Distribution patterns and possible influencing factors of As speciation in ornithogenic sediments from the Ross Sea region, East Antarctica

Chuangneng Lou [a], Xiaodong Liu [a,*], Wenqi Liu [b], Libin Wu [a], Yaguang Nie [a], Steven D. Emslie [c]

[a] Institute of Polar Environment, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China
[b] Instruments' Center for Physical Science, University of Science and Technology of China, Hefei 230026, China
[c] Department of Biology and Marine Biology, University of North Carolina Wilmington, 601 S. College Road, Wilmington, NC 28403, USA

HIGHLIGHTS

- Inorganic As is the predominant species in ornithogenic sediments.
- As in fresh guano is largely composed of DMA.
- Diagenetic processes may influence the distribution of As species in guano.
- Redox conditions and algae abundance may control As species in studied sediments.

GRAPHICAL ABSTRACT
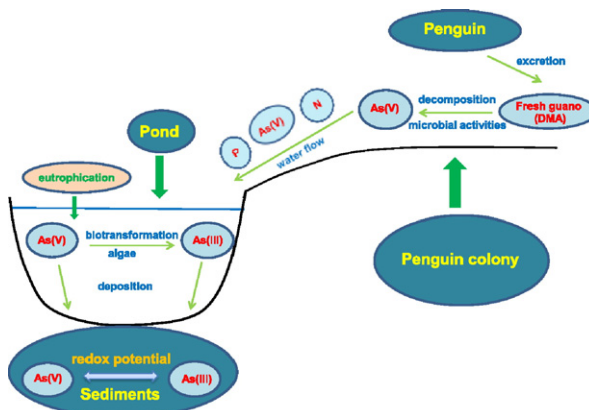
ARTICLE INFO

ABSTRACT

Ornithogenic sediments are rich in toxic As (arsenic) compounds, posing a potential threat to local ecosystems. Here we analyzed the distribution of As speciation in three ornithogenic sediment profiles (MB6, BI and CC) collected from the Ross Sea region, East Antarctica. The distributions of total As and total P (phosphorus) concentrations were highly consistent in all three profiles, indicating that guano input is a major factor controlling total As distribution in the ornithogenic sediments. The As found in MB6 and CC is principally As(V) (arsenate), in BI As(III) (arsenite) predominates, but the As in fresh guano is largely composed of DMA (dimethylarsinate). The significant difference of As species between fresh guano and ornithogenic sediment samples may be related to diagenetic processes after deposition by seabirds. Based on analysis of the sedimentary environment in the studied sediments, we found that the redox conditions have an obvious influence on the As speciation distribution. Moreover, the distributions of As(III) and chlorophyll *a* in the MB6 and BI profiles are highly consistent, demonstrating that aquatic algae abundance may also influence the distribution patterns of As speciation in the ornithogenic sediments.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

As is a toxic metalloid element found throughout the natural world, and it has received increased attention by both scientists and the

* Corresponding author.
  E-mail address: ycx@ustc.edu.cn (X. Liu).

general public in recent decades as a result of problems encountered with excessive As content of groundwater in Southeast Asia (Harvey et al., 2002; Polizzotto et al., 2008). Apart from the earth's crust, soils, sedimentary materials and other natural sources, man-made sources such as mining and fossil fuel industries, industrial waste and products containing As (pesticides, fertilizers and food additives) have all enhanced the presence of As within the environment (Bissen and Frimmel, 2003). The principal pathways of As into the human body include drinking water, food and air. Of these, excessive levels of As in drinking water pose the greatest threat to human health (Smedley and Kinniburgh, 2002). Following progress in research into As epidemiology, its carcinogenic nature and consequent threat to human health have received increased attention (Mandal and Suzuki, 2002; Smith et al., 2002).

The breeding activities of seabirds in coastal areas act as a 'biological pump' in the transference of nutrients between marine and terrestrial ecosystems (Sun et al., 2000). Struvite (MgNH$_4$PO$_4 \cdot$6H$_2$O), originating from diagenetic processes on seabird guano, is an important and sustainable source of phosphate fertilizer (Ma and Rouff, 2012). However, seabird behavior is also an important medium for the transfer of some harmful pollutants (Blais et al., 2005; Brimble et al., 2009). Many studies have shown that As is one of the bio-elements from guano input in ornithogenic sediments (Liu et al., 2006, 2013; Huang et al., 2009; Xu et al., 2011). Intense seabird behavior can cause an obvious accumulation of As in soils and sedimentary materials close to their habitats, having a potentially harmful effect upon the local ecosystem (Xie and Sun, 2008; Brimble et al., 2009). Seabirds carry species-specific mixtures of metals (or metalloids) to their nesting sites. Some heavy metals such as Hg (mercury) and Cd (cadmium) can enter and gradually accumulate in the food chain through biological magnification, but As is generally not considered to exhibit similar characteristics (Michelutti et al., 2010; Zheng et al., 2015). As typical elements transformed by seabirds, Hg and Cd in guano appear in far greater concentrations than in background soils and sediments (Nie et al., 2012; Liu et al., 2013). However, As content in seabird guano is at lower levels than in the sediments influenced by guano input, and even in the weathered soils (Liu et al., 2006, 2013; Huang et al., 2009). The possible reason for this discrepancy may be related to As speciation transformation processes in guano after deposition in the sediments. However, the exact enrichment mechanism of As in the ornithogenic sediments requires further research.

Fractionation distribution reflects the specific bound state of elements in soils and sediments and induces a crucial impact upon their mobility and bioavailability in the environment (Wenzel et al., 2001). Based on our reported results of As fractionation distribution in ornithogenic sediments from the Ross Sea region, residual As holds a dominant position, suggesting a relatively weak mobility of As (Lou et al., 2015). Since the speciation of As to a large degree determines the toxicity and behavior of arsenicals within the environment (Jain and Ali, 2000), comprehensive analysis of As fractionation with speciation can provide more detailed information on the ecotoxicological impact and risk associated with the presence of As in the ornithogenic sediments. Relevant toxicological studies reveal that the toxicity of inorganic As is much greater than that of organic As, and that its toxic sequence is As(III) > As(V) > DMA > MMA (monomethylarsonate) > AsC (arsenocholine) and AsB (arsenobetaine) (Bissen and Frimmel, 2003). In most cases, As in soils and sediments is mainly inorganic. Soil oxidation and reduction potential (Ma and Rouff, 2012), microbial behavior (Saalfield and Bostick, 2009), mineral absorbability (Huang et al., 2011) and organic qualities (Harvey et al., 2002) play important roles in the process of As species transformation and migration. Prior to now, comparative research on the analysis of As speciation in seabird guano and the surrounding environment have not been reported, and geochemical research on As in seabird habitats remains with the general study of total As.

