Transport of nutrients and contaminants from ocean to island by emperor penguins from Amanda Bay, East Antarctic

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HIGHLIGHTS

• Emperor penguins transfer nutrients and contaminants from ocean to island and lake or pond system.
• Stable carbon and nitrogen isotopes in determining sources of organic matters in lake sediments
• Differences in biotransfer efficiency between emperor and Pygoscelis penguins

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ABSTRACT

Penguins play important roles in the biogeochemical cycle between Antarctic Ocean and land ecosystems. The roles of emperor penguin Aptenodytes forsteri, however, are usually ignored because emperor penguin breeds in fast sea ice. In this study, we collected two sediment profiles (EPI and PI) from the N island near a large emperor penguin colony at Amanda Bay, East Antarctic and performed stable isotope and element analyses. The organic C/N ratios and carbon and nitrogen isotopes suggested an autochthonous source of organic materials for the sediments of EPI (C/N = 10.21 ± 0.26, n = 17, δ13C = −13.48 ± 0.50‰, δ15N = 8.35 ± 0.55‰, n = 4) and an allochthonous source of marine-derived organic materials for the sediments of PI (C/N = 6.15 ± 0.08, δ13C = −26.85 ± 0.11‰, δ15N = 21.21 ± 0.02‰, n = 20). The concentrations of total phosphorus (TP), selenium (Se), mercury (Hg) and zinc (Zn) in PI sediments were much higher than those in EPI, the concentration of copper (Cu) in PI was a little lower, and the concentration of element lead (Pb) showed no difference. As measured by the geoaccumulation indexes, Zn, TP, Hg and Se were from moderately to very strongly enriched in PI, relative to local mother rock, due to the guano input from juvenile emperor penguins. Because of its high trophic level and transfer efficiency, emperor penguin can transport a large amount of nutrients and contaminants from ocean to land even with a relatively small population, and its roles in the biogeochemical cycle between ocean and terrestrial environment should not be ignored.

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Hills in Antarctica, *Pygoscelis* penguins could transfer about $4.0 \times 10^5$ kg of phosphorus per year from ocean to islands and coastal lands (Qin et al., 2013). *Pygoscelis* penguins transported large amounts of marine heavy metals and organic pollutants from both natural and anthropogenic sources to lands, lakes or ponds in the form of guanos, feathers and eggshells (Roosens et al., 2007; Xie and Sun, 2008; Brasso et al., 2012). These transported nutrients and contaminants were deposited in land and lakes and then formed penguin ornithogenic soils and sediments. Unlike *Pygoscelis* penguins, emperor penguins have been less studied for their roles in the biogeochemical cycle between ocean and land, likely due to the fact that adult emperor penguins breed in sea ice and rarely visit land (Le Maho, 1977).

During several field investigations, we observed many juvenile emperor penguins in the N island near their colony, even though their population is smaller than that of the land-based *Pygoscelis* penguins. To study possible impacts by juvenile emperor penguins on land environment, in this study, we collected two sediment cores (named as EPI and PI) from the N island near a large emperor penguin colony at Amanda Bay, East Antarctic and performed stable C and N isotope and elemental analyses. By comparing stable isotope values, elemental concentrations and sedimentary characteristic, we identified the sources of organic matters in EPI and PI. Therefore, we have studied the biogeochemical cycle between ocean and land, likely due to the fact that adult emperor penguins breed in sea ice and rarely visit land (Le Maho, 1977).

During several field investigations, we observed many juvenile emperor penguins in the N island near their colony, even though their population is smaller than that of the land-based *Pygoscelis* penguins. To study possible impacts by juvenile emperor penguins on land environment, in this study, we collected two sediment cores (named as EPI and PI) from the N island near a large emperor penguin colony at Amanda Bay, East Antarctic and performed stable C and N isotope and elemental analyses. By comparing stable isotope values, elemental concentrations and sedimentary characteristic, we identified the sources of organic matters in EPI and PI, calculated the geoaccumulation index of elements in PI, and discussed emperor penguins’ roles in transfer of nutrients and contaminants from ocean to island and freshwater systems.

