



## Palaeobiodiversity research based on stable isotopes: Correction of the sea spray effect on bone carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ by Gaussian Mixture Model clustering



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### ABSTRACT

Transport of sea spray aerosol in coastal areas (“sea spray” effect) can have a marked influence on isotopic ratios of terrestrial ecosystems shifting terrestrial isotopic ratios towards unusual high values masking the original terrestrial signature. It is unclear so far if and to what extend sea spray influences other stable isotopes besides sulphur. In this study, we examined if the effect was also detectable in carbon, nitrogen, and oxygen stable isotopes of bone collagen and carbonate, respectively.

Multi-isotope data of mammals sampled from the Viking Haithabu and medieval Schleswig sites in Northern Germany were analysed according to a previously developed approximation procedure and Gaussian Mixture Model (GMM) clustering in order to quantify the sea spray effect in the isotopes under study.

While we were able to approximate an influence of the sea spray effect of at least 32.8% and 62.8% in  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$ , respectively, it was not possible to validate or approximate this effect in  $\delta^{13}\text{C}_{\text{coll}}$  and  $\delta^{15}\text{N}_{\text{coll}}$ . Indeed, detection of the sea spray effect not only in  $\delta^{34}\text{S}_{\text{coll}}$ , but also in  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  is of particular importance for studies on both prehistoric and recent material.

GMM clustering on terrestrial herbivorous and marine piscivorous mammals was used to confirm the existing influence and to validate the approximated correction for the sea spray effect in the respective isotopic ratios ( $\delta^{13}\text{C}_{\text{carb}}$ ,  $\delta^{18}\text{O}_{\text{carb}}$ ,  $\delta^{34}\text{S}_{\text{coll}}$ ) and the correction for the limnic influence on  $\delta^{15}\text{N}_{\text{coll}}$  approximated in a previous study. After correction, the clustering results markedly changed corresponding to the actual diet and habitat preference of the examined species. Although our study focused on palaeoecology, we suggest that GMM clustering also constitutes a very useful tool for modern landscape ecology based on stable isotope analyses.

### 1. Introduction

Palaeobiodiversity research, particularly the reconstruction of changes in the spatial distribution and abundance of vertebrate species, benefits substantially from stable isotope analyses of archaeological vertebrate bone finds. This archaeometric approach constitutes a useful tool for the assessment of important aspects of palaeobiodiversity such as feeding and habitat preference of taxa, and migration and import of vertebrate species.

Interpretation of stable isotopic signals in archaeological bones is particularly complex in brackish water environments because they offer a diversity of ecological niches characterised by a mixture of different salinity levels, from freshwater to marine, in the intertidal zone. Moreover, isotopic signatures in vertebrates that roam coastal areas can be markedly influenced by the so called “sea spray” effect. This effect is well documented for stable sulphur isotopes (e. g. Wadleigh et al., 1994), because atmospheric transport of sulphate through sea spray aerosol leads to an enrichment of  $^{34}\text{S}$  in terrestrial systems thereby

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mimicking marine values. As already detected by Wakshal and Nielsen (1982) sulphate is isotopically enriched close to the coast, while it becomes isotopically lighter with increasing distance from the sea. However, the sea spray effect in  $\delta^{34}\text{S}$  can be detected in a coastal corridor of about 100 km (Nehlich, 2015), where individuals can be enriched in  $^{34}\text{S}$  due to the marine sea spray signal. This also depends on the prevailing wind as demonstrated for Ireland by Zazzo et al. (2011). While the sea spray was still detectable about 100 km inland from the west coast, individuals located closer to the east coast (60–70 km) exhibited much lower average  $\delta^{34}\text{S}$  values. This can be explained by the fact that the prevailing wind in the examined site (Ireland) is between south and west (Zazzo et al., 2011).

Plants capture the natural enrichment in  $^{34}\text{S}$  in the sulphate molecules of their cells. Since only a small net fractionation against  $^{34}\text{S}$  occurs during sulphur uptake, sulphated metabolites in plants show quite similar  $\delta^{34}\text{S}$  values compared to substrate sulphur (Monaghan et al., 1999; Tcherkez and Tea, 2013). The only sources of sulphur for animals are diet and drinking water (Schmidt et al., 2015). As herbivores gain 10–40% of their sulphur supply by sulphate relatively enriched in  $^{34}\text{S}$  and another 60 to 90% by organic sulphur relatively  $^{34}\text{S}$ -depleted (Tanz and Schmidt, 2010), we expect a distinct influence of marine sulphate taken up by herbivores as well as in the course of the trophic chain. This is even more probable as the only reaction accompanied by fractionation of sulphur isotopes in animals is the sulphur activation for biosynthesis of sulphate esters (Schmidt et al., 2015).

