Sources and distribution of particulate organic carbon in Great Wall Cove and Ardley Cove, King George Island, West Antarctica

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Abstract Concentrations of chlorophyll-a (Chl-a), particulate organic carbon (POC) and its stable carbon isotope composition (δ13C) were analyzed to investigate the biogeochemical characteristics and sources of POC in Great Wall Cove (GWC) and Ardley Cove (AC) during the austral summer. POC concentrations ranged from 50.51 to 115.41 μg·L −1 (mean±1 standard deviation: 77.69±17.27 μg·L−1) in GWC and from 63.42 to 101.79 μg·L −1 (82.67±11.83 μg·L−1) in AC. The POC δ13C ranged from −30.83‰ to −26.12‰ (−27.40‰±0.96‰) in GWC and from −28.21‰ to −26.65‰ (−27.45‰±0.47‰) in AC. The temperature and salinity results showed distinct runoff signals in both GWC and AC, although the δ13C data and POC distribution indicate a negligible influence of land sources upon POC. The δ13C values suggest that POC is of predominantly marine origin. The POC/Chl-a ratio and the relationship between POC and Chl-a indicate that phytoplankton, organic detritus and heterotrophic organisms are significant contributors to POC in GWC and AC.

Keywords    POC, Chl-a, δ13C, Great Wall Cove, Ardley Cove, Antarctica


1 Introduction

Particulate organic carbon (POC) is a key component of the marine food web and plays an important role in the global carbon cycle. Its flux is controlled by primary productivity and other biological activities[1], and it is the main component of precipitation, transformation and transport of marine organisms[2]. The relationship between carbon, nitrogen and phosphorus in POC provides information regarding the sources and biogeochemical processes controlling the POC. In the Antarctic ocean, POC distribution varies both geographically and with depth[3-4]. POC is more abundant in surface waters than in bottom waters[5-7].

Changes to glacial ablation, permafrost degradation and other effects of recent global warming have altered the nature of organic carbon input into the ocean. This may have affected primary productivity, phytoplankton communities and the input of ancient organic carbon stored in land soil in the Antarctic region.

King George Island is the biggest island of the South Shetland Islands[8]. Near to the northwestern tip of the Antarctic Peninsula, the island is within one of the most rapidly warming regions on Earth[9]. This region has a typical maritime climate, with little annual variation in atmospheric temperature, high relative humidity and constant cloud cover[10]. Great Wall Cove (GWC) is located at the southwest
end of King George Island, east of Great Wall Station. GWC runs north to south, from the shared territory between Ardley Island and Fields Peninsula, to Maxwell Bay. It is 1.3 km long and 0.7 km wide, with an area of 0.71 km\(^2\)\(^{[11]}\). Ardley Cove (AC) lies to the north of Ardley Island. It has an area slightly larger and is deeper than GWC. The depth of GWC is variable with complex bathymetry. The depth inside the bay is \(~35\) m, with depths >50 m outside the bay\(^{[12]}\). Both coves are extensions of Maxwell Bay.

Many studies have been conducted at the Great Wall Station, including research regarding meteorological conditions\(^{[13]}\), snow accumulation and melt processes\(^{[14]}\), land pollution\(^{[15]}\), ecosystem dynamics\(^{[16]}\), and the hydrological conditions of GWC\(^{[11,17-18]}\). Biogeochemistry parameters such as dissolved oxygen\(^{[19]}\), nutrient levels, phytoplankton\(^{[20-22]}\), chlorophyll-\(a\) (Chl-\(a\))\(^{[23-26]}\), and their relationships\(^{[27-28]}\) have also been investigated. International research in this area includes examination of the biogeochemistry conditions in the adjacent Antarctic Peninsula\(^{[29-31]}\) and King George Island coastal areas\(^{[9,32-34]}\). All these studies indicate that global climate change impacts upon these marine ecosystems, and will further affect the composition of marine organisms as well as burial efficiency.