### 2. Materials and methods

#### 2.1. Study area and sample collection

Amanda Bay is located at the Ingrid Christensen Coast of Princess Elizabeth Land, East Antarctica, about 20 km northeast of Chinese Zhongshan Station (Larsemann Hills) and nearly 80 km to the west of Australian Davis Station (Vestfold Hills). It is approximately 3 km wide and 6 km long, and opens northwest into the much larger Prydz Bay. The southwest side of the bay is flanked by the Flatnes Ice Tongue. The eastern and southern sides are bounded by the ice cliffs of the Hovde Glacier, with Hovde Island in the northeast. There are some small islands within the bay. Fast ice within the Prydz Bay renders the sea ice unstable for most of the year and provides the emperor penguin colony in Amanda Bay with good access to the sea for feeding. Colonies of several thousand pairs of emperor penguins occupy variable positions in the southwest corner of Amanda Bay (Wienecke and Pedersen, 2009).

During the field investigation, two sediment cores (EPI and PI) were collected at the N island, on the southwest side of the Amanda Bay (Fig. 1). EPI core was extracted from a pond with a 19 m height above sea level while PI core was collected from a pond with a 1.5 m height above sea level. The PI core pond was near the emperor penguin colony and many penguin feathers and even a little mummified penguin were found near the pond. In the laboratory, the cores were opened. EPI was sectioned at 1 cm intervals to obtain 17 subsamples; PI was sectioned at 0.5 cm interval on the top 4.5 cm and at 1.0 cm interval on the layer below 4.5 cm, to obtain a total of 20 subsamples. Penguin remains such as bones and feathers were found in PI sediment core and were handpicked. All the subsamples as well as local bedrock samples were stored frozen prior to analysis.

#### 2.2. Stable isotope and elemental analysis

All the samples from EPI and PI were analyzed for the organic C/N ratio; 4 samples in EPI and 20 samples in PI were analyzed for the stable C and N isotope ratios. Samples were air-dried, powdered, acidified with 4 mol/L HCl of 20 ml to remove inorganic carbon, washed repeatedly with Millipore water to neutral pH, dried at 40 °C again. Samples and standards were weighed accurately into tin capsules and loaded into elemental analyzer–isotope ratio mass spectrometer (Flash EA 1112 HT-Delta V Advantages, Thermo). The instrument precision is ±0.25‰ for δ^{13}N, ±0.20‰ for δ^{13}C and ±0.25‰ for C and N content. Standard deviation of the insert standard samples ($n = 5$) is <2.0‰ for δ^{13}C, <0.30‰ for δ^{15}N, and <0.8‰ and <0.7‰ for C and N content, respectively. Stable isotope results are presented in δ (%) and expressed relative to air for δ^{15}N and Vienna Pee Dee Belemnite (VPDB) for δ^{13}C according to the equation: \( \delta \% = \left[ \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 10^3 \), where \( \delta \% \) represents the δ^{15}N or δ^{13}C value, \( R_{\text{sample}} \) is the isotopic ratio of the sample, and \( R_{\text{standard}} \) is the isotopic ratio of the air and VPDB.

For elemental analyses, about 0.25 g of sediment and bedrock powder was taken, weighed, and digested (HNO₃–HF–HClO₄) in a Teflon...
crucible with electric heating. The digested samples were analyzed for TP, Cu, Zn and Pb by inductively coupled plasma-optical emission spectrometry (ICP-OES, Perkin Elmer DV2100) and for Hg and Se by atomic fluorescence spectrophotometry (AFS-930, Titan Instruments Co., Ltd.). Standard sediment reference materials were included with every batch of samples. The analytical values for major elements and trace elements were within ±0.5% and ±5% of the certified standards, respectively. According to the equation given by Müller (1979) \( I_{geo} = \log_2 \left[ \frac{C_n}{B_n} \right] \), the geoaccumulation index of 6 elements in PI sediment was calculated, where \( C_n \) represents the elemental concentrations in PI sediments, \( B_n \) the elemental concentrations in local bedrock, and 1.5 is a correction factor.

2.3. Statistical test for isotopic and elemental data between PI and EPI

To assess the significance of the difference in stable isotope ratios (\( \delta^{13}C \) and \( \delta^{15}N \), \( n = 20 \) for PI and \( n = 4 \) for EPI) and elemental concentrations (C/N, TP, Cu, Zn, Hg, Se and Pb, \( n = 20 \) for PI and \( n = 17 \) for EPI) between PI and EPI, we performed two-step statistical tests by using SPSS 16.0. First, we performed the nonparametric one-sample Kolmogorov–Smirnov test to verify if the data follow normal distribution. The results showed that all of our data in PI and EPI follow normal distribution (asymptotic \( p \) value > 0.10 with no presence of ties). Second, we performed parametric independent samples t-test and used 0.05 for the level of significance.

