

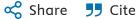
# Palaeogeography, Palaeoclimatology, Palaeoecology

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# Ornithogenic sedimentary profiles of *n*alkanes and PAHs constrain breeding penguin population dynamics at Cape Bird, Ross Island, Antarctica, over the past 1,500 years

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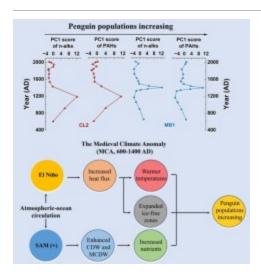
# Highlights

- *n*-Alkanes and PAHs can function as proxy indicators for historical penguin guano input.
- PC 1 scores for *n*-alkanes and PAHs correlate with guano input intensity metrics and bioelements.
- Penguin population significantly increase in mid Cape Bird during the Medieval Climate Anomaly.
- Atmospheric-ocean circulation influences penguin population dynamics.

#### Abstract

Ornithogenic sediment may contain important paleoecological information concerning past bird population dynamics. In this paper, we analyse the distribution of n-alkanes and polycyclic aromatic hydrocarbons (PAHs) in two sedimentary profiles collected from abandoned penguin colonies at Cape Bird, Ross Island, Antarctica. The geochronology of the sediment profiles was determined using <sup>210</sup>Pb and AMS <sup>14</sup>C dating techniques, and spans the past 1500 years. We observe low levels of n-alkanes (0.93–2.67  $\mu$ gg<sup>-1</sup>) and PAHs (20.5–  $46.8 \,\mathrm{ngg^{-1}}$ ) concentrations dominated by short-chain n-alkanes, low-molecular-weight and alkyl PAHs. Principal Component Analysis (PCA) shows that the PC 1 scores for *n*-alkanes and PAHs are significantly correlated with the input intensity of penguin guano and penguin bioelements. Using these proxies in combination with Generalized Additive Model (GAM), we reveal that breeding penguin population growth reaches a historical peak during the Medieval Climate Anomaly (MCA) prior to 1550CE. This growth in population size corresponds to the extent of sea ice cover and the activity of the local atmospheric-ocean circulation. Warming induced by El Niño and the positive phase of the Southern Annular Mode, along with the expansion of ice-free zones and increased oceanic nutrient and food availability, are considered primary factors contributing to the growth of breeding penguin populations. Additionally, variations in sea ice extent and Amundsen Sea Low significantly influence penguin population dynamics. Our study suggests that *n*-alkanes and PAHs may be valuable organic proxies for reconstructing historical changes in breeding penguin populations, with the local sea ice extent and atmospheric-oceanic circulation exerting a major influence on Antarctic penguin population dynamics.

#### Graphical abstract



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#### Introduction

*n*-Alkanes are saturated straight-chain aliphatic hydrocarbons with a variable number of carbon atoms. They exhibit high environmental durability owing to the absence of reactive functional groups in their structures (Li et al., 2020). In marine environments, *n*-alkanes are the primary components of biological hydrocarbons and are, commonly found in organisms such as algae, bacteria, fungi, and macrophytes (Ficken et al., 2000). As common organic bio-indicators in the Antarctic, *n*-alkanes are crucial for distinguishing between natural and anthropogenic inputs (Martins et al., 2021; Chatterjee et al., 2023; Van Overmeiren et al., 2024). Polycyclic aromatic hydrocarbons (PAHs) are semi-volatile compounds with two or more aromatic rings in linear, angular, or clustered configurations (Xia et al., 2024a, Xia et al., 2024b). They are highly toxic pollutants of global concern and fall within the purview of international regulations, such as the European Convention on Long-Range Transboundary Air Pollution (EU, 2004). PAHs infiltrate the biogeosphere from biogenic or anthropogenic sources and have been consistently detected throughout Antarctica (Palmer et al., 2022; Iriarte et al., 2023; Van Overmeiren et al., 2024). Despite extensive research on the presence, transport, and sources of *n*-alkanes and PAHs in pristine and remote parts of Antarctica, their temporal trends and variation with environmental and ecological factors, remain largely unknown.

Diligent efforts have focused on retrieving natural archives to reconstruct the chronology of n-alkanes and PAHs in response to anthropogenic activities. Sedimentary n-alkanes are used as organic bio-indicators, recognising historical changes in inputs and sources, to reconstruct short- or long-term changes in the marine environment (Martins et al., 2021). Sedimentary PAHs, which act as indicators of pyrogenic activities, are commonly analyzed in areas near industrial hubs or with high population densities to gauge the impact of anthropogenic activities on the fate of PAHs (Arp et al., 2015). Investigations into the transport pathways and environmental changes during which PAHs are subject to bio-and/or photo-degradation contribute to unravelling the biogeochemical cycle of PAHs (Da et al., 2019; Love et al., 2021; Fan et al., 2023). Additionally, sedimentary PAHs convey the signatures of burning vegetation, enabling their use as proxies for the occurrence and types of ancient wildfires across diverse spatial and temporal scales (Wang et al., 2017; Zrkrzewski and Kosakowski, 2021; Vachula et al., 2022).