To improve the current understanding of carbon cycling in the Antarctic region, this study examines the hydrogeochemical conditions and biogeochemical parameters such as POC/Chl-\(a\) and the POC stable carbon isotope (\(\delta^{13}C\)) signatures within GWC and AC, with the aim of determining the distribution and sources of POC in these coves.

## 2 Materials and methods

### 2.1 Sampling and sample preparation

Nutrients, POC, Chl-\(a\), temperature and salinity were observed in GWC and AC on 17 and 23 January 2013, during the twenty-ninth Chinese National Antarctic Research Expedition (29th CHINARE). There were five sampling stations in each cove, named G1–G5 in GWC and A1–A5 in AC (Figure 1). Seawater was sampled with a 5-L Niskin sampler. For POC collection, 0.5–2.0 L seawater was filtered on GF/F filters (47 mm, 0.7 μm) that had been pre-combusted for 4 h at 450°C. For Chl-\(a\) analysis, 0.5 L seawater was filtered on GF/F filters (47 mm, 0.7 μm). All samples were stored at \(-20°C\).

**Figure 1** Sampling stations in Great Wall Cove and Ardley Cove.

### 2.2 Analytical methods

Filters for detecting POC were dried at 50°C until constant weight and then de-carbonated by fumigating with hydrochloric acid. Carbon concentrations were analyzed using an Elementar Vario MICRO cube elemental analyzer and \(\delta^{13}C\) was analyzed using a Thermal MAT 253 isotope ratio mass spectrometer. The filters for Chl-\(a\) analysis were
extracted in 90% acetone and kept in the dark at −20°C for 24 h. Chl-α concentrations were determined according to fluorescence readings using a Turner fluorometer (Turner10-AU). Dissolved oxygen was measured using the Winkler titration method according to the Chinese “Specification for Oceanographic Survey” (State Bureau of Quality and Technical Supervision, 2007). Seawater temperature and salinity were measured in situ with a conductivity, temperature and depth logger (RBRconcerto CTD).

3 Results

3.1 Temperature, salinity and nutrients

Water temperature in GWC was in the range 0.49–1.15°C (mean: 0.72°C) and 0.72–1.36°C (mean: 1.02°C) in AC. Salinity in GWC ranged from 34.02 to 34.21 and from 33.97 to 34.14 in AC. One-way ANOVA tests show that the differences in temperature and salinity between the two coves are both statistically significant (p<0.05). This indicates a difference in the hydrological regimes of the two coves, most likely because of differences in river discharge and variations in bathymetry.

Both temperature and salinity showed similar trends in the two coves: Temperature decreased with depth, while salinity increased from the inner regions to the outer regions of the coves. Higher temperatures and lower salinities were at depths <10 m in both coves. As shown in Figure 2, temperature and salinity show a negative correlation ($r = -0.79$, $p < 0.01$, $n = 37$) where higher seawater temperature corresponds to lower salinity. Although no runoff records are available for this region, this pattern implies that meltwater discharge from King George Island affects both coves, especially the upper layer of seawater.

Concentrations of nitrate (GWC: 24.94 μmol·L⁻¹, AC: 24.92 μmol·L⁻¹), phosphate (GWC: 1.94 μmol·L⁻¹, AC: 1.96 μmol·L⁻¹) and silicate (GWC: 78.61 μmol·L⁻¹, AC: 79.32 μmol·L⁻¹) showed little difference between the two coves. Concentrations of these compounds in the river discharge into the two coves are in the range of 0.95–3.10 μmol·L⁻¹ for nitrate, 0.12–0.21 μmol·L⁻¹ for phosphate and 19.32–39.02 μmol·L⁻¹ for silicate, much lower than those of GWC and AC (Gao et al, 2015, submitted). Nitrate shows a weak positive correlation with salinity ($r = 0.54$, $p = 0.01$, $n = 37$) because of the greater difference between the river and seawater nitrate concentrations. No significant correlations between salinity and phosphate ($r = 0.13$, $p > 0.05$, $n = 37$) and silicate ($r = 0.05$, $p > 0.05$, $n = 37$) were found. The patterns of temperature, salinity and nutrient levels suggest that river runoff dilutes nutrient concentration in these two coves.