3. Results

3.1. C/N ratios and stable isotopes

The C/N ratios of the PI sediments range from 5.38% to 6.66% with a mean of 6.15 ± 0.08% (mean ± standard error of mean, \( n = 20 \)). The C/N ratios of the EPI sediments range from 9.83% to 11.82% with a mean of 10.21 ± 0.28% (\( n = 17 \)). There is a significant difference in the C/N ratios of sediments between PI and EPI (\( t = 6.984, p = 0.005 \)). The \( \delta^{13}C \) values in the PI sediments range from -21.1 ± 2.02% to -12.3% with a mean of \(-26.85 \pm 0.11\%\) (\( n = 20 \)); the \( \delta^{15}N \) values have a greater range from 15.05% to 47.09% with a mean of 21.2 ± 2.02% (\( n = 20 \)). The \( \delta^{13}C \) values in the EPI sediments range from -12.05% to -14.29% with a mean of -13.48 ± 0.50% (\( n = 4 \)); the \( \delta^{15}N \) values range from 6.98% to 9.64% with a mean of 8.35 ± 0.55% (\( n = 4 \)). Stable C and N isotope values between PI and EPI show a significant difference (\( \delta^{13}C: t = 26.202, p < 0.001; \delta^{15}N: t = 6.139, p < 0.001 \)), and they are plotted vs. C/N ratios in the Fig. 2.

3.2. Elemental concentrations and geoaccumulation index (\( I_{geo} \))

The mean concentrations of TP, Hg, Se, Zn, Cu and Pb in sediments of PI are 2.5 ± 0.3%, 281 ± 25 ng g\(^{-1}\), 9.1 ± 1.1 mg kg\(^{-1}\), 652 ± 86 mg kg\(^{-1}\), 22.3 ± 2.1 mg kg\(^{-1}\) and 23.8 ± 1.7 mg kg\(^{-1}\), respectively. The mean levels of corresponding elements in EPI are 0.29 ± 0.01%, 55.5 ± 2.1 ng g\(^{-1}\), 2.9 ± 0.2 mg kg\(^{-1}\), 138 ± 19 mg kg\(^{-1}\), 35.3 ± 3.1 mg kg\(^{-1}\) and 20.5 ± 1.3 mg kg\(^{-1}\), respectively. Elemental concentrations vs. C/N ratios in PI and EPI are plotted in Fig. 3. PI has higher levels of TP, Hg, Se and Zn and lower levels of Cu than EPI, and the differences are significant for TP, Hg, Se, Zn and Cu (\( t = 6.411, p < 0.001 \); Hg: \( t = 8.231, p < 0.001 \); Se: \( t = 4.979, p < 0.001 \); Zn: \( t = 5.377, p < 0.001 \); Cu: \( t = 3.485, p = 0.002 \)) and insignificant for Pb (\( t = 1.464, p = 0.152 \)).

The geoaccumulation indexes (\( I_{geo} \)) of 6 elements in PI are shown in Fig. 4. TP, Hg, Se and Zn have high \( I_{geo} \) values with a mean of 2.8 ± 0.2, 2.9 ± 0.1, 5.6 ± 0.2 and 1.2 ± 0.2, respectively; Cu and Pb have negative \( I_{geo} \) values.

Fig. 2. Isotope values vs. C/N ratios in EPI and PI. a: \( \delta^{13}C \); b: \( \delta^{15}N \), triangle for PI, and dot for EPI.

4. Discussion

4.1. Sources of organic matter in PI and EPI

The ecosystem of Antarctic islands and coastal ice free land areas is relatively simple. The organic matters in Antarctic lake or pond sediments are mainly from autochthonous algae or allochthonous floras and faunas (e.g. Sun et al., 2013). During the core section, visual inspection showed a homogenous lithostratigraphy for EPI and PI cores. EPI is composed of mainly peat and PI of mainly black mud with a strong unpleasant smell of penguin guano. Mean C/N ratios of PI and EPI (6.15 ± 0.08% and 10.21 ± 0.28%) are within the range of 4%–10% (Fig. 2), indicating a lacustrine or marine organic sedimentation (Meyers, 1994). PI has C/N ratios closer to those of sedimentary organic matters from Southern Ocean (mean: 6.2 ± 0.5%, range: 5.0%–6.9%, \( n = 11 \), data from Sigman et al., 1999) than EPI. Though the difference in C/N ratios between PI and EPI sediments is significant, we cannot distinguish their exact original sources since the C/N ratios in PI and EPI are within the range of both lacustrine and marine organic materials.

