



Sedimentary organic bromine as indicator for marine organic carbon: a proxy for primary productivity in paleo-records

Cecile S. Hilgen¹, Gert-Jan Reichart^{1,2}, Wim Boer², Marcel T. J. van der Meer³, Francesca Sangiorgi¹, Rick Hennekam²

¹Department of Earth Sciences, Utrecht University, 3584 CB Utrecht, The Netherlands

²Department of Ocean Systems, NIOZ Royal Netherlands Institute for Sea Research, 1790 AB, Den Burg, The Netherlands

³Department of Marine Microbiology and Biogeochemistry, NIOZ Royal Netherlands Institute for Sea Research, 1790 AB, Den Burg, The Netherlands

Correspondence to: Cecile S. Hilgen (c.s.hilgen@uu.nl)

Abstract. The efficiency of the ocean as a carbon sink requires estimates for marine primary productivity and for the fraction of this primary productivity that is ultimately buried in the sediment. Partitioning sedimentary total organic carbon (TOC) into marine (OC_{mar}) and terrestrial (OC_{ter}) components is thereby essential for distinguishing the contribution of land-derived organic matter versus locally produced organic matter in a marine setting. Previous studies have proposed sedimentary organic-bound bromine (Br_{org})-to-TOC (Br/OC) ratio as a proxy for OC_{mar} , as marine organic matter is enriched in bromine relative to terrestrial organic matter. Yet, the influence of other environmental and depositional conditions on Br_{org} and thereby its potential as a quantitative tool for unravelling terrestrial versus marine organic matter remain poorly constrained. To address this, we present a multi-regional dataset of Br_{org} in core-top sediments from the Baltic Sea and North Sea to the Atlantic Ocean, Black Sea, and Mediterranean Sea ($n = 55$). We investigate environmental controls on the Br/OC ratio and compare the performance of Br_{org} with traditional marine organic matter indicators such as the carbon isotope composition of bulk organic matter ($\delta^{13}C_{org}$) and the carbon-to-nitrogen (C/N) ratio in capturing OC_{mar} contributions. By better constraining the marine carbon flux, Br_{org} not only distinguishes OC_{mar} but also directly reflects its link to marine net primary productivity (NPP), as sedimentary OC_{mar} is primarily derived from NPP. Across all studied basins, Br_{org} shows a strong positive relationship with TOC ($R^2 = 0.86$). After accounting for preservation effects using bottom-water oxygen concentrations (oxic versus anoxic settings), we show that sedimentary Br_{org} deposited under oxic conditions exhibits the strongest relationship with NPP ($R^2 = 0.65$), compared to TOC ($R^2 = 0.43$), $\delta^{13}C_{org}$ -derived OC_{mar} ($R^2 = 0.38$), and C/N -derived OC_{mar} ($R^2 = 0.26$). This suggests that Br_{org} not only traces OC_{mar} more effectively than traditional proxies but also outperforms them in reconstructing productivity signals. However, this relationship applies mainly to sediments deposited under oxic conditions (North Sea, Atlantic Ocean, and Mediterranean Sea). Under anoxic conditions (Baltic and Black Seas), reduced oxygen exposure may enhance the preservation of labile, Br-rich organic matter, causing these sediments to follow a different Br_{org} -NPP relationship than oxic settings. Finally, we apply this Br_{org} -NPP relationship to a North Sea sedimentary record by calibrating X-ray fluorescence core scanning Br data to Br_{org} using a multivariate log-ratio calibration. As such, this approach allows high-resolution Br_{org} records downcore to be generated and used to trace OC_{mar} and for quantitative past NPP (paleoproductivity) reconstructions.



1. Introduction

Long-term sequestration of organic carbon (OC) in marine sediments is a critical component of the global carbon cycle (Berner, 1982; Burdige, 2007) and changes therein potentially affect climate. To infer long term (marine) OC sequestration, sedimentary proxies are essential to reconstruct past variations in organic matter (OM) sources, marine productivity, and OC degradation. OC sequestration occurs predominantly in river deltas and on (shelf) continental margins, where high sedimentation rates and efficient particle trapping promote OC deposition (Archer et al., 2002; Hedges & Keil, 1995). These dynamic settings may receive substantial carbon inputs from both marine primary production (OC_{mar}) and from terrestrial ecosystems (OC_{ter}), resulting in sedimentary OC of mixed origins. A fundamental challenge is hence to deconvolve marine and terrestrial OC contributions, which differ in composition, provenance, fluxes, and degradation pathways.

Proxies that distinguish OC_{mar} from OC_{ter} should ideally be directly and unambiguously linked to either marine or terrestrial OC fluxes. Typically, approaches used to estimate the relative contributions of OC_{mar} and OC_{ter} rely on stable carbon isotope ratios of bulk OM ($\delta^{13}C_{org}$) and elemental carbon-to-nitrogen (C/N) ratio of this OM (e.g., Malcolm & Price, 1984; Seki et al., 2019). Two-endmember mixing models with a terrestrial (typical terrestrial $\delta^{13}C_{org} = -30$ to -24‰ and $C/N > 12$ for C_3 plants and > 30 for C_4 plants) and marine (typical marine $\delta^{13}C_{org} = -22$ to -18‰ and $C/N = 4$ to 10) endmember are used to calculate relative contributions. These approaches, however, often rely on ambiguous source signatures due to overlapping geochemical values of sources and/or mixed inputs, as demonstrated by their endmember ranges (Fry, 2006; Lamb et al., 2006; Meyers, 1994). Consequently, there is a need for an alternative approach to better, quantitatively, distinguish marine and terrestrial OC sources which preferably does not rely on endmembers.