We have already shown previously that it is possible to approximate the sea spray effect on collagen  $\delta^{34}\text{S}$  by use of appropriate mathematical methods (Göhring et al., 2015). At the Haithabu and Schleswig sites which date from Viking to Medieval times (see below), a local sea spray influence between about 16.5 and 21.9% shifted bone  $\delta^{34}\text{S}_{\text{coll}}$  of terrestrial mammals, terrestrial and freshwater birds, as well as humans towards unusual high values (Göhring et al., 2015). Uncorrected measurement data would therefore lead to biased palaeodietary and habitat reconstructions. Correction of  $\delta^{34}\text{S}_{\text{coll}}$  according to the local sea spray effect leads to much more reliable dietary reconstructions, which are compatible with the actual diet or habitat of the examined taxa (Göhring et al., 2015).

The atomic weight of sulphur considerably exceeds the atomic weights of the elements carbon, nitrogen, and oxygen. It therefore appears rather unlikely that these lighter atoms would not be prone to the sea spray in a similar way. Both Richards et al. (2006) and Virginia and Delwiche (1982), for instance, indeed found some evidence for sea spray effect on  $\delta^{15}\text{N}_{\text{coll}}$  values in animals and plants, respectively, manifested by an enrichment with  $^{15}\text{N}$ . No attempts have been made so far for an approximation of the magnitude of this effect in archaeological remains. Furthermore, to our knowledge, the influence of sea spray on other isotope systems is not yet verified at all. Therefore, the aim of this study was to evaluate if there was a detectable influence of the sea spray on  $\delta^{13}\text{C}_{\text{coll}}$ ,  $\delta^{13}\text{C}_{\text{carb}}$ ,  $\delta^{15}\text{N}_{\text{coll}}$ , and  $\delta^{18}\text{O}_{\text{carb}}$  values, respectively, and, if applicable, to approximate the magnitude of the effect, similar to the approximation procedure of the sea spray effect on  $\delta^{34}\text{S}_{\text{coll}}$  (Göhring et al., 2015). Gaussian Mixture Model (GMM) clustering (see below) was used to detect clusters in the data set as well as to illustrate the isotopic signature of the examined specimens before and after correction.

## 2. Materials and methods

The large isotopic data set of animal bones recovered from the Viking Haithabu (804–1066 CE) and medieval Schleswig (1070–1350 CE) sites in Northern Germany located on the Jutland peninsula (Grupe et al., 2013; Hilberg, 2008) in close proximity to the Baltic Sea (Fig. 1) was used for an examination of the sea spray effect on stable carbon, nitrogen, and oxygen isotope values. A subsample of 111 terrestrial and 27 marine mammals was analysed (Tables S1 and S2). Another smaller subsample ( $n = 33$ ) additionally including  $\delta^{34}\text{S}$  was

used for a demonstration of clustering in the five-dimensional case (Tables S1 and S2). The original isotopic data are published by Doppler et al. (2010) and Göhring et al. (2015).

Both Haithabu and Schleswig were important trading centres at their time. Consequently, a considerable amount of animals excavated at these sites was probably imported (Becker and Grupe, 2012; Doppler et al., 2010; Grupe et al., 2009). The area around Haithabu and Schleswig is particularly influenced by the brackish environment of the Baltic coast. The salinity level of the Baltic Sea increases from the northern part (Bothnian Bay) with 2–5 psu (practical salinity units) to the western part (Arkona Basin) with a salinity between 5 and 10 psu (Emeis et al., 2003; Fig. 1). As dietary reconstructions can be quite complex in the case of a brackish environment and one might also expect at least some influence of sea spray (see above), this data set is well suited for our study. However, the primarily unknown proportion of imported animals exhibiting a non-local isotopic signature has to be kept in mind.