Distributions of POC, Chl-α and δ¹³C

Distributions of POC, Chl-α and δ¹³C in GWC and AC are shown in Figure 3. POC was in the range of 50.51–115.41 μg·L⁻¹ (mean: 77.69±17.27 μg·L⁻¹) in GWC and 63.42–101.79 μg·L⁻¹ (mean: 82.67±11.83 μg·L⁻¹) in AC. The concentration of POC in GWC gradually increased from the inner cove to the outer cove. The highest concentration was recorded at station G5, but this station also had a low POC concentration in the surface layer. However, the distribution of POC in AC exhibited higher concentrations at station A1 and A4, with the lowest concentration observed at station A3, in the middle of the cove.

Chl-α was in the range of 0.42–3.08 μg·L⁻¹ (mean: 1.29 ±0.60 μg·L⁻¹) in GWC and 0.81–1.48 μg·L⁻¹ (mean: 1.08 ±0.20 μg·L⁻¹) in AC. Higher concentrations of Chl-α were found in the inner cove region of GWC, while in AC, higher
concentrations were found in the middle of the cove. 

$\delta^{13}C$ was in the range of $-30.83\%$ to $-26.12\%$ (mean: $-27.40\%\pm0.96\%$) in GWC and $-28.21\%$ to $-26.65\%$ (mean: $-27.45\%\pm0.47\%$) in AC. As Figure 3 shows, the minimum $\delta^{13}C$ value was observed in the surface water of station G2 whereas the maximum value was observed in the surface water of G4. $\delta^{13}C$ in AC shows a vertical distribution pattern, with more negative values at station A2 and A3. The minimum value was observed at 10 m depth at station A2, and the maximum value was observed at 5 m depth at A5.

4 Discussion

4.1 Influence of hydrological and chemical conditions on POC distribution

During the austral summer, the south of the South Shetland Islands is occupied by the “shelf surface water” with salinity of 34.1–34.2[35]. The northern waters of the Bransfield Strait, where King George Island is located, mainly originate from the surface water of the Bellingshausen Sea, which is a warm water mass with lower salinity[36]. The monthly mean precipitation at the Great Wall Station was ~50–60 mm during January and February, which are typically the wettest months of the year[37]. Warmer fresh water from river runoff flowing into the two coves, along with solar radiation heating, causes water in the inner cove regions and the upper layer of seawater to be comparatively fresher and warmer. The patterns of temperature and salinity of homologous positions in GWC and AC were roughly similar (Figure 4a). As shown in Figure 4b, POC concentrations at station G5 were distinctly higher, with higher salinity and lower temperature. POC in the surface water is higher in other Antarctic areas than in GWC (Table 1), and it is most likely that the lateral transportation of a water mass with high POC by the Bransfield Current contributed to the high POC value of station G5. POC concentrations were distinctly lower in the surface water of G1 and G3 because of dilution by fresh water.

Phytoplankton is an important source of POC. In shallow Antarctic waters, light limitation due to high turbidity and the strong mixing of the upper water layers (a consequence of the heavy winds) have been suggested as controls upon phytoplankton abundance[33]. Antarctic coastal waters are usually considered to be replete with nutrients, except during local phytoplankton blooms in areas west of the Antarctic Peninsula[39] or close to receding ice edges[40]. The concentrations of nitrate, phosphate and silicate in GWC and AC are high, similar to the high nutrient concentrations in Antarctic and sub-Antarctic waters in general. The average N/P ratio was 13.60±0.26 in GWC and 13.20±0.27 in AC. Normally, phytoplankton in the ocean uptake dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) according to the Redfield ratio, which is a ratio of carbon, nitrogen and phosphorus of 106:16:1. Justić[41] suggested that an N/P ratio close to the Redfield ratio (10–22) is indicative of high productivity. As nutrient concentrations are not the limiting factors for phytoplankton growth in the two coves, there is no significant relationship between nutrient levels and POC.
Additionally, although differences in temperature and salinity between the two coves were both statistically significant \( (p<0.05) \), differences between Chl-\( \text{a} \) and POC concentrations were not significant \( (p>0.05) \). This indicates that hydrological conditions do not strongly influence the distribution of Chl-\( \text{a} \) and POC.