Since Antarctica is so geographically remote and human interference is limited, it is an ideal environment in which to investigate the influence of seabird biovectors under natural conditions. The primary objective of this study is to analyze the distribution of As speciation in guano and ornithogenic sediments from the Ross Sea region, East Antarctica, and to better understand the biogeochemical process and enrichment mechanism of As in seabird habitats.

2. Materials and methods

All three ornithogenic sediment cores (MB6, BI, CC) and environmental materials (fresh guano, fresh-water algae samples) were collected in the Ross Sea region, East Antarctica (Fig. 1). Of these, profiles MB6 and CC were collected at Cape Bird and Cape Crozier, respectively, and BI was at Beaufort Island. The detailed description of sampling sites and sectioning of the sediment profiles used in this study were reported by Nie et al. (2012). All the samples were kept at −20 °C until indepth studies were conducted. Prior to chemical analysis, sediments were freeze-dried, homogenized and ground using an agate mortar and pestle, and then passed through a 200-mesh sieve.

As(III) stock standard solution was purchased from the National Institute of Metrology (China). Standards of As(V), DMA and MMA were purchased from Dr. Ehrenstorfer GmbH (Germany), and stock standard solutions of these (containing 100 mg L^{-1} of As) were prepared using deionized water. All stock solutions were kept in the dark at a constant 4 °C, and mixed standard solutions for analysis were prepared daily. In the analysis of As species, 0.6 g subsamples and 10 mL of mixed extractant (1.0 mol L^{-1} H$_3$PO$_4$ and 0.1 mol L^{-1} ascorbic acid) were placed in Pyrex extraction vessels, then subjected to microwave digestion procedures under 80 °C for 20 min. Next, the extracting solution was leached through a 0.45 μm filterable membrane, and the acidity was adjusted using deionized water to approximately 0.2 mol L^{-1} H$_3$PO$_4$. The mixed standard solutions (200 μg L^{-1} with respect to each As speciation) for the analysis were prepared daily, and then diluted to 20, 40, 60, 80 and 100 μg L^{-1} respectively for running standard curves. A 15 mmol L^{-1} (NH$_4$)$_2$HPO$_4$ solution was used as a mobile phase to separate As species. The pH of the mobile phase was adjusted to 6.0 by 10% (v/v) methanoic acid, and then leached using a 0.45 μm filterable membrane and degassed by ultrasonic shaking before analysis. A 7% (v/v) hydrochloric acid was applied as a current-carrying agent, and the reductant was a mixed solution of 0.5% (m/v) potassium hydroxide and 1.5% (m/v) potassium borohydride. All these solutions were prepared daily. High performance liquid chromatography coupled to hydride generation atomic fluorescence spectrometry (HPLC-HG-AFS, SA-10, Titan Instruments, Beijing, China) was used to detect As speciation. A 250 × 4.1 mm Hamilton PRP-X100 anion exchange column with its corresponding guard column (Hamilton, Reno, NV) was applied as part of the separation process of As species. A MARS Xpress 5 microwave oven (CEM, Matthews, NC, USA) was employed in the extraction procedure. The acidity of the mobile phase was monitored by a PHS-3C Lei-ci precision acidimeter (Shanghai Precision Scientific Instruments, China). The analytical method of As speciation and principal operating conditions of HPLC-HG-AFS were reported in detail by Lou et al. (2014).

For total As, 0.25 g subsamples were precisely weighed and digested (HNO$_3$—HCl—HClO$_4$) in colorimeter tubes with electric heating, followed by AFS-930 detection. For P, 0.25 g subsamples were precisely weighed and acid digested (HNO$_3$—HF—HClO$_4$) in Teflon tubes with electric heating, followed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer 2100DV) detection. TOC (total organic carbon) was measured by determining the samples' potassium dichromate oxidation capacity. Analysis of N (nitrogen) content was conducted on an element analyzer (Vario EL III). Organic carbon isotope analysis of acid-treated (HCl about 1 mol L^{-1}) sediment samples were performed using the sealed tube combustion method. All the above analytical methods and data have been reported in detail by Liu et al. (2013). The chlorophyll *a* concentration of sediment samples was analyzed using high performance liquid chromatography coupled with atmospheric pressure chemical ionization mass spectrometry
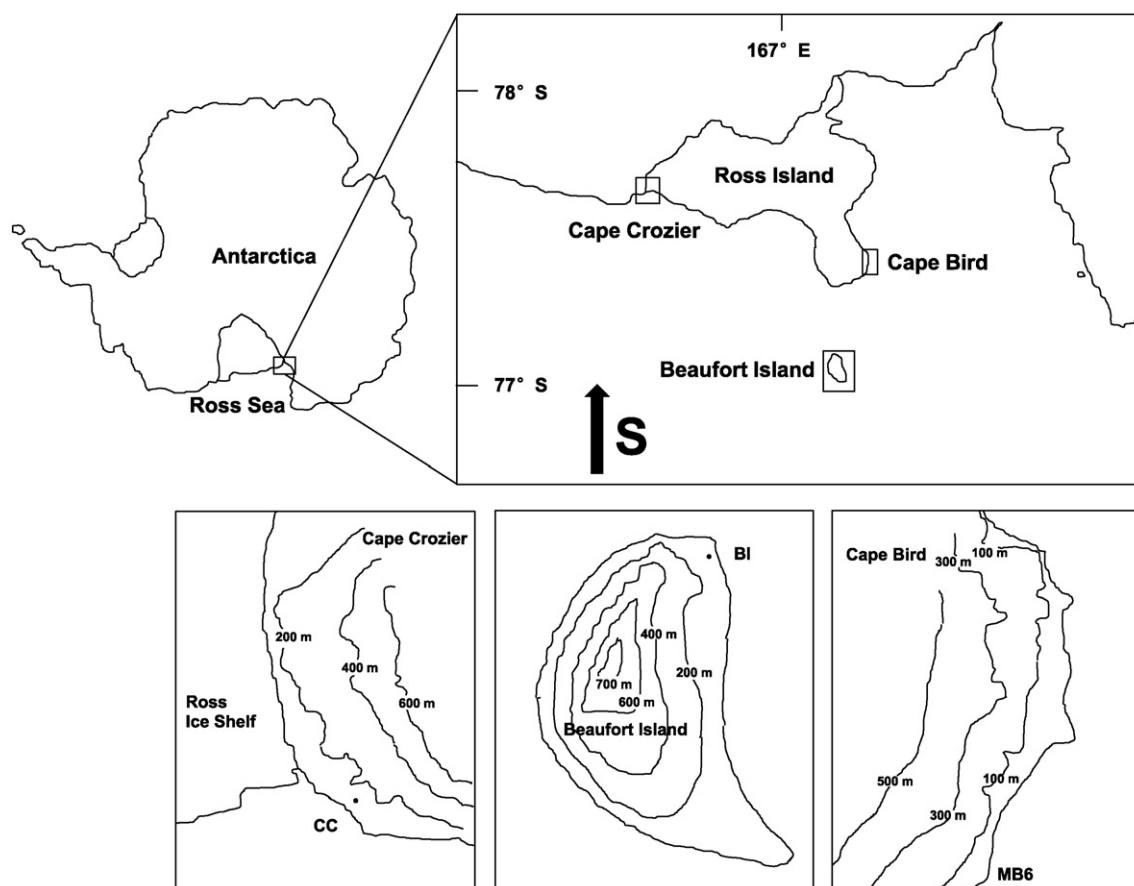
Fig. 1. Sampling sites in the Ross Sea region.