Sedimentary organic-bound bromine (Br_{org}) has been suggested as a potential tracer for OC_{mar} due to its strong association with marine OM. It is highly enriched in marine organisms, including algae, eukaryotes, seaweeds, and sponges and comparatively depleted in terrestrial biomass (Cortizas et al., 2016; Dembitsky, 2002; Leri et al., 2010, 2019; Leri & Myneni, 2012). Enrichments in bromine (Br) in the marine environment are driven by biogenic bromination, a process where enzymes (e.g., bromoperoxidase) oxidize bromide (Br^-) from seawater using hydrogen peroxide (H_2O_2), producing reactive Br species that can be incorporated into OM (Butler and Carter-Franklin, 2004; Gribble, 2000, 2003; Van Pée & Unversucht, 2003), and abiotic oxidative processes, in which photochemically generated reactive Br species (e.g., $HOBr$, Br_2 and Br radicals) react with OM and promote OM bromination in seawater (Tamtam and Chiron, 2012; Leri et al., 2014; Méndez-Díaz et al., 2014). These processes and the relatively high seawater Br^- concentrations render Br_{org} a potential proxy for OC_{mar} provided that the mechanisms involved and the different environmental factors that impact Br_{org} formation are well constrained and Br_{org} can be measured reliably.

The mechanisms underlying OM bromination itself are recognized, but the environmental controls on OM bromination in seawater remain poorly constrained. While factors such as light, temperature, salinity, Br^- and H_2O_2 concentrations, pH, redox conditions, and OM composition may all modulate the production of (volatile) short-lived brominated compounds (Abrahamsson et al., 2003; Hill & Manley, 2009; Joe-Wong et al., 2019; Liu et al., 2015), the effects of environmental variables



on sedimentary Br_{org} are not known. To unravel which environmental factors (e.g., primary productivity, nutrients, salinity) control Br_{org} and thereby its use as OC_{mar} proxy, core-top calibration studies provide an opportunity to link modern environmental conditions with the integrated bromination signal preserved in surface sediments.

Previous core-top studies have repeatedly shown strong correlations between Br_{org} and total organic carbon (TOC) on a regional scale within individual marine basins (Malcolm & Price, 1984; Pedersen & Price, 1980; Price & Calvert, 1978; Price et al., 1970). These results led to the proposal of the Br_{org} -to-TOC (Br/OC) ratio as indicator to distinguish OC source using an endmember model for Br/OC , where marine Br/OC is 7.7 mg g^{-1} and terrestrial Br/OC is 0.43 mg g^{-1} (Mayer et al., 1981; 2007), with even lower terrestrial endmember values (0.13 mg g^{-1}) reported by Zheng et al. (2026). However, broader applicability of Br_{org} and Br/OC ratio as an indicator of OC_{mar} remains unresolved. A systematic evaluation across environmental gradients is therefore needed, using surface sediments directly linked to modern environmental conditions.

Here we address this knowledge gap using a multi-regional core-top dataset covering a wide range of environmental conditions (i.e., salinity, temperature, marine primary productivity, nutrient concentrations, and redox conditions). We measure Br_{org} in 55 surface sediments from 5 marine basins: Baltic Sea, North Sea, Atlantic Ocean, Black Sea, and Mediterranean Sea (Fig. 1). Br determination remains challenging due to its high volatility, which can lead to substantial losses during oxidative digestion of OM at high temperatures (He et al., 2018; Mesko et al., 2016). We therefore test four oxidative digestion of OM methods (i.e., H_2O_2 with 20°C , 50°C , 80°C , and using ultraviolet light) to identify the most accurate method to determine Br in certified reference materials (RMs) by inductively coupled plasma mass spectrometry (ICP-MS). We then use this method on the core-top dataset to identify environmental controls (e.g., sea surface salinity, water depth, and bottom-water oxygen concentrations) on Br enrichment using the Br/OC ratio (Sect. 3.1) and evaluate the association between Br_{org} and sedimentary OC (Sect. 3.2). We further evaluate the performance of Br_{org} relative to traditional proxies (i.e., TOC, $\delta^{13}\text{C}_{\text{org}}$, and C/N ratio) in capturing OC_{mar} contributions and compare the relationships between these proxies and marine net primary productivity (NPP) (Sect. 3.3). Because preservation may influence Br_{org} independently of productivity, we also evaluate whether enhanced preservation of Br-rich labile marine OM can offset the Br_{org} -NPP relationship using bottom-water oxygen levels.

In paleoceanography, continuous high-resolution records of Br from sediment cores are mostly measured by X-ray fluorescence (XRF) core scanning. Br, often normalized to Ti as Br/Ti or to Cl as Br/Cl , has been used as a proxy for OC_{mar} and/or marine productivity (e.g., Agnihotri et al., 2008; Bokhari-Friberg et al., 2025; Caley et al., 2011; Cartapanis et al., 2011; McHugh et al., 2008; Ren et al., 2009; Seki et al., 2019; Thomson et al., 2006; Ziegler et al., 2010). Here, we test approaches to correct XRF-derived Br for pore-water Br and to effectively calibrate XRF core scanner Br data against independently measured Br_{org} using the core-top dataset and a sedimentary record from the Norwegian Trench. This allows us to evaluate the potential of XRF-derived Br_{org} for quantitative paleoproductivity reconstructions (Sect. 3.4).

