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

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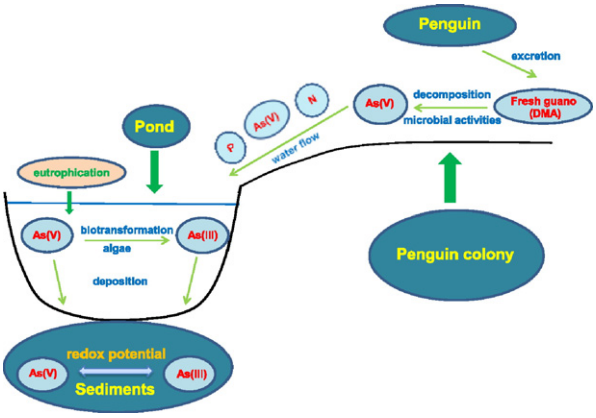
## HIGHLIGHTS

- 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

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## 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.



## 1. Introduction

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

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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 ($MgNH_4PO_4 \cdot 6H_2O$), 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 in-depth 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 $L^{-1}$ $H_3PO_4$ 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 $L^{-1}$ $H_3PO_4$. 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 $L^{-1}$ $(NH_4)_2HPO_4$ 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