### Table 1
Concentrations of POC in different regions, Antarctica

<table>
<thead>
<tr>
<th>Area</th>
<th>POC/(μg·L(^{-1}))</th>
<th>Depth</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prydz Bay(^{6})</td>
<td>482.90</td>
<td>surface</td>
<td>2006</td>
</tr>
<tr>
<td>Prydz Bay(^{38})</td>
<td>480</td>
<td>surface</td>
<td>2013</td>
</tr>
<tr>
<td>Prydz Bay(^{6})</td>
<td>352.2</td>
<td>25 m</td>
<td>2006</td>
</tr>
<tr>
<td>Prydz Bay(^{5})</td>
<td>279.11</td>
<td>surface</td>
<td>1999</td>
</tr>
<tr>
<td>Ross Sea(^{7})</td>
<td>226.91</td>
<td>euphotic layer</td>
<td>1989</td>
</tr>
<tr>
<td>South Atlantic(^{3})</td>
<td>106.40</td>
<td>——</td>
<td>1989/1990</td>
</tr>
<tr>
<td>Drake Passage(^{1})</td>
<td>88.90</td>
<td>——</td>
<td>1989/1990</td>
</tr>
</tbody>
</table>

### 4.2 \( \delta^{13} \)C of particulate organic matter

Particulate organic matter (POM) in the ocean originates largely from plankton in the euphotic zone and reflects living plankton populations\(^{42}\). The \( \delta^{13} \)C value of marine organic matter represents a mixed isotope signal from land plant detritus, primary production by aquatic organisms, and microbial biomass\(^{42}\). A culture experiment with marine microalgae\(^{43}\) showed that phytoplankton \( \delta^{13} \)C depends on several factors, including cell wall permeability, growth rate, cell size and the ability of the cell to actively assimilate inorganic carbon. It has been reported that between 40°N and 40°S, \( \delta^{13} \)C of POM varies between −18.5‰ and −22‰, with significantly lighter values in cold euphotic waters and the high latitudes of the Southern Ocean\(^{45}\). This is consistent with the reported trend of increasing surface ocean \( \delta^{13} \)C toward the tropics in both hemispheres\(^{44,45}\) (Table 2). For example, in Prydz Bay, latitude 64°–69°S, phytoplankton is the major contributor of POC\(^{5,6,38}\), and the POC \( \delta^{13} \)C is −28.01‰.

As described above, terrestrial organic matter is a significant contributor to marine POC and strongly influences the \( \delta^{13} \)C. There are no available \( \delta^{13} \)C data for the Fields Peninsula; however, it has been reported that it has similar vegetation to that of other ice-free regions around Maxwell Bay\(^{16,46}\). The vegetation is predominantly composed of lichens and mosses\(^{15}\), along with some algae and macro fungi, and a single type of phanerogam named Deschampsia Antarctica. Lee et al.\(^{46}\) reported that terrestrial plants on Barton Peninsula showed species-specific carbon and nitrogen isotope compositions, with \( \delta^{13} \)C values ranging between −26.9‰±0.5‰ and −23.6‰±2.5‰. Along the coast of Admiralty Bay, the largest fjord-like embayment on King George Island, \( \delta^{13} \)C of lichens ranges from −21.13‰ to −18.43‰ and mosses from −25.99‰ to −21.64‰\(^{47}\). However, the average POC \( \delta^{13} \)C value for GWC and AC was −27.43‰±0.74‰, lighter than that of the terrestrial plants \( \delta^{13} \)C mentioned above.