\( \delta^{13}C \) is a useful proxy in tracing organic sources in sediments (Meyers, 1994). The \( \delta^{13}C \) values of lake algae are usually around -27‰ (Meyers, 1994), but they can increase to reach as high as -9‰ when the algae begin to use dissolved bicarbonate as the carbon source (Meyers, 2003). Marine phytoplankton typically has \( \delta^{13}C \) values between -22‰ and -20‰, and the \( \delta^{13}C \) values of particulate organic carbon in Southern Ocean are around -26‰ (Berg et al., 2011). The mean \( \delta^{13}C \) value of -13.48 ± 0.50‰ in the EPI sediments indicates freshwater algae sedimentation, and this is further supported by the observed sedimentary characteristic. High \( \delta^{13}C \) values in lake sediments are also observed in the nearby Larsemann Hills (mean: -9.9‰, range: -11.31‰– -8.92‰, \( n = 63 \), Liu et al., unpublished results). These high \( \delta^{13}C \) values of lake sediments in East Antarctica suggest
that lake algae use bicarbonate as carbon sources. The \( \delta^{13}C \) values of the PI sediments range from \(-25.76\)‰ to \(-27.35\)‰ with a mean of \(-26.85 \pm 0.11\)‰, indicating either freshwater or marine original organic sources. Since the freshwater algae sedimentations in both the N island (EPI) and the nearby Larsemann Hills have high \( \delta^{13}C \) values, the distinctly low \( \delta^{13}C \) values in PI suggest a marine source of its organic matters. Average \( \delta^{13}C \) values of Pygoscelis penguin ornithogenic sediments from Ardley Island and Ross Island in Antarctica are \(-22.61\)‰ (n = 12) and \(-24.06\)‰ (n = 116), respectively (Liu et al., 2006, 2013); and they are very close to the values of PI sediments, a further indication of the marine source of the organic matters in PI.

In contrast to carbon isotope ratio (\( \delta^{13}C \)), stable nitrogen isotope ratio (\( \delta^{15}N \)) is much enriched in consumers relative to that of prey and consequently it usually serves as indicator of a consumer trophic position (e.g. Emslie and Patterson, 2007; Huang et al., 2011b). The mean \( \delta^{15}N \) value in the PI sediments is \(21.21 \pm 2.02\)‰, much higher than that of EPI (\(8.35 \pm 0.55\)‰). According to the local sedimentary environment, PI should be ornithogenic sediments as the result of juvenile emperor penguins’ guano input. The high \( \delta^{15}N \) values in PI are very likely due to substantial fractionation in the penguin guanos from ammonia volatilization, during which lighter nitrogen-14 is emitted with ammonia and heavier nitrogen-15 is enriched in the remaining sediments. Similarly high nitrogen isotopic ratios are observed in Adélie penguin

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**Fig. 3.** Elemental concentrations vs. C/N ratios in the sediments of PI and EPI. Triangle is for PI, and dot for EPI.

**Fig. 4.** Geoaccumulation index of elements in the PI sediments (data was presented by mean ± standard error of mean, n = 20).
ornithogenic soils (32.2±n, n = 6, Mizutani et al., 1986), Adélie penguin guanos (25.0±n, n = 3), ornithogenic sediments (28.4±n, n = 11, Huang et al. unpublished results), and seal excrement sediments (24.0±n, n = 32, Liu et al., 2004). By comparing stable C and N isotope values of PI and EPI, we conclude that PI sediments are affected by emperor penguin’s guano input while EPI sediments are from natural lake algal sedimentation.

4.2. Emperor penguins transfer nutrients and contaminants from ocean to island

The transport of large amount of nutrients and contaminants from ocean to the Antarctic islands and coastal ice free land areas by the land-based Pygoscelis penguins have been studied (e.g. Sun and Xie, 2001; Roosens et al., 2007; Nedzarek, 2010). Emperor penguins’ role in such transport, however, is usually ignored because they are sea ice breeding species (Le Maho, 1977). Our stable isotope analyses suggest that penguin’s guano input while EPI sediments are from natural lake and EPI, we conclude that PI sediments are affected by emperor penguins.