(HPLC-APCI-MS) (Chen et al., 2013). Following the procedure reported by Sanei and Goodarzi (2006), Rock-Eval analysis was conducted at the State Key Laboratory of Organic Geochemistry in Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Of Rock-Eval's parameters, S1, S2 and S3 respectively indicate the volatile hydrocarbons, hydrocarbon components produced due to thermal degradation of humic substances, and the amount of oxycarbide created during pyrolysis. T_{max} is the temperature of the pyrolysis oven recorded at the top of peak S2, which is a well-known indicator for organic matter maturity in ancient sediments. Hydrogen Index (HI) represents the hydrocarbon potential of the total organic matter, and Oxygen Index (OI) gives the oxygen content of the organic matter, both of which may be used to differentiate different sources of organic matter in sediments (Meyers and Lallier-Vergès, 1999; Jacob et al., 2004). The results of Rock-Eval analysis from three sediment profiles and environmental material samples are given in Fig. S1 and Table. S1 in the Supporting Information, respectively. The analysis of active iron in sediment samples was after the method of Wallmann et al. (1993) and Haese et al. (1997).

3. Results and discussion

3.1. As speciation distribution in the ornithogenic sediments

The vertical distributions of As speciation, total P, TOC and total N contents in the three profiles of MB6, BI and CC are given in Fig. 2. Of these, the MB6 profile exhibits a significant change in its element contents at ~24 cm depth, and this is believed to be related to the migration history of penguin populations within Cape Bird, Ross Island (Nie et al., 2015). Thus, in the following discussion the profile was divided into two layers for analysis. The major As species concentrations in the three profiles exhibit similar vertical distribution patterns with total As (Fig. 2).

The prominence of As(V) is present in samples from the upper layers of MB6 and its concentrations rise gradually with increasing depth. Also, small quantities of As(III) and DMA were still detected. As(V) and As(III) in samples from the deeper sediment layers of MB6 are the principal species and no organic As was detected. Total P and As contents in the MB6 profile exhibit a sharp increase just below the sediment layer of ~24 cm, and As speciation also experiences similar changes. Of these, the increase in As(III) is the most noticeable. As(III) and As(V) in samples from the BI profile are the primary species, and their concentrations increase gradually from the bottom to the top (excluding the abnormally high values in the deeper sediment layers). Furthermore, in samples from the recent layers, small quantities of DMA were still detected. As(V) and As(III) in the profile of CC are the main species, and their concentrations increase gradually towards the surface sediments.

In summary, we discovered that As exists principally in inorganic species in the ornithogenic sediment samples from the Ross Sea region, and As(V) accounts for the largest proportion in the profiles of MB6 and CC, whereas As(III) is the predominant species in BI. In addition, the composition of As speciation in fresh penguin guano samples from the Ross Sea region was measured (Table 1). The results show that the predominant species of As in fresh guano is DMA, with a small quantity of As(III), which are obviously different from the ornithogenic sediment samples. Furthermore, total As contents in the fresh guano (below 1.5 μg g^{-1}) are much lower than those in the ornithogenic sediment samples (mostly over 5 μg g^{-1}).