Furthermore, the average \( \delta^{13} \)C value given by Fry and Sherr\(^{48}\) for 12 species of benthic macroalgae sampled in AC was −22.41‰±6.97‰ \((n=26)\), implying that phytodetritus of

### Table 2
\( \delta^{13} \)C of phytoplankton from various latitudes

<table>
<thead>
<tr>
<th>Regions</th>
<th>Phytoplankton ( \delta^{13} )C/‰</th>
<th>Latitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canada Basin(^{49})</td>
<td>−27.1</td>
<td>80°N</td>
</tr>
<tr>
<td>Mackenzie Shelf(^{50})</td>
<td>−27.31</td>
<td>70°N</td>
</tr>
<tr>
<td>Prydz Bay(^{38})</td>
<td>−28.01</td>
<td>64°–69°S</td>
</tr>
<tr>
<td>GWC (this study)</td>
<td>−27.40±0.96</td>
<td>62°N</td>
</tr>
<tr>
<td>AC (this study)</td>
<td>−27.45±0.47</td>
<td>62°N</td>
</tr>
<tr>
<td>Scotia Shelf(^{51})</td>
<td>−25.3±2.8</td>
<td>55°–60°S</td>
</tr>
<tr>
<td>Laoshan Bay (winter)(^{51})</td>
<td>−25.2</td>
<td>36°N</td>
</tr>
<tr>
<td>Bering Sea(^{31})</td>
<td>−24.4</td>
<td>53°–63°N</td>
</tr>
<tr>
<td>Torres Strait(^{51})</td>
<td>−21.8±0.9</td>
<td>10°S</td>
</tr>
</tbody>
</table>

Notes: \( \delta^{13} \)C values of Canada Basin, Mackenzie Shelf, Prydz Bay, GWC and AC are POC \( \delta^{13} \)C‰. There were strong positive correlations between Chl-\( \text{a} \) and POC in these regions except GWC and AC.
bacterial macroalgae is likely not a major source of POC. Although runoff made distinct contributions to other seawater parameters in GWC and AC, the amount of organic carbon washed into the sea from the Fields Peninsula is negligible. Although more riverine and phytoplankton samples would be required to better constrain the various terrestrial POC sources, our results suggest that terrestrial organic matter and benthic macroalgae do not significantly influence POC in these two coves. This indicates that the POC is of predominantly marine origin.

4.3 Contribution of phytoplankton and heterotrophic organisms to POC

Antarctic coasts are usually considered productive areas. However, some shallow coastal areas are known to be high-nutrient, low-chlorophyll (HNLC) systems where even with favorable conditions for phytoplankton growth, phytoplankton biomass remains low[33]. Chl-a concentration is taken as representative of the living phytoplankton biomass, which is an important source of POC. In GWC, the main source of Chl-a was primary producers such as phytoplankton (namely diatoms, dinoflagellates and chrysophyceae) and benthic algae[16]. Reported diatom to total phytoplankton ratios are 93%[20], 96.63%[16], with dominant in summer. The POC/Chl-a of fresh phytoplankton ranges between 33 and 100[32], which is close to the range seen in regions of high primary productivity. In rivers, lakes and regions where primary productivity is not a major contributor to POC, the POC/Chl-a will be high, reaching ~250–2 500[51]. The POC/Chl-a in GCW and AC was 74.62 ± 27.97, which is higher than that of sub-Antarctic water (50–60)[50] but lower than that of the Ross Sea (116–150)[53] and Prydz Bay (~118)[51]. The POC/Chl-a profile (Figure 5) exhibit a similar pattern to that of POC.

Strong linear relationships between Chl-a and POC ($r = –0.89$) have been reported in Prydz Bay and the Ross Sea[5–7,38]. This correlation was not seen in either GWC or AC, where POC did not increase as Chl-a increased ($r = –0.40$, $p < 0.05$). This indicates that other marine organisms as well as phytoplankton also contributed to POC in these two coves.