The geoaccumulation index (Igeo) by Müller (1979) has been extensively used for evaluating contamination and enrichment of elements in sediments. Fürstner et al. (1993) classified sediments into seven classes based upon Igeo, from practically unpolluted level (class 0, Igeo < 0) to very strong pollution level (class 6, Igeo > 5). The Igeo of elements in PI are plotted in Fig. 4. Nutrient element Se has the highest Igeo value of 5.6 ± 0.8, indicating a very strong enrichment, apparently because of the very high concentration of Se in emperor penguin ornithogenic sediments and the very low level in local mother rock. High concentration of Se in Pygoscelis penguin guanos and ornithogenic sediments from Ardley Island, Victoria Land and Vestfold Hills in Antarctica was also observed (Sun et al., 2000; Hofstere et al., 2006; Huang et al., 2009a). The Igeo of nutrient element TP and pollution element Hg in PI are 2.8 ± 0.2 and 2.9 ± 0.1, indicating moderate to strong enrichment and pollution of them, apparently due to penguin guano input. The Igeo of heavy metal of Zn in PI is 1.2 ± 0.2, a moderately pollution level. The Igeo of Cu and Pb in PI are negative, indicating that Cu and Pb are not affected by penguin guano input. Different homeostatic processes from non-essential elements Hg and Pb in contrast to essential elements TP, Se, Cu and Zn may cause a bias in our dataset. However, the non-essential element Hg has an Igeo value comparable to that of the essential element TP and Pb has much lower value of Igeo than TP and Hg; thus the effects of the homeostatic processes of elements on the dataset in the present study are likely insignificant. The geoaccumulation index values of elements in PI and EPI showed that juvenile emperor penguins transferred a large number of nutrients and contaminants from ocean to island system.

Trophic position of seabirds influences their efficacy in transferring pollutants from ocean to land. Seabirds of higher trophic position are more efficient transferer (Michelutti et al., 2010) because many pollutants become biomagnified through food webs. Pb level does not show any substantial difference between emperor penguin ornithogenic sediments PI and Pygoscelis penguin ornithogenic sediments Y2 (23.8 ± 1.7 mg kg⁻¹ vs. 15.7 ± 0.7 mg kg⁻¹, data from this study and Sun and Xie, 2001), mainly because Pb is not bioaccumulated through food chain (Sun and Xie, 2001). The concentration of Hg, however, increases in living organisms along the trophic chain through bioaccumulation and biomagnification (Risgaard and Hansen, 1990). The Hg level in PI is as high as 281 ± 25 ng g⁻¹, much higher than those in Adélie penguin ornithogenic sediments from Ardley Island and Vestfold Hills (55 ± 2 ng g⁻¹ (n = 46) and 10 ± 0.4 ng g⁻¹ (n = 55), respectively) (Sun et al., 2006; Huang et al., 2009a) and even those in pure Adélie penguin guanos from Ross Island (150 ± 8 ng g⁻¹, n = 3) (Nie et al., 2012). The great differences in Hg concentration between Adélie and emperor penguin ornithogenic sediments are mainly due to their different trophic positions. Unlike Adélie penguins, which mainly feed on krill of lower trophic level, emperor penguins eat fishes of higher trophic level and occupy a higher trophic position (Cherel, 2008). Because of their high transfer efficiency, emperor penguins’ role in transferring materials from ocean to land should not be underestimated or even ignored, especially in the barren Antarctic terrestrial systems, even though the population of juvenile emperor penguins that visited on land is smaller than that of Adélie penguins.

5. Conclusion

Based on stable isotope and elemental geochemical analyses on two sediment cores EPI and PI from the N island near Amanda Bay, we conclude that EPI is composed of natural freshwater alga sedimentation and PI is strongly influenced by emperor penguin guano input. The Igeo values of elements in PI sediments show that emperor penguins at Amanda Bay have significant impacts on local island and pond systems. Juvenile emperor penguins transfer large amounts of nutrients and contaminants from Southern Ocean to island environment, and lead to substantial enrichment of Se, TP and Hg in lake sediments. Though the population of emperor penguins that have direct impacts on land systems is small, emperor penguins’ role in the biogeochemical cycle between ocean and land should not be ignored, especially in the Antarctic land systems.

Conflict of interest

The authors declare no conflict of interests.

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