3.2. Effects of guano input and diagenesis on As speciation distribution

As shown in Fig. 2, apart from several samples from the deeper layers of BI, total As concentrations in the three profiles displayed
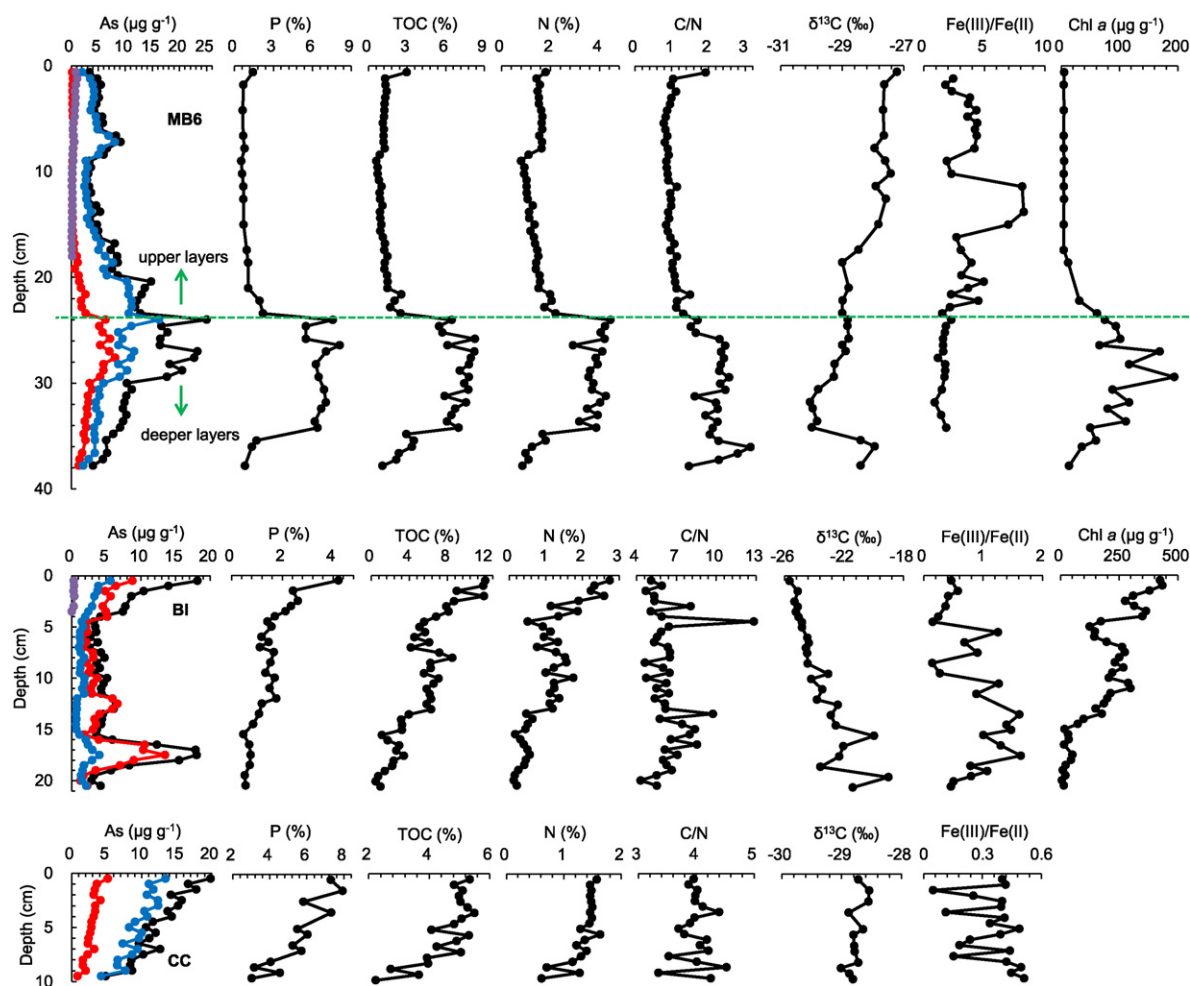
Fig. 2. Variable curves showing the distributions of As speciation, total P, TOC, total N, C/N ratio, δ^{13}C (organic carbon isotope), Fe(III)/Fe(II) active iron values and Chl a content in the sediment profiles of MB6, BI and CC. In the As speciation distribution chart, the black, blue, red and purple dots represent total As, As(V), As(III) and DMA, respectively.

similar trends with total P, TOC and total N, reflecting that the distributions of these components in the sedimentary profiles may be subject to the same environmental factor. The average values of total P content in the deeper sediment layers of MB6 and the CC profile were significantly higher than in the upper layers of MB6 and the BI profile (*T*-test, p < 0.01), and the distribution of total As average concentrations in all three profiles showed clear accordance with total P averages (Fig. 3, A and B). According to our previous research, and excluding the abnormally high values in the deeper layers of BI, total As in the three profiles exhibits significant positive correlations with total P concentrations (Liu et al., 2013), indicating that the amount of guano input is a major factor controlling the distribution of total As concentrations in these three profiles. Based on our published data of grain size in studied sediments (Lou et al., 2015), we suggest the abnormally high As values in the deeper layers of BI may be related to the migration effect of As(III), benefiting from relatively strong migratory aptitude of As(III) and coarse grain

size in the upper sediment layers of BI. To better understand the effect of guano input on the distribution of As speciation in the three profiles, we compared the average As(III)/As(V) value with the average total P content in each profile (Fig. 3, A and C). The results showed no obvious correspondence between these two parameters in the sedimentary samples. Together with the weak Pearson correlations between As(III)/As(V) and P concentration in all the studied sediment samples (Fig. S2), we suggest that the distribution of As speciation in these ornithogenic sediments is not determined by the amount of guano input, although this is an important factor controlling total As contents.

The significant difference of As species in fresh guano and ornithogenic sediment samples is of interest. Some studies have shown that under microbial influence DMA in soils can be transformed into inorganic As through demethylation and redox processes, specifically described by the sequence DMA(V) → MMA(V) → MMA(III) → inorganic As (Huang et al., 2007; Yoshinaga et al., 2011). Thus, we suggest that the diagenetic process after the excretion of fresh guano should be the main factor in explaining the difference of As speciation composition in fresh guano and ornithogenic sediment samples. Moreover, it can also explain why small quantities of DMA were detected in the surface layers of sedimentary samples, as well as why the As from the deeper sediment samples mainly consisted of inorganic species (Fig. 2). Here, we hypothesize the transformation and accumulation mechanisms of As speciation in the ornithogenic sediments as follows (see the Graphical abstract). In the initial stage of guano dehydration, a large amount of organic matter (e.g., uric acid) is decomposed, probably leading to a

Table. 1
As speciation distribution patterns in fresh guano samples.

