

onset of human-induced eutrophication in the North Sea and Skagerrak regions. In the following, we will investigate the isotopic enrichment of organic matter in sediment from the Danube-influenced Black Sea shelf to reconstruct nitrogen sources to this region. Specifically, we combine observations on N isotopes and nitrogen content to identify N sources and turnover processes. Briefly, if the $\delta^{15}\text{N}$ value of organic matter changes but the N content remains stable, this can indicate a change in the N source, whereas an increase in $\delta^{15}\text{N}$ and a concomitant decrease in N content is indicative of remineralisation (Möbius, 2013).

The present study aims to identify present and historic nitrogen sources to the Danube-influenced north-western (NW) shelf of the Black Sea by analysing sediment cores along a transect from the Danube Delta towards the shelf break. Similar studies by Fulton et al. (2012) and Cutmore et al. (2025) focussed on sediment from the deep basins and the continental slope of the Black Sea but did not cover the north-western shelf, where major rivers discharge into the Black Sea. Aiming to close this gap, we sampled along a transect from the Danube Delta towards the shelf break. Our samples reflect a gradient from Danube River Plume dominated to Black Sea-dominated water masses, which both imprint the specific signature of their respective nitrogen sources to the sediment record. We analysed the sediment for organic carbon and nitrogen, and the nitrogen stable isotope composition to identify natural and anthropogenic nitrogen sources over the past 6000 years.

2 Material and Methods

2.1 Working area and samples

Sampling was performed in early May 2016 during R/V *Mare Nigrum* cruise MN 148 in the Romanian Shelf area at four stations that span a transect from nearshore to offshore (Table 1, Fig. 1). Water depth at the sampling stations ranged from 22 m (Station 2) to 80 m (Station 6). From each station, sediment cores (20–40 cm length, 6 cm in diameter) were taken with a Multicorer. The sediment cores were immediately sliced in 1 cm intervals and frozen for further analysis. The sediment from stations 4 and 6 was wet sieved through a 400 μm sieve after slicing to collect mussel shells for radiocarbon dating. The < 400 μm fraction was freeze-dried and homogenized for analysis of $\delta^{15}\text{N}$, organic carbon and nitrogen content.

2.2 Analyses of sediment samples

The sediment samples were analysed for total carbon and total nitrogen content with an elemental analyser (Carlo Erba NA 1500) via gas chromatography, calibrated against acetanilide. The total organic carbon content (TOC) was analysed after a threefold removal of inorganic carbon using 1 mol L⁻¹ hydrochloric acid. Sediment carbonate content

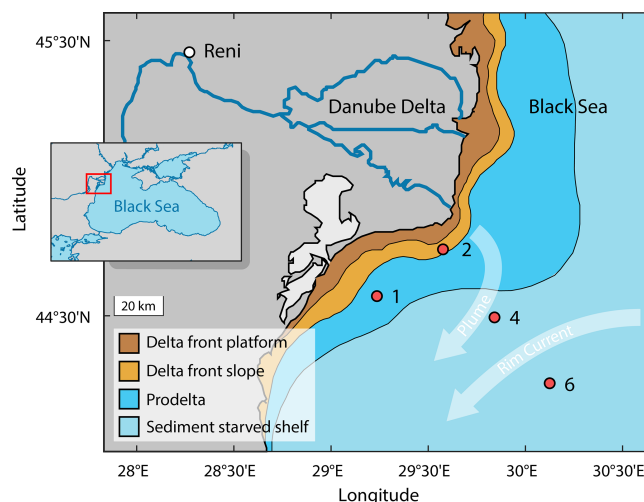


Figure 1. Sampling stations of the sediment cores 1, 2, 4 and 6 in the northwestern Black Sea during R/V *Mare Nigrum* cruise 148 and major depositional units of the Danube Delta (after Panin et al., 2016). Light arrows indicate the general surface water currents of Danube River Plume and Rim Current. Insert: Study area (red rectangle) within the Black Sea region.

Table 1. Summary of metadata of sediment cores from Mare Nigrum cruise 148.

Core	Latitude	Longitude	Water depth (m)	Core length (cm)
	TS1			
1	45°58.4'	29°18.8'	30	42
2	44°74.9'	29°58.2'	22	35
4	44°49.9'	29°84.8'	62	29
6	44°25.2'	30°13.1'	80	27

was then calculated as the difference of total carbon content and TOC content. The standard deviation of sediment samples was less than 0.6 % for TOC and 0.08 % for nitrogen.

Nitrogen isotope analyses were performed with a CE 1108 elemental analyser (ThermoFinnigan) connected to a mass spectrometer (Finnigan 252) via a split interface (Conflow). Two international standards were used for calibration (IAEA-N1: $\delta^{15}\text{N} = 0.4\text{‰}$, IAEA-N2: $\delta^{15}\text{N} = 20.3\text{‰}$), and an additional, internal standard was measured for further quality assurance. The standard deviation for repeated measurements was < 0.2 ‰.

2.3 Radiocarbon Dating

The radiocarbon ages of organic sediment (TOC) were obtained from 2 bulk sediment samples from Station 4, and 6 bulk sediment samples from Station 6. Additionally, 6 bivalve shells from different sediment layers of Station 6 (two samples of *Modiolula phaseolina* and four samples of *Mytilus galloprovincialis*) were analysed to date the carbonate. These two species were used because the top 8 cm