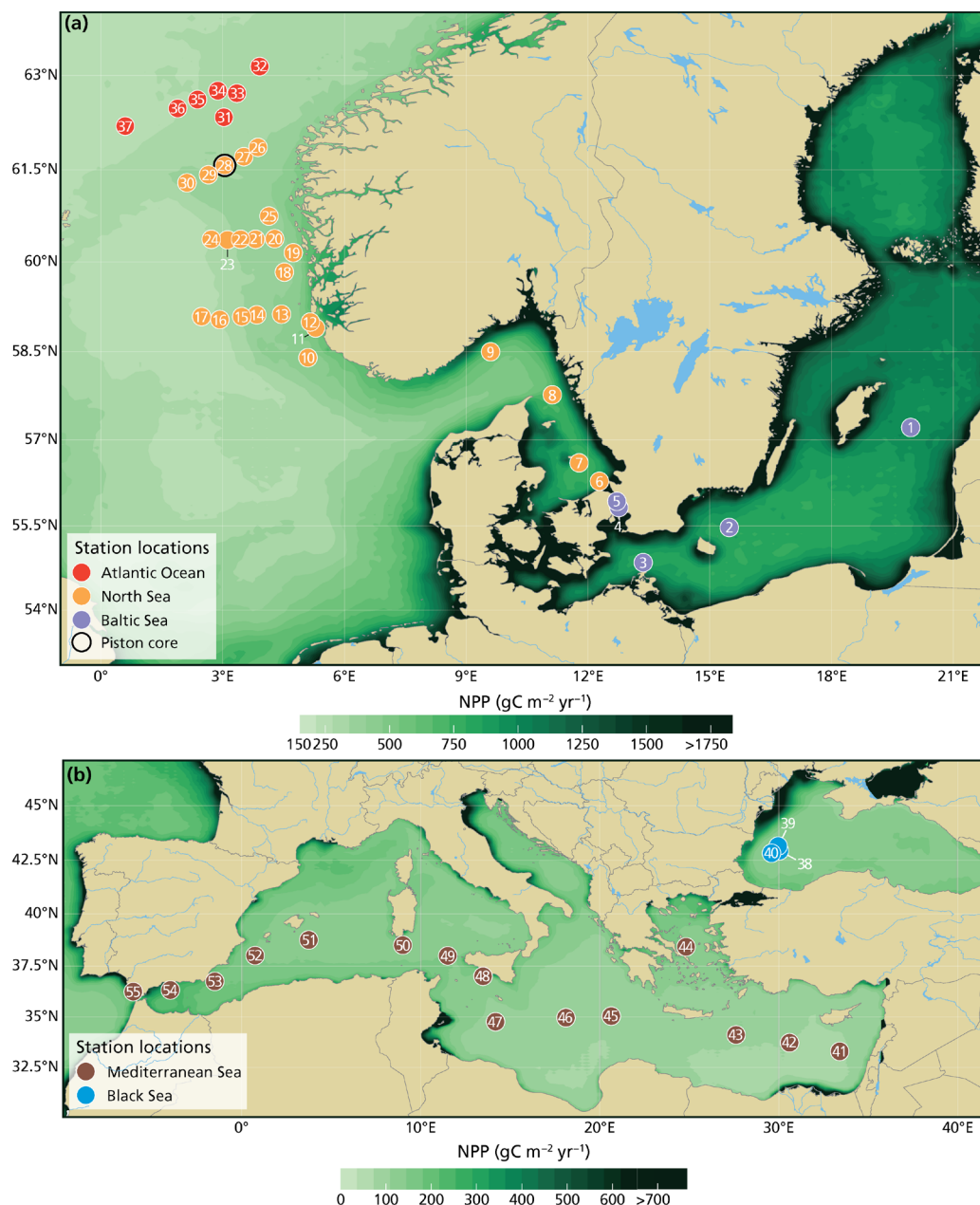


Figure 1: Maps showing net primary productivity (NPP) based on annual mean surface chlorophyll-a concentrations for the period 2003-2023 (Behrenfeld & Falkowski, 1997; Silsbe et al., 2016) and the station locations of the 55 retrieved core-top samples (<https://www.naturalearthdata.com/>, last access: 8 February 2026, scale: 1:10m). Note that color scale of NPP differs per panel and the colors of the station locations are assigned based on their geographic region. See detailed information per location in Table S1. a: Baltic Sea-North Sea-Atlantic Ocean transect. b: Black Sea and Mediterranean Sea.



2. Material and Methods

2.1 Study area

100 We focus on five oceanographic regions: the Baltic Sea, North Sea, Atlantic Ocean, Black Sea, and Mediterranean Sea. Sampling transects include contrasting productivity regimes (Fig. 1), ranging from high productivity of the eutrophic, river-influenced Kattegat and Baltic Sea (Rydberg et al., 2006; Voss et al., 2011) to the low productivity of the warm and oligotrophic Mediterranean Sea (Poulos, 2020). Simultaneously, a pronounced salinity gradient is captured (Raegan et al., 2024), spanning from the brackish Baltic Sea and Black Sea to the highly saline evaporation-driven Mediterranean Sea, with sampling sites
105 ranging from coastal areas receiving significant terrestrial carbon to offshore environments where this contribution is small. Moreover, the selected stations encompass a full range of bottom-water redox conditions, including fully oxygenated waters in the North Sea, Atlantic Ocean, and Mediterranean Sea, seasonally hypoxic conditions in the stratified Baltic Sea (Bergman Sjöstrand et al., 2025), and permanently anoxic and sulfidic (euxinic) waters in the Black Sea (Codispoti et al., 1991).