Guano sample	As(III) (μg g^{-1})	DMA (μg g^{-1})	MMA (μg g^{-1})	As(V) (μg g^{-1})	As$_{total}$ (μg g^{-1})
G-1	0.31	1.12	–	–	1.43
G-2	0.33	1.14	–	–	1.35
G-3	0.30	1.05	–	–	1.22

Note: "–" indicates that the contents in measured samples are below the detection limit according to the method reported by Lou et al. (2014).
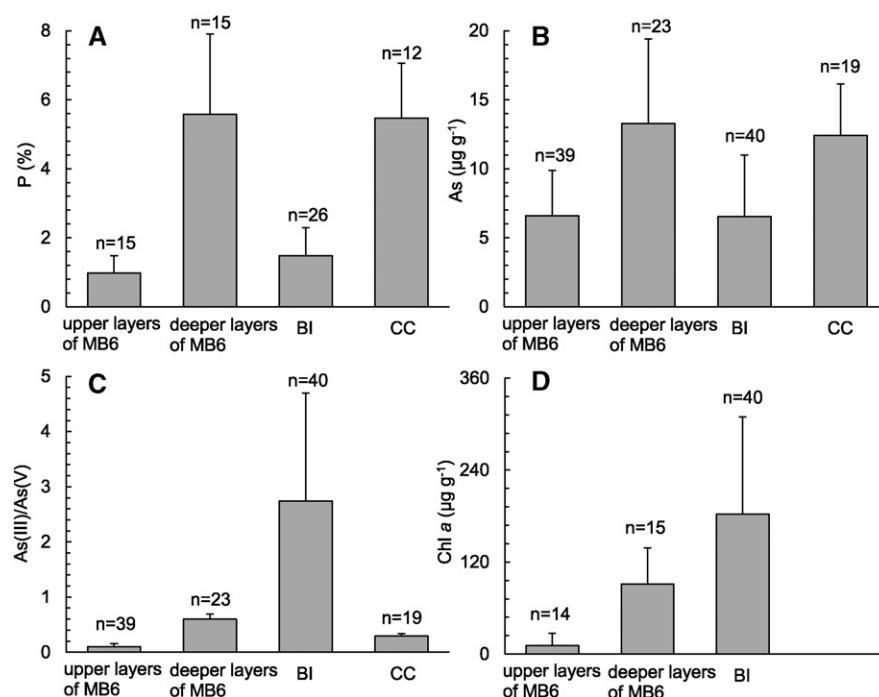
Fig. 3. Total P, total As, As(III)/As(V) and Chl *a* average values in the upper and deeper layers of MB6, BI and CC profiles.

remarkable enrichment of As in guano. This process can be confirmed by the data of As speciation and TOC in modern and ancient guano samples collected from Xisha Islands (see Fig. S3 in the Supporting Information). The DMA in fresh guano gradually transforms into inorganic As in the historical process of diagenesis, and then it is transported by water flow into low-lying pools nearby and accumulated in the sediments. Finally, the sedimentary environment and biogeochemical process may be the main cause leading to an obvious difference of As speciation distribution in the MB6, BI and CC profiles.

3.3. Effects of sedimentary characteristics on As speciation distribution

To our knowledge, the redox potential of soils and sediments play a crucial role in the process of As species transformation (Ma and Rouff, 2012). To assess the influence of sedimentary environment on the distribution patterns of As speciation in the ornithogenic sediments, detailed analysis on the redox conditions of MB6, BI and CC profiles was conducted. OI shows a potential for organically-produced carbon oxide, to a certain degree reflecting the redox nature of sediments (Meyers and Lallier-Vergès, 1999; Jacob et al., 2004). Active iron is extremely sensitive to changes in the sedimentary environment, and $Fe(III)/Fe(II)$ values in sediment samples are good indicators of redox conditions in this environment (Wallmann et al., 1993; Haese et al., 1997). As a result, we compared As(III)/As(V), OI, and $Fe(III)/Fe(II)$ average values in the three profiles of MB6, BI and CC (Fig. 4), and analyzed the effect of the sedimentary environment on the distribution of As species. The results show that OI and $Fe(III)/Fe(II)$ data have a good correspondence. Of these three profiles, on the whole MB6 corresponds to an relatively oxidized environment, and As(III)/As(V) values are also correspondingly at their relatively low level, demonstrating that redox conditions may have an important influence upon the distribution patterns of As speciation in the ornithogenic sediments. BI and CC are similar and correspond to a relatively reduced environment. However, the As(III)/As(V) values in the BI profile are much higher than those in CC. This finding implies that the sedimentary environment is not the unique factor determining the distribution patterns of As species in the ornithogenic sediments. Moreover, Pearson correlation analysis between As(III)/As(V) and OI, $Fe(III)/Fe(II)$ showed no obvious

correlations between As(III)/As(V) and redox conditions in these three profiles (Fig. 5). However, for the MB6 profile, As(III)/As(V) ratios do have significant correlations with redox proxies. These results further indicated that the factors controlling the distributions of As species in
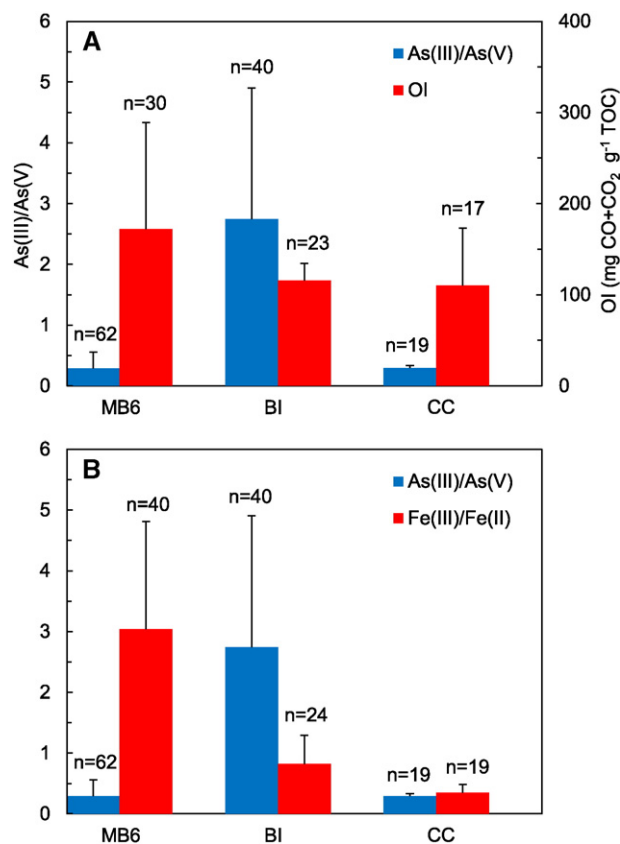

Fig. 4. As(III)/As(V), OI and $Fe(III)/Fe(II)$ average values in the sediment profiles of MB6, BI and CC.

these three profiles may be different. As demonstrated by the high Fe(III)/Fe(II) values, the MB6 profile has a relatively strong oxidized environment, and so the redox condition may be an important factor controlling the distribution of As speciation in this profile. Nevertheless, for the CC profile, although its sedimentary environment was relatively reduced, this seemed not enough to cause a significant effect on As species transformation from As(V) to As(III), since the profiles of MB6 and CC had similar As(III)/As(V) values. Regarding BI, the influencing factors of As speciation are more complex, and we speculate the algae abundance may also play an important role in the As species distribution.

