998) and Ahn & Kim (1999) reported that Cd concentrations were high in herbivorous Antarctic limpets living intertidally in Marian Cove. Kang *et al.* (1998) found that this resulted from bioaccumulation along the Marian Cove food chain: phytoplankton absorb Cd directly from the seawater and are consumed by diatom-feeding limpets. The settling particles in Marian Cove contained enriched concentrations of Cd in spring and summer (EF value > 1), but during other seasons, the EF values were ~ 1 (Fig. 4d). Peak Cd concentrations were coincident with those of biogenic particle components (OC, BSi, TN, and OP), implying that Cd enrichment occurred via biogenic debris. The seasonal variations in Cd concentration seem to be controlled by organic matter

deposition during the study period.

Lead showed the most distinctive pattern of temporal EF value variation of all the metals, with high values in winter and autumn rather than in summer, and the greatest observed peak occurring in March 1998 (Fig. 4e). This seasonal pattern of Pb distribution in settling particle coincides with that in snow and ice. Lead concentrations of snow in autumn/winter were 2–4 times those in spring/summer at Dolman Island and Livingston Island (Suttie & Wolff 1992, Hong *et al.* 1999, Wolff *et al.* 1999). These authors concluded that lead flux in the Antarctic region was generally higher in winter than in summer. Hong *et al.* (1999) also reported that the Pb concentration of snow around King Sejong station was ~ 46 times that of Livingston Island, and suggested that this elevated lead concentration might be of anthropogenic rather than natural origin. This is supported by the finding that Pb concentrations in lichens, sampled around the King Sejong station, decrease sharply with distance from the station. Therefore, the high EF values of Pb (> 1) in winter are probably affected by both large-scale patterns of Pb flux in the Antarctic region and localized anthropogenic pollution (i.e. the amount of fuel burned at the station).

Conclusion

We found large seasonal and interannual variability in TMF in a subtidal benthic environment in Marian Cove. As in other Antarctic regions, lithogenic particles comprised the majority of the total particles, and lithogenic particle input was the major factor controlling TMF variability. The negatively linear relationship between snow depth and lithogenic particle flux in Marian Cove demonstrates that in these coastal environments, where the land surface is seasonally exposed and covered by snow, snow depth might be a good estimator of meltwater stream volume and, consequently, of the input of lithogenic particles. The biogenic particle flux showed distinct seasonal variability, with peaks in spring rather than in summer, decoupled from patterns in lithogenic particle flux. Comparisons between biological particle flux and Chl *a* concentration show that there was a gap of one month between biological production and deposition during the study period. The similarity of the timing of the peaks for both flux and content of OC, BSi, TN and OP implies that siliceous plankton dominated during the study period, and was thus the major source of organic matter deposition in Marian Cove. Among metals in settling particles, Cu, Cd and Pb showed characteristic biogeochemical cycles. Affected by Cu-enriched terrestrial rock, Cu enrichment factors were high (> 4) throughout each year, and were related to lithogenic particle flux. However, the correlations between biogenic particle flux and high enrichment factor values in spring suggests that particulate Cd originates mainly from organic matter rather than from anthropogenic sources. Lead showed the most

distinct seasonal variability, with high values in winter and low values in summer. Further study is needed to quantify variability in Pb levels, as they were affected by both large-scale patterns of Pb flux in the Antarctic region and localized anthropogenic pollution.

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