2.2 Sample collection

110 In total, 55 surface sediment samples were collected from core-tops in the Baltic Sea (n = 5), North Sea (n = 25), Atlantic Ocean (n = 7), Black Sea (n = 3), and Mediterranean Sea (n = 15) (Table S1; Fig. 1). Sampling sites coverage ensured representation of marginal seas, temperate shelves, and open ocean environments. Surface sediments were collected using multi-, box-, and trip-corers to retrieve undisturbed surface layers (0-0.5 cm or 0-1 cm), which were subsequently freeze-dried and homogenized for analysis. To ensure age control, we sampled the sediment-water interface and for samples from the North
115 Sea and Atlantic Ocean, recent deposition was confirmed by ^{234}Th and ^{210}Pb core-top analyses (Hilgen et al., 2026a).

A piston core 110PC (719 cm in length 61°32.2'N, 2°55.6'E at 293 m water depth) was taken at station 28 during the 64PE517 cruise with R/V *Pelagia* to the Norwegian Trench, offshore Norway (Fig. 1a). The sediment collected mainly consisted of clay. In total, 11 downcore samples were selected from the piston core. Water content ((wet weight – dry weight)/wet weight * 100) was determined at 2–12 cm intervals (average = 9 cm), and values between measured depths were
120 interpolated.

2.3 Water-column properties

Environmental properties describe surface water and bottom water conditions and include sea surface temperature (SST; °C), sea surface salinity (SSS; unitless), sea surface inorganic nutrients (nitrate, phosphate, and silicate; $\mu\text{mol kg}^{-1}$), sea surface oxygen (O_2 ; $\mu\text{mol kg}^{-1}$), net primary productivity (NPP; $\text{gC m}^{-2} \text{year}^{-1}$), water depth, and bottom-water oxygen (BWO; $\mu\text{mol kg}^{-1}$). Water depth was determined during sediment collection on board a single beam echo sounder. All other variables were
125 extracted as annual means and spatially averaged within a 50 km radius of each station.

NPP was derived from the Vertically Generalized Production Model (VGPM; Behrenfeld & Falkowski, 1997) using chlorophyll-a data from MODIS-Aqua.R1.1



(<https://orca.science.oregonstate.edu/1080.by.2160.monthly.hdf.vgpm.m.chl.m.sst.php>, last access: 10 January 2026) with a
0.1° spatial resolution for the period 2003 to 2023. As the Black Sea is not covered by the VGPM product, NPP data from the
Carbon, Absorption, and Fluorescence Euphotic-resolving (CAFE; Silsbe et al., 2016) model
(<https://orca.science.oregonstate.edu/1080.by.2160.monthly.hdf.cafe.m.php#monthly>, last access: 26 January 2026) was
adjusted to be comparable with VGPM estimates using an empirically derived exponential regression based on the station data.

SST, SSS, nutrients, O₂, and BWO were derived from the World Ocean Atlas 2023 (Reagan et al., 2024). Surface ocean
conditions were extracted at 20-meter water depth. SST and SSS were derived from 0.25° spatial resolution for the period
1955 to 2022, whereas nutrients, O₂, and BWO were derived from 1° spatial resolution for the period 1965 to 2022. BWO data
were retrieved from the corresponding station depths, and missing values are filled through vertical and horizontal interpolation
of oxygen concentrations to the sampled depths and coordinates.

2.4 Bulk sediment organic carbon and nitrogen

We measured total organic carbon (TOC; wt%), total nitrogen (TN; wt%), stable organic carbon isotope ratio ($\delta^{13}\text{C}_{\text{org}}$; ‰),
and stable nitrogen isotope ratio ($\delta^{15}\text{N}$; ‰) on all bulk sediment samples (core-top and downcore). Core-top data from the
Baltic Sea, North Sea, and Atlantic Ocean were obtained from Hilgen et al. (2026b), while data from the Black Sea and
Mediterranean Sea and piston core were generated as part of this study. For TOC and $\delta^{13}\text{C}_{\text{org}}$, ~1 g of freeze-dried and
homogenized sediment was decalcified by adding excess HCl overnight to remove inorganic carbon. TOC and $\delta^{13}\text{C}_{\text{org}}$ were
subsequently measured on the decalcified samples, whereas TN and $\delta^{15}\text{N}$ were determined on untreated sediment. All samples
were analyzed using an elemental analyzer (Fisons Instruments NA 1500, TCD) coupled to an isotope ratio mass spectrometer
(IRMS, FinniganMat Delta Plus). TOC and TN were reported as weight percentage (wt%) of dry sediment with an analytical
error of 0.01 wt% (TOC) and 0.02 wt% (TN) based on the relative standard deviation of replicate runs of laboratory certified
standards (nicotinamide and GQ2-1). The carbon-to-nitrogen (C/N) ratio is calculated by dividing the molar amount of carbon
by the molar amount of nitrogen. TN is assumed to represent total organic nitrogen (TON) consistent with common practice
in sedimentary studies (Meyers, 1997; Müller, 1977), as it is analytically difficult to determine organic nitrogen directly. $\delta^{13}\text{C}_{\text{org}}$
values are reported relative to the Vienna Pee-dee Belemnite (VPDB) standard and $\delta^{15}\text{N}$ values relative to atmospheric
nitrogen, with precisions of 0.03 ‰ and 0.09 ‰, respectively, as determined by repeated analyses of international and
laboratory certified standards (ammonium sulfate and GQ2-1).