In aquatic ecosystems, the metabolic process of phytoplankton may have some influence on the distribution pattern and transformation process of As speciation (Rahman and Hasegawa, 2012). Our previous research indicated that the organic matter in the MB6 and BI profiles mainly originated from externally-sourced guano and endogenous algae, while the CC profile did not contain algae, and guano was the main source of organic matter (Chen et al., 2013; Liu et al., 2013). The detailed discussion of organic matter composition in the studied ornithogenic sediments can be found in the Supporting Information. To assess the influence of algae growth on the distribution patterns of As speciation, correlation analysis of As speciation and algae productivity in the MB6 and BI profiles were performed (Fig. 6). The results show that As(III) concentrations in the both profiles have significant positive correlations with Chl a contents, and also As(III)/As(V) and C/N are positively correlated, with the exception of the abnormally high As values in the deeper layers of BI. These results indicate that the distribution patterns of As speciation in the ornithogenic sediments may be related to algae abundance. Furthermore, we conducted a comparative analysis of averaging As(III)/As(V) and Chl a content in the profiles of BI and MB6 (Fig. 3, C and D). Of these two profiles, the average values of As(III)/As(V) in BI are markedly higher than those in the sediment samples from the deeper layers of MB6 (T-test, p < 0.01), and the sediments in the upper layers of MB6 render the lowest values. The consistent trends of Chl a content and As(III)/As(V) value support the finding that algae growth may also have an impact upon the distribution patterns of As speciation in the ornithogenic sediments. Thus, for the studied ornithogenic profiles, we suggest that the distribution patterns of As speciation are likely subject to the comprehensive impacts of sedimentary characteristics including redox conditions and algal abundance.

It is still unclear how algae impact the As species in the ornithogenic sediments. Here we only propose a hypothesis to explain this finding based on some reported results. Because As(V) has a similar chemical structure to phosphate, and the metabolic process of algae absorbs great quantities of phosphate in the water, it may also mistakenly absorb some As(V). Once As(V) has entered a cell, it may then trigger a series of biological responses as follows: As(V) → As(III) → MMA → DMA (Rahman and Hasegawa, 2012; Rahman et al., 2012). Of these biotransformation processes, the redox step of As(V) → As(III) performs rapidly, whereas the later methylation step is relatively slow (Hellweger et al., 2003; Hellweger, 2005). Seabirds introduce a large quantity of nutrients (P, N) into low-lying pools around their habitats, creating a nutritionally-rich aquatic environment (Chen et al., 2013). Along with nutrients entering seabird habitats, the guano chemically degrades and discharges plenty of As(V), which is then transported by surface water flow into neighboring ponds. According to some published studies on the metabolism of algae in eutrophic lakes (Hellweger and Lall, 2004; Rahman et al., 2012), algae populations experience explosive growth when water is phosphate-rich, and cells absorb substantial quantities of phosphates and As(V). As(V) in cells is quickly reduced to As(III), and due to the later process of methylation being slow, cells trigger a detoxification mechanism to discharge the As(III). Thus, the metabolism of algae may explain the difference of As speciation in the sediment profiles of BI and CC with similar redox conditions. We point out the above explanation is tentative, and more work is needed to confirm this hypothesis in future studies.

4. Conclusions

Total As concentrations exhibit similar trends with total P, TOC and total N in the MB6, BI and CC profiles, and the guano input is considered
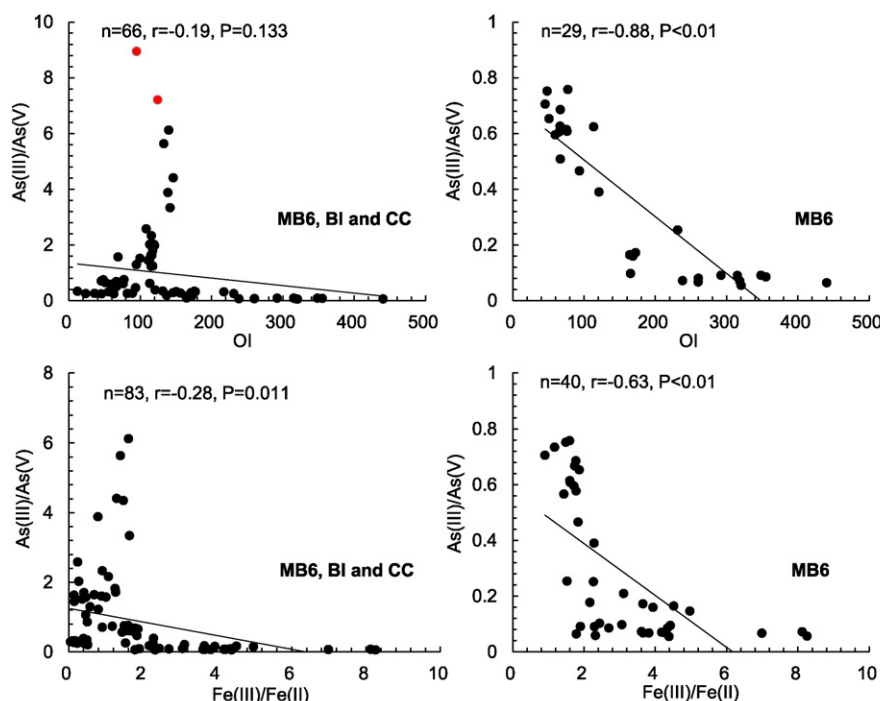
Note: The red dots indicate the sediment samples with abnormally high As concentrations in the deeper layers of BI.