Ornithogenic soil, a by-product of seabird excrement at nesting sites, acts as a signal of penguin activity in ornithogenic sediments. It has been extensively utilised to reconstruct

the ecological history of penguins in Antarctica (Nie et al., 2012, Nie et al., 2014, Nie et al., 2015, Nie et al., 2022; Hu et al., 2013; Liu et al., 2013; Zheng et al., 2022; Yang et al., 2018a). Emphasis has been placed on revealing historical changes in penguin populations and plant communities by leveraging proxies such as biological elements, organic markers, and isotopes of C and Hg. For instance, Liu et al. (2013) demonstrated that the organic matter and nutrients in ornithogenic sediment profiles predominantly originated from penguin guano inputs and established a profile of guano-derived elements, such as P, S, Cu, Zn, F, As, Se, and Hg. Hu et al. (2013) evaluated organic biomarkers (cholesterol and cholestanol) in an ornithogenic sediment profile to reconstruct penguin occupation history, indicating increased penguin populations in different regions of Antarctica during both the warmer Medieval Climate Anomaly (MCA, 600–1400CE) and the colder Little Ice Age (LIA, 1500– 1850CE). Zheng et al. (2015) indicated the dominant sources of methylmercury originating from in situ Hg methylation for marine biota based on Hg stable isotope compositions (e.g.,  $\delta^{202}$ Hg and  $\Delta^{199}$ Hg/ $\Delta^{201}$ Hg) in an ornithogenic soil profile. Recently, Zheng et al., 2022, Zheng et al., 2023 successfully reconstructed historical penguin population changes using a generalized additive model (GAM) combining multiple proxies, and attributed the surge in penguin population to atmosphere-ocean circulation patterns.

Given the simplicity of Antarctic ecosystems, previous palaeoecological records have renewed our interest in establishing connections between n-alkane, PAHs, and breeding penguin population dynamics. This study investigated n-alkanes and PAHs in two sedimentary cores from abandoned penguin colonies in mid Cape Bird, Ross Island, Antarctica. Our objectives were to (1) explore the distribution, sources, and historical trends of n-alkanes and PAHs; (2) analyse the feasibility of using n-alkanes and PAHs as indicators of penguin guano inputs to reconstruct the historical dynamics of breeding penguin populations; (3) assess the relationship between Antarctic atmospheric–oceanic circulation patterns and changes in penguin populations, and (4) determine the mechanisms driving the ecological and climatic changes that influenced penguin populations.

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# Section snippets

# Site description and sampling

Ross Island, a volcanic formation with a total land area of  $2460\,\mathrm{km^2}$ , is intricately linked to Victoria Land in eastern Antarctica through the Ross Ice Shelf in the McMurdo Sound, as shown in Fig. 1a and b. This island, which has an annual average temperature of  $-18\,^\circ$ C, is predominantly enveloped by ice, with three principal ice-free zones: Cape Crozier ( $\sim 18\,\mathrm{km^2}$ ), Cape Royds ( $\sim 13\,\mathrm{km^2}$ ), and Cape Bird ( $\sim 15\,\mathrm{km^2}$ ). These ice-free zones have witnessed a remarkable congregation and proliferation of...

#### Organic matter provenance

Organic geochemical indicators, such as TOC, TN, and  $\delta^{13}$ C (Table S3 and S4), are commonly used for discerning the origin of organic matters (Jin et al., 2021; Liu et al., 2013; Nie et al., 2014). Previous research has shown that bedrock weathering products, penguin guano, and freshwater algae are the primary constitutes of sediments in the Ross Sea region (Nie et al., 2014). Notably, penguin guano and algae exhibit elevated TOC values, in contrast to bedrock differentiation products, which...

#### **Conclusions**

This study discusses the profiles of n-alkanes and PAHs within depositional environments. The n-alkanes and PAHs primarily originated from penguin guano inputs as well as from natural contributions such as local algae and aquatic plants. The distributions of n-alkanes and PAHs correlated significantly with indicators of penguin guano input intensity and biological elements, which underscores the potential of using n-alkanes and PAHs as organic proxies to analyse historical variations in...

# CRediT authorship contribution statement

**Zhixiang Liu:** Methodology, Investigation. **Yaguang Nie:** Writing – original draft, Resources, Conceptualization. **Ruwei Wang:** Writing – review & editing, Supervision, Conceptualization. **Qing Huang:** Methodology, Investigation. **Hong Yan:** Writing – review & editing, Methodology. **Ming Hung Wong:** Writing – review & editing....

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper....

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