2.5 Bromine concentrations measured with ICP-MS

Sedimentary bromine (Br) speciation and analyses are complex due to the high volatility of this element, which can lead to
substantial losses during oxidative digestion of organic matter (OM) at high temperatures (He et al., 2018; Mesko et al., 2016).
Therefore, here we investigated the best digestion method with varying temperatures and ultraviolet (UV) exposure. The
analytical workflow for determining Br concentrations using inductively coupled plasma mass spectrometry (ICP-MS) is
summarized in Fig. 2. During this method testing we evaluated three components. First, we evaluated four oxidative digestion



methods to extract Br through chemical oxidation of OM using certified reference materials (RMs) (Sect. 2.5.1). Second, we determined salt-associated bromine (Br_{salt}) to assess the relative contribution of Br_{salt} to sedimentary organic-bound bromine (Br_{org}) (Sect. 2.5.2). Third, we used the most accurate method, based on our test on RMs (Sect. 2.5.3), to quantify Br_{org} in all core-top and downcore samples (Sect. 2.5.4).

165 2.5.1 Reference materials and method evaluation

We evaluated the Br extraction through repeated analyses of seven standard RMs (Jochum et al., 2005), including BCSS-1 (marine sediment; $78 \pm 3 \mu\text{g g}^{-1}$), GBW07309 (stream sediment; $1.35 \pm 0.15 \mu\text{g g}^{-1}$), JCP-1 (Porites coral; $3.25 \mu\text{g g}^{-1}$), JLK-1 (lake sediment; $8.7 \pm 0.6 \mu\text{g g}^{-1}$), JSd-1 (stream-sediment; $1.65 \pm 0.35 \mu\text{g g}^{-1}$), JSd-3 (stream-sediment; $3.9 \pm 0.3 \mu\text{g g}^{-1}$), and MAG-1 (marine sediment; $251 \pm 1 \mu\text{g g}^{-1}$). The certified values of these RMs included both Br_{salt} and Br_{org} , therefore method
170 evaluation was performed on total bromine (TBr) concentrations. The approach is depicted in Fig. 2 by following the pathway that starts at the green box and follows the long-dashed black line and the solid black line to the ICP-MS analysis, thus skipping the removal of Br_{salt} step (Sect. 2.5.2).

To study potential loss of Br, we evaluated four digestion methods that differ in temperature and UV exposure (Fig. 2: orange boxes): method 1 at 20 °C, method 2 at 50 °C, method 3 at 80 °C, and method 4 with UV light at room temperature.
175 He et al. (2018) proposed an optimal digestion temperature and time of 140 °C and 15 min. However, the soils and sediments analyzed in that study contain Br concentrations $< 25 \mu\text{g g}^{-1}$, substantially lower than those expected for marine sediments (Leri et al., 2010). To avoid potential loss at higher temperature we maximized the temperatures used to 80 °C, which is commonly applied in studies of marine sediments (Jilbert et al., 2021; Ziegler et al., 2008). UV-assisted digestion was included here as a low-temperature approach to accelerate OM oxidation while minimizing Br volatilization losses.

180 For all four digestion methods we followed the same general workflow. We weighed $\sim 0.1 \text{ g}$ of material and oxidized the material to release Br by addition of 5 ml 35% H_2O_2 . During the oxidation step, the vials were closed hand-tight to prevent the loss of Br and were shaken intermittently to avoid excessive pressure build up. The temperature methods (1 to 3) were processed in a temperature-controlled shaking bath, while method 4 samples were transferred to PFA vials and placed in a UV box on an orbital shaker for 24 h. After the reaction was finished (i.e., the bubbling stopped), the samples were centrifuged
185 and filtered (0.45 μm PTFE). Of the residual digest, a 100 μL aliquot was diluted to 2.5 mL and measured using ICP-MS.

To compare the performance of the four digestion methods, we applied several statistical tests. Accuracy was assessed by comparing the measured TBr to their certified values using three complementary metrics: (i) mean and median recovery (%), expressing the measured concentration as a percentage of the certified concentration to indicate the percentage of the analyte that is successfully extracted, (ii) mean and median bias ($\mu\text{g g}^{-1}$), representing the difference between measured and
190 certified concentrations to indicate whether the approach systematically over- or underestimates the certified value, and (iii) mean and median relative error (%), quantifying the size of the error relative to the certified value.