Fig. 5. Correlation analysis between As(III)/As(V) and OI, Fe(III)/Fe(II) in the sediment samples of MB6, BI and CC.
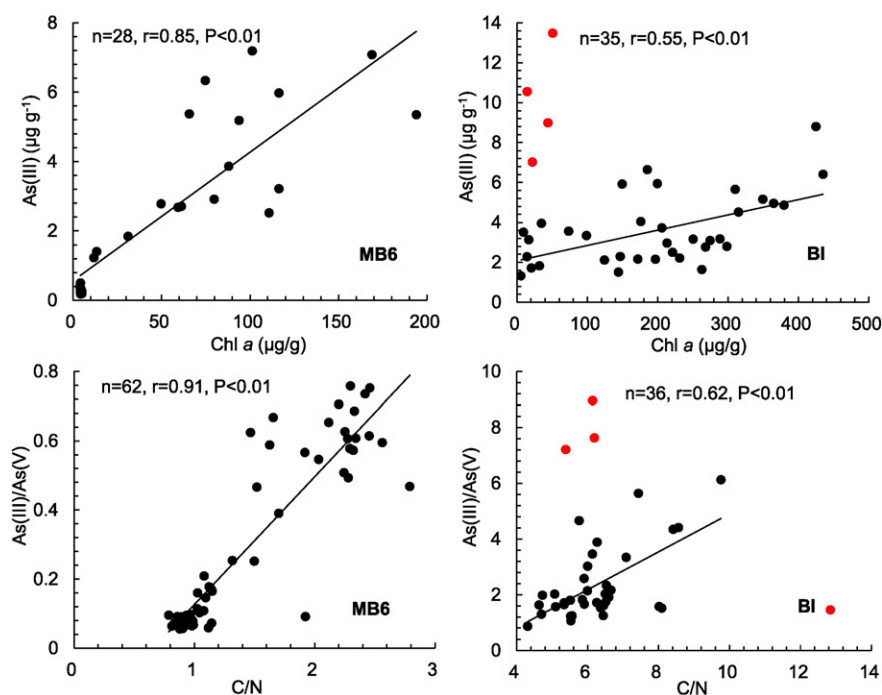
Note: Apart from the abnormally high C/N ratio shown by one red dot, the other red dots indicate abnormally high As concentrations in the samples from the deeper layers of BI.

Fig. 6. Correlation analysis between As(III) and Chl *a*, As(III)/As(V) and C/N ratio in the sediment samples from the MB6 and BI profiles.

to be a major factor controlling the distribution of total As in the ornithogenic sediments. Inorganic As is the predominant species in the ornithogenic sediments. Of such species, As(V) is mainly found in MB6 and CC, whereas As(III) is the predominant species in the BI profile. Average As(III)/As(V) values in each profile demonstrate an unclear relation to total P content, indicating that the distribution patterns of As speciation in the ornithogenic sediments are not determined by guano input. As in fresh guano is principally composed of DMA, and so we suggest that the diagenetic process after guano excretion is the main reason for transformation of organic As in fresh guano to inorganic As in the ornithogenic sediments. OI and active iron results show that the sedimentary environment is one of the important factors controlling As speciation distribution patterns in the ornithogenic sediments. Furthermore, the changes of As(III) and Chl *a* content in the MB6 and BI profiles are in accordance, indicating that the algal growth promoted by large guano nutrient input may also have an effect on the As speciation distribution patterns in the studied sediments.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.02.053.

References

Bissen, M., Frimmel, F.H., 2003. Arsenic — a review. Part I: occurrence, toxicity, speciation, mobility. Acta Hydrochim. Hydrobiol. 31, 9–18.

Blais, J.M., Kimpe, L.E., McMahon, D., Keatley, B.E., Mallory, M.L., Douglas, M.S.V., Smol, J.P., 2005. Arctic seabirds transport marine-derived contaminants. Science 309, 445.

Brimble, S.K., Foster, K.L., Mallory, M.L., Macdonald, R.W., Smol, J.P., Blais, J.M., 2009. High arctic ponds receiving biotransported nutrients from a nearby seabird colony are also subject to potentially toxic loadings of arsenic, cadmium, and zinc. Environ. Toxicol. Chem. 28, 2426–2433.

Chen, Q., Liu, X., Nie, Y., Sun, L., 2013. Using visible reflectance spectroscopy to reconstruct historical changes in chlorophyll a concentration in East Antarctic ponds. Polar Res. 32 (19932). http://dx.doi.org/10.3402/polar.v32i0.19932.

Haese, R.R., Wallmann, K., Dahmke, A., Kretzmann, U., Müller, P.J., Schulz, H.D., 1997. Iron species determination to investigate early diagenetic reactivity in marine sediments. Geochim. Cosmochim. Acta 61, 63–72.

Harvey, C.F., Swartz, C.H., Badruzzaman, A.B.M., Keon-Blute, N., Yu, W., Ali, M.A., Jay, J., Beckie, R., Niedan, V., Brabander, D., Oates, P.M., Ashfaque, K.N., Islam, S., Hemond, H.F., Ahmed, M.F., 2002. Arsenic mobility and groundwater extraction in Bangladesh. Science 298, 1602–1606.

Hellweger, F.L., 2005. Dynamics of arsenic speciation in surface waters: As(III) production by algae. Appl. Organomet. Chem. 19, 727–735.

Hellweger, F.L., Lall, U., 2004. Modeling the effect of algal dynamics on arsenic speciation in Lake Biwa. Environ. Sci. Technol. 38, 6716–6723.

Hellweger, F.L., Farley, K.J., Lall, U., Di Toro, D.M., 2003. Greedy algae reduce arsenate. Limnol. Oceanogr. 48, 2275–2288.

Huang, J.H., Scherr, F., Matzner, E., 2007. Demethylation of dimethylarsinic acid and arsenobetaine in different organic soils. Water Air Soil Pollut. 182, 31–41.