### 2.1. Stable isotope analysis

The laboratory protocols for purification of bone collagen and structural carbonate including the validation of the isotopic signatures was previously published by Doppler et al. (2010). For the analysis of  $\delta^{13}\text{C}_{\text{coll}}$  and  $\delta^{15}\text{N}_{\text{coll}}$  0.3–0.5 mg of the extracted gelatine weighed into tin capsules were combusted in a CHN-analyser (Carlo-Erba 1110) and afterwards analysed by mass spectrometry (Thermo Finnigan Delta Plus; Geo-Center of Northern Bavaria, University of Erlangen, Germany) (Doppler et al., 2010). Stable carbon and nitrogen isotopic ratios were expressed against the VPDB (Vienna Pee Dee Belemnite) and the AIR (atmospheric nitrogen) standard, respectively, provided by the Section of Isotope Hydrology of the International Atomic Energy Agency (IAEA) in Vienna, Austria. Replicate analysis of laboratory standards calibrated to the international standard USGS 40 ( $\delta^{13}\text{C} = -26.3\text{‰} \pm 0.10\text{‰}$ ,  $\delta^{15}\text{N} = -4.52\text{‰} \pm 0.08\text{‰}$ ,  $n = 43$ ; IAEA) was used to test for reproducibility and accuracy of carbon and nitrogen isotope analyses.

For  $\delta^{34}\text{S}_{\text{coll}}$  measurements, extracted gelatine samples were further processed at the Max-Planck-Institute for Evolutionary Anthropology in Leipzig (Germany): After ultrafiltration with a 30 kDa filter in order to remove degraded molecules, salts and other impurities (see Nehlich and Richards, 2009) samples were analysed with a mass spectrometer (Thermo Finnigan Delta V plus) coupled with an elemental analyser (Heka EuroVector) with a measurement precision of  $\pm 0.4\text{‰}$ . Stable sulphur isotope values were expressed against the VCDT (Vienna Cañon-Diablo Troilite; IAEA) standard. Reproducibility of sulphur isotope analyses was monitored by replicate analyses of laboratory standards calibrated to the international standards NBS 127 ( $\delta^{34}\text{S} = +20.30\text{‰} \pm 0.19\text{‰}$ ,  $n = 23$ ; IAEA), IAEA-S1 ( $\delta^{34}\text{S} = -0.43\text{‰} \pm 0.18\text{‰}$ ,  $n = 24$ ), IAEA-S2 ( $\delta^{34}\text{S} = +21.25\text{‰} \pm 0.28\text{‰}$ ,  $n = 24$ ), IAEA-S3 ( $\delta^{34}\text{S} = -30.75\text{‰} \pm 5.22\text{‰}$ ,  $n = 21$ ), IAEA-SO-5 ( $\delta^{34}\text{S} = +0.17\text{‰} \pm 0.24\text{‰}$ ,  $n = 24$ ), Liver 1577b ( $\delta^{34}\text{S} = +7.62\text{‰} \pm 0.16\text{‰}$ ,  $n = 43$ ; Iso-Analytics), as well as a laboratory protein standard ( $\delta^{34}\text{S} = +6.25\text{‰} \pm 0.21\text{‰}$ ,  $n = 72$ ; IVA certified).

The extracted bone apatite was measured using a Gasbench II/Delta plus system (Thermo Finnigan) where the samples react with 100% phosphoric acid at 70 °C for 1 h, coupled to the mass spectrometer (Thermo Finnigan Delta Plus; Geo-Center of Northern Bavaria) with a measurement precision of  $\pm 0.1\text{‰}$  (Doppler et al., 2010). Stable carbon and oxygen isotopic ratios were expressed against the VPDB (Vienna Pee Dee Belemnite; IAEA) standard. The extraction procedure was controlled using laboratory standards, namely NBS 120c ( $\delta^{18}\text{O} = +21.80\text{‰} \pm 0.56\text{‰}$ ,  $n = 14$ ; National Institute of Standards and Technology NIST, Florida, USA) and NIST 1400 ( $\delta^{18}\text{O} = +17.01\text{‰} \pm 0.32\text{‰}$ ,  $n = 8$ ; NIST, Florida, USA). The laboratory standard NBS Erl ( $\delta^{18}\text{O} = +22.55\text{‰} \pm 0.18\text{‰}$ ,  $n = 23$ ; Geo-Center of Northern Bavaria) was used to test for reproducibility and accuracy

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