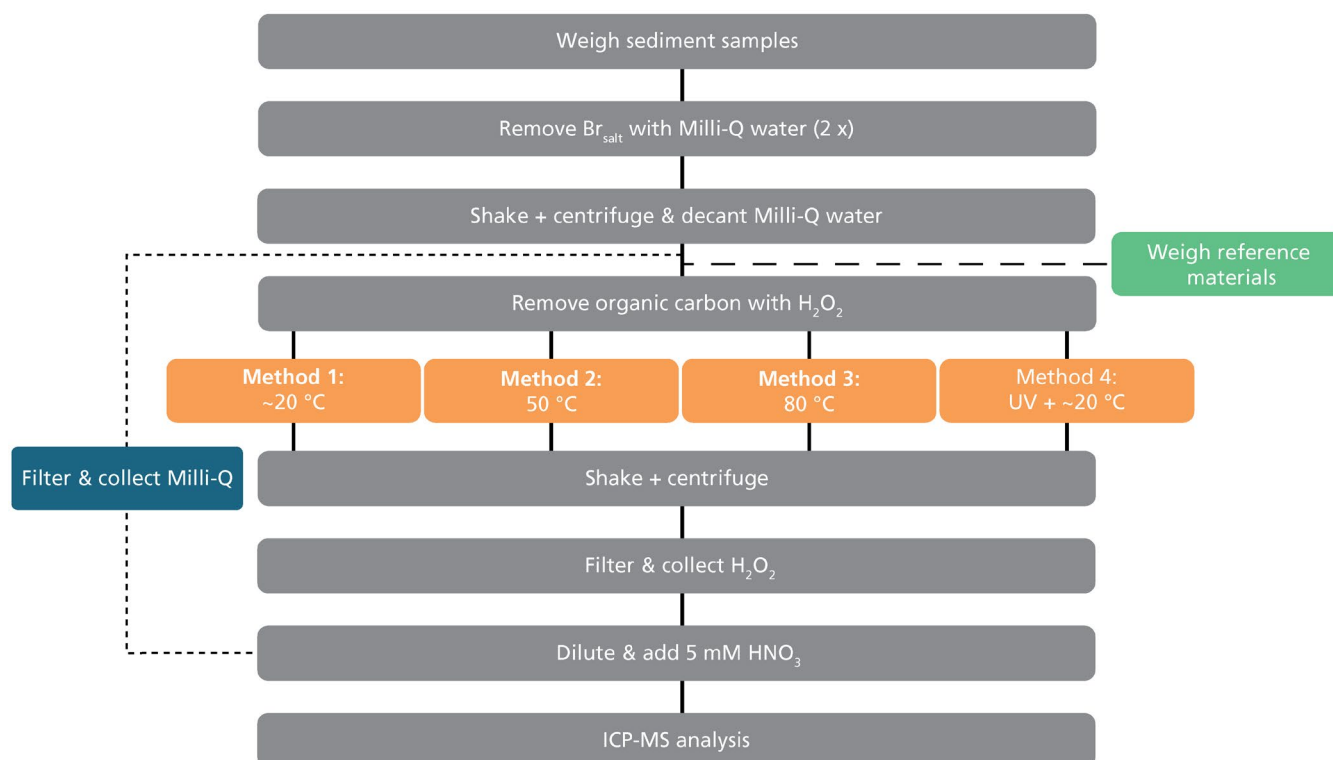


Figure 2: Schematic workflow for the quantitative measurement of bromine (Br) in marine sediments using inductively coupled plasma-mass spectrometry (ICP-MS). The long-dashed black line originating from the green box indicates the procedure used to evaluate four digestion methods (orange boxes) with certified reference materials. The short-dashed black line via the blue box originating from the upper gray box indicates the procedure for determining the salt-associated Br (Br_{salt}). The full sequence of gray boxes, including method 2, represents the procedure for determining organic-bound Br.

2.5.2 Salt-associated bromine

195 In addition to testing the four digestion methods on RMs, different procedures were also applied to five core-top sediment samples; one from each basin: stations 4, 13, 37, 39, and 41 (Fig. 1). To isolate Br_{org} , these samples were rinsed to remove residual pore-water salts containing bromide (Br^-) (Zheng et al., 2026; Ziegler et al., 2008). Br_{salt} was measured to evaluate the relative contribution of Br_{salt} and Br_{org} . This corresponds to the second pathway indicated by the solid black line starting at the top and following the short-dashed black line through the blue box in Fig. 2.

200 Br_{salt} was removed by rinsing ~ 0.1 g of sediment twice with 10 mL Milli-Q water (15 min shaking, 10 min centrifugation at 2500 rpm). The residual Milli-Q water was filtered ($0.45 \mu\text{m}$ PTFE), and a $100 \mu\text{L}$ aliquot as diluted to 2.5 mL and analyzed by ICP-MS to quantify Br_{salt} .



2.5.3 Evaluation of methods for determining total bromine concentrations in certified reference materials

The results of the statistical tests for each digestion method are summarized in Table 1, and the recoveries of the measured TBr concentrations for each method and RM are shown in Fig. S1. Comparing the recoveries confirms that temperature and time play a central role in the efficiency and practicality of Br extraction. Methods 2 and 3 show the best overall performance, yielding the highest recoveries, the lowest bias, and the smallest relative errors. Nevertheless, oxidizing OM at 50 °C (method 2) consistently produced recoveries closest to the certified TBr concentrations. This temperature strikes an optimal balance between two competing processes. Low temperatures (i.e., method 1) extend the oxidation step in time and do not fully oxidize the organic matrix, leaving part of Br_{org} bound (as indicated by lower recoveries). High temperatures (i.e., method 3) may volatilize Br compounds, through which Br is lost (also indicated by lower recoveries). UV light (method 4) led to a large spread in the data and values far from the certified values and is therefore the least reliable of the four methods. This variability may partly be caused by frequent switching between sample vials during analysis, as sample material needed to be transferred to UV-transparent quartz glass vials, which likely caused contamination and the high and strongly biased recoveries.