Huang, J.H., Voegelin, A., Pombo, S.A., Lazzaro, A., Zeyer, J., Kretzschmar, R., 2011. Influence of arsenate adsorption to ferrihydrite, goethite, and boehmite on the kinetics of arsenate reduction by Shewanella putrefaciens strain CN-32. Environ. Sci. Technol. 45, 7701–7709.

Huang, T., Sun, L., Wang, Y., Liu, X., Zhu, R., 2009. Penguin population dynamics for the past 8500 years at Gardner Island, Vestfold Hills. Antarct. Sci. 21, 571–578.

Jacob, J., Disnar, J.R., Boussafir, M., Sifeddine, A., Turcq, B., Spadano Albuquerque, A.L., 2004. Major environmental changes recorded by lacustrine sedimentary organic matter since the last glacial maximum near the equator (Lagoa do Caçó, NE Brazil). Palaeogeogr. Palaeoclimatol. Palaeoecol. 205, 183–197.

Jain, C.K., Ali, I., 2000. Arsenic: occurrence, toxicity and speciation techniques. Water Res. 34, 4304–4312.

Liu, X., Nie, Y., Sun, L., Emslie, S.D., 2013. Eco-environmental implications of elemental and carbon isotope distributions in ornithogenic sediments from the Ross Sea region, Antarctica. Geochim. Cosmochim. Acta 117, 99–114.

Liu, X.D., Zhao, S.P., Sun, L.G., Luo, H.H., Yin, X.B., Xie, Z.Q., Wang, Y.H., Liu, K.X., Wu, X.H., Ding, X.F., Fu, D.P., 2006. Geochemical evidence for the variation of historical seabird population on Dongdao Island of the South China Sea. J. Paleolimnol. 36, 259–279.

Lou, C., Liu, W., Liu, X., 2014. Quantitative analysis of arsenic speciation in guano and ornithogenic sediments using microwave-assisted extraction followed by high performance liquid chromatography coupled to hydride generation atomic fluorescence spectrometry. J. Chromatogr. B 969, 29–34.

Lou, C., Liu, X., Nie, Y., Emslie, S.D., 2015. Fractionation distribution and preliminary ecological risk assessment of As, Hg and Cd in ornithogenic sediments from the Ross Sea region, East Antarctica. Sci. Total Environ. 538, 644–653.

Ma, N., Rouff, A.A., 2012. Influence of pH and oxidation state on the interaction of arsenic with struvite during mineral formation. Environ. Sci. Technol. 46, 8791–8798.

Mandal, B.K., Suzuki, K.T., 2002. Arsenic round the world: a review. Talanta 58, 201–235.

Meyers, P.A., Lallier-Vergès, E., 1999. Lacustrine sedimentary organic matter records of Late Quaternary paleoclimates. J. Paleolimnol. 21, 345–372.

Michelutti, N., Blais, J.M., Mallory, M.L., Brash, J., Thienpont, J., Kimpe, L.E., Douglas, M.S.V., Smol, J.P., 2010. Trophic position influences the efficacy of seabirds as metal biovectors. Proc. Natl. Acad. Sci. 107, 10543–10548.

Nie, Y., Liu, X., Sun, L., Emslie, S.D., 2012. Effect of penguin and seal excrement on mercury distribution in sediments from the Ross Sea region, East Antarctica. Sci. Total Environ. 433, 132–140.

Nie, Y., Sun, L., Liu, X., Emslie, S.D., 2015. From warm to cold: migration of Adélie penguins within Cape Bird, Ross Island. Sci. Report. 5, 11530.

Polizzotto, M.L., Kocar, B.D., Benner, S.G., Sampson, M., Fendorf, S., 2008. Near-surface wetland sediments as a source of arsenic release to ground water in Asia. Nature 454, 505–508.

Rahman, M.A., Hasegawa, H., 2012. Arsenic in freshwater systems: influence of eutrophication on occurrence, distribution, speciation, and bioaccumulation. Appl. Geochem. 27, 304–314.

Rahman, M.A., Hasegawa, H., Lim, R.P., 2012. Bioaccumulation, biotransformation and trophic transfer of arsenic in the aquatic food chain. Environ. Res. 116, 118–135.

Saalfield, S.L., Bostick, B.C., 2009. Changes in iron, sulfur, and arsenic speciation associated with bacterial sulfate reduction in ferrihydrite-rich systems. Environ. Sci. Technol. 43, 8787–8793.

Sanei, H., Goodarzi, F., 2006. Relationship between organic matter and mercury in recent lake sediment: the physical–geochemical aspects. Appl. Geochem. 21, 1900–1912.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517–568.

Smith, A.H., Lopipero, P.A., Bates, M.N., Steinmaus, C.M., 2002. Arsenic epidemiology and drinking water standards. Science 296, 2145–2146.

Sun, L., Xie, Z., Zhao, J., 2000. Palaeoecology: A 3,000-year record of penguin populations. Nature 407, 858.

Wallmann, K., Hennies, K., König, I., Petersen, W., Knauth, H.D., 1993. New procedure for determining reactive Fe (III) and Fe (II) minerals in sediments. Limnol. Oceanogr. 38, 1803–1812.

Wenzel, W.W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., Adriano, D.C., 2001. Arsenic fractionation in soils using an improved sequential extraction procedure. Anal. Chim. Acta 436, 309–323.

Xie, Z., Sun, L., 2008. A 1,800-year record of arsenic concentration in the penguin dropping sediment, Antarctic. Environ. Geol. 55, 1055–1059.

Xu, L.Q., Liu, X.D., Sun, L.G., Yan, H., Liu, Y., Luo, Y.H., Huang, J., 2011. Geochemical evidence for the development of coral island ecosystem in the Xisha Archipelago of South China Sea from four ornithogenic sediment profiles. Chem. Geol. 286, 135–145.

Yoshinaga, M., Cai, Y., Rosen, B.P., 2011. Demethylation of methylarsonic acid by a microbial community. Environ. Microbiol. 13, 1205–1215.

Zheng, W., Xie, Z., Bergquist, B.A., 2015. Mercury stable isotopes in ornithogenic deposits as tracers of historical cycling of mercury in Ross Sea, Antarctica. Environ. Sci. Technol. 49, 7623–7632.