The process of phytoplankton photosynthesis releases dissolved oxygen (DO) and POC rich in phytoplankton is generally consistent with higher DO values. A weak positive correlation between Chl-a and DO ($r = 0.48$, $p < 0.01$) was found for GWC and AC. In general, when POC sinks through the water column, the degradation of organic matter results in lower POC concentrations and higher apparent oxygen utilization (AOU). However, in GWC and AC, POC and DO showed a negative correlation ($r = –0.43$, $p < 0.01$), while POC and AOU showed a positive correlation ($r = 0.53$, $p < 0.01$), although neither correlation was significant. This indicates POC formation in these two coves is a strong DO-consuming process, most likely respiration or the heterotrophic synthesis of POC. Within the microbial food loop, heterotrophic bacteria play a key role in the formation of organic carbon, because unlike other organisms, they can transform dissolved organic carbon (DOC) into POC[56–57]. The increase in DOC released during rapid phytoplankton growth stimulates bacteria growth[59]. Bacteria biomass comprises more than one third of the microbial community biomass in GWC and AC, with values of 10.770 μgC·L−1 reported for the upper 10 m of GWC and 10.424 μgC·L−1 for AC[56]. In the sea adjacent to King George Island, only ~2% of phytoplankton are consumed by zooplankton. At least 90% of phytoplankton are mineralized in the water or sink down through the water column[59]. Therefore, it is possible that the high nutrient concentrations and phytoplankton biomass provided support to the heterotrophic organisms, which consumed DO.

Additionally, seashore organisms may also play a role. On land and in the shore zone macroalgae are a source of organic matter and nutrients[60]. During our survey, there was visible macroalgae washed up on the beach and deposited on the shores of GWC and AC. After being deposited on land, the macroalgae are subject to decomposition and join the material cycle between sea and land[60].

There are also large penguin populations living on Ardley Island that produce a considerable volume of excreta, much of which is deposited in the coastal region of AC. However, there are no penguin colonies around the shores of GWC. Despite this, the POC concentrations of the two coves are similar, indicating the penguins’ impacts are minimal in the two coves.

While the contributions of all the various POC sources are difficult to quantify, it can be concluded that phytoplankton, organic detritus and heterotrophic organisms all contributed to POC in GWC and AC.

5 Conclusions

This study studied the distribution and sources of POC in GWC and AC in January 2013, during the 29th CHINARE.
Our observations illustrate that the higher concentration of POC at station G5 is the result of lateral transport of the Bransfield Strait current on the outer cove, whereas the lower concentration of POC in surface waters of stations G1 and G3 indicates dilution of surface waters in the inner cove.

Although temperature and salinity values for the two coves display clear runoff signals, $\delta^{13}C$ values and POC distributions indicate that the amount of organic carbon from riverine and terrestrial sources was negligible. The $\delta^{13}C$ values also suggest that POC was of predominantly marine origin. Based on the relationship between POC and Chl-$a$, it can be concluded that phytoplankton, organic detritus and heterotrophic organisms all contribute to POC in GWC and AC.

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References

36 Yang T Z, Zhao J S, Xu J P. Water masses and circulation around the South Shetland Islands in summer. Proceedings of China first symposium on Southern Ocean expedition (Hangzhou, China), the Academic Committee on Antarctic Research of China and the Second Institute of Oceanography, SOA, 1988
38 Yin X J, Li Y H, Qiao L, et al. Distribution of particulate organic carbon(POC) and $\delta^{13}$C in surface waters in summer in Prydz Bay, Antarctica. Chin J Polar Res(Chinese Edition), 2014, 26: 159-166
42 Hoefs J. Stable Isotope Geochemistry, Sixth Edition. Berlin: Springer-Verlag, 2009
44 Goericke R, Fry B. Variations of marine plankton $\delta^{13}$C with latitude, temperature, and dissolved CO2 in the world ocean. Global Biogeochem. Cycles, 1994, 8: 85-90
56 Dai J C. The Composition and Function of the Main Group of Microbial Food Loop in Offshore of Polar Region. 2006