Table 1: Overview of the statistical tests to compare total bromine concentration and certified values of the reference materials (RMs) per method (M1-4).

Information			Recovery		Bias		Relative error	
Method	Number RMs	Reaction time	Mean (%)	Median (%)	Mean (µg g ⁻¹)	Median (µg g ⁻¹)	Mean (%)	Median (%)
M1 (~20 °C)	7	±29 days	87.7	89.2	-16.2	-0.4	25.0	33.3
M2 (50 °C)	7	±27 hours	103.2	91.0	-1.6	-0.5	19.8	17.2
M3 (80 °C)	7	±17 hours	91.2	92.3	-6.1	-0.3	13.5	9.1
M4 (UV)	7	±24 hours	147.0	87.7	-18.1	-0.4	96.1	47.0

2.5.4 Organic-bound bromine

Method 2 (50 °C) shows values closest to the certified values and hence is here identified as the optimal approach (see Sect. 2.5.3 for details) and is, therefore, applied to all 55 core-top samples and 11 downcore samples. All samples were rinsed with Milli-Q water to remove Br_{salt} (see Sect. 2.5.2). Then, Br_{org} was liberated from OM through chemical oxidation using H₂O₂ at 50 °C (see Sect. 2.5.1). For each sample, we calculated Br_{org} to TOC (Br/OC) ratio (mg g⁻¹). To examine relationships between Br_{org} and Br/OC ratio and sediment properties and water-column conditions, Pearson correlation coefficients were calculated (Pearson, 1895), and statistical significance is defined as $p < 0.05$. Linear regressions were shown for strong relationships ($|r| \geq 0.71$; $R^2 \geq 0.5$).



2.5.5 ICP-MS analysis

Processed samples of TBr (Sect. 2.5.1), Br_{salt} (Sect. 2.5.2), and Br_{org} (Sect. 2.5.4) were analyzed with a Thermo Fisher Scientific Element 2 sector-field ICP-MS (SF-ICP-MS) at the Royal Netherlands Institute of Sea Research (NIOZ). A low-molarity ultrapure HNO₃ solution (5 mmol L⁻¹) was used to minimize washout times, and Rh was added as an internal standard to correct for instrumental drift. The Br isotopes ⁷⁹Br and ⁸¹Br could not be measured in low-resolution mode due to polyatomic interferences from ⁴⁰Ar³⁸Ar¹H and ⁴⁰Ar⁴⁰Ar¹H, respectively. In medium-resolution (MR) mode, ⁷⁹Br was fully resolved, whereas ⁸¹Br remained partially unresolved. Complete separation of ⁷⁹Br was further confirmed in high-resolution (HR) mode. Br concentrations were therefore quantified using the ⁷⁹Br signal measured in MR mode and a five-point calibration curve prepared in the same 5 mmol L⁻¹ HNO₃ matrix.

In addition to ⁷⁹Br, isotopes ³¹P, ³²S, ⁴⁴Ca, ⁶⁰Ni, ⁶³Cu, ¹⁰³Rh, and ¹¹⁵In were monitored in MR. In HR mode, ⁷⁵As, ¹⁰³Rh, and ¹¹⁵In were monitored. Quantification was carried out using a five-point calibration curve prepared in the same 5 mmol L⁻¹ HNO₃ matrix. The internal and external precision of Br_{org} is 1.3 RSD% and 9 RSD%, respectively, based on multiple analyses of the drift samples (n=18) and the repeated analyses of samples.

2.6 Bromine measured with XRF core scanner

X-ray fluorescence (XRF) core scanning was performed on the 55 core-top samples and a piston core from the North Sea using an Avaatech XRF core scanner at NIOZ. The core-top samples were freeze-dried, homogenized and measured in small sample cups (6 mm diameter, measured with a 4 × 4 mm window size in the scanner). The samples were measured before and after rinsing with Milli-Q water to remove the dissolved salt fraction (Sect. 2.5.2). Al, Ca, Cl, K, Si, and Ti were measured at 10 kV (0.8 mA, 40 s, no filter), and Br, Cu, Fe, Ni, Sr, Rb, Zn, and Zr were measured at 30 kV (0.5 mA, 60 s, Pd-thick filter). Downcore measurements (1-cm resolution, measured with a 10 x 10 mm window size in the scanner) from the North Sea core 64PE517-110PC (location 28; Fig. 1) were carried out on wet split-core surfaces. Al, Ca, Cl, Cr, K, Mg, S, and Ti were measured at 10 kV (0.5 mA, 10 s, no filter), Fe and Mn were measured at 20 kV (0.3 mA, 20 s, Al filter), Br, Co, Cu, Ni, Pb, Sr, Rb, Zn, and Zr were measured at 30 kV (1.75 mA, 20 s, Pd-thick filter), and Ba and Mo were measured at 50 kV (0.25 mA, 20 s, Cu filter). Before scanning, all sediment surfaces were flattened and covered with a thin 4 μm Ultralene film and reference materials and monitor scans were measured to assess instrumental stability.

Because XRF core scanning generates elemental counts rather than absolute concentrations, we need to calibrate XRF-scanning-derived signals against independently quantified concentrations. For many elements, such conversion had been done by combining XRF data with discrete measurements using multivariate log-ratio calibration (MLC; Weltje et al., 2015). For Br, however, this calibration is more complicated because Br may escape during traditional oxidative digestion, requiring a separate extraction method to quantify Br. Hence, we used the same extraction method with H₂O₂ at 50 °C at regular intervals (n = 11) to independently measure Br_{org} concentrations calibrate and validate XRF-scanning-derived Br signals as proxies for Br_{org}.



Core-top XRF measurements were used to evaluate which XRF-scanning-derived Br signal best reflects measured Br_{org} and modern NPP. Ideally, such indicators would allow high-resolution Br records to be converted to Br_{org} , and subsequently to NPP, with minimal additional discrete measurements. Therefore, four XRF-scanning-derived Br indicators, described below, were evaluated in the core-top dataset: Br_{xrf} , Br_{rinsed} , Br/Cl , and $Br_{\%}$.

The first indicator was raw Br counts from the untreated cup measurements, here referred as Br_{xrf} . This indicator was included to test whether uncorrected Br counts already reflect Br_{org} or whether correction for salt is required since the total XRF-scanning Br signal can include both dissolved Br from pore water ($Br_{xrf,salt}$) and Br associated with sedimentary OM ($Br_{xrf,org}$):

$$Br_{xrf} = Br_{xrf,salt} + Br_{xrf,org} \quad (1)$$

We here assume that Br-bearing minerals or other non-organic Br components are not present or negligible compared to the $Br_{xrf,salt}$ and $Br_{xrf,org}$ fractions. The second indicator was the Br signal measured after rinsing (Br_{rinsed}), which provides an estimate of the Br signal remaining after removal of pore-water salt ($Br_{xrf,org}$):

$$Br_{rinsed} = Br_{xrf,org} \quad (2)$$

For the third indicator, the ratio between raw Br counts and raw chlorine (Cl) counts (Br/Cl) was tested (e.g., used in Thomson et al., 2006). This indicator was included because Cl measured with XRF (Cl_{xrf}) is primarily derived from pore-water salt ($Cl_{xrf,salt}$) and does not have an appreciable organic form in sediment. Because the Br/Cl ratio of marine pore water is approximately constant, the Br_{salt} fraction is proportional to the Cl_{salt} fraction:

$$\frac{Br}{Cl} = \frac{Br_{xrf}}{Cl_{xrf}} = \frac{Br_{xrf,salt} + Br_{xrf,org}}{Cl_{xrf,salt}} \quad (3)$$

Elevated Br/Cl values may therefore indicate Br enrichment which is not related to pore-water salt contribution. For the fourth indicator, total Br counts were normalized to total counts of selected elements ($Br_{\%}$), following the normalization approach of Bertrand et al. (2024):

$$Br_{\%} = \frac{Br_{xrf}}{\sum 11 \text{ selected element intensities}} * 100 \quad (4)$$

The 11 selected elements were Al, Br, Ca, Fe, K, Rb, Si, Sr, Ti, Zn, and Zr.

All indicators, except Br_{rinsed} , were applied to a downcore record. The rinsing approach was used only for the core-top samples because it requires discrete sampling, drying, homogenization, and rinsing and is therefore not ideal when dealing with long sediment cores where the main advantage of XRF core scanning is the generation of rapid, high-resolution Br records



from wet surfaces. To examine relationships between Br_{org} and XRF-scanning-derived indicators in both the core-top and downcore datasets, Pearson correlation coefficients were calculated (Pearson, 1895), and statistical significance is defined as $p < 0.05$. Linear regressions are shown for strong relationships ($|r| \geq 0.71$; $R^2 \geq 0.5$).

Calibration against independently measured Br_{org} is required to convert the XRF-scanning-based indicators into quantitative Br_{org} estimates. The core-top cup calibrations were used to assess proxy behavior, but the calibration equations were not transferred directly to the downcore data because the dry sediment measurements in cups and wet-core scans differ in sample surface area and XRF-scanning settings. Therefore, the continuous downcore records were evaluated separately against discrete Br_{org} concentrations by averaging the XRF data over one to two measurements closest to each discrete sample depth.

In addition to the three indicators that can be calculated directly from XRF-scanning data (Br_{xrf} , Br/Cl , and $Br\%$), two other approaches were applied to the downcore record: a water-content based salt correction and MLC. Following Ziegler et al. (2008), Br_{xrf} was normalized to water content (WC) and plotted against TOC:

$$\frac{Br_{xrf}}{WC} = a \times TOC + b \quad (5a)$$

where a is the slope and b the intercept. The intercept b represents the Br_{salt} contribution per unit water content and is used to correct Br based on water content ($Br_{org,wc}$):

$$Br_{org,wc} = Br_{xrf} - (b * WC) \quad (5b)$$

Furthermore, Br_{org} was predicted from the downcore XRF dataset using Avaaxelerate (Bloemsma, 2015; Weltje & Tjallingii, 2008) following the MLC approach of Weltje et al. (2015). In addition to the piston core samples, four samples from multi-core 64PE517-79MC, collected at the same location (location 28; Fig 1; Table S1), were included to extend the calibration dataset. These multi-core samples were processed simultaneously with the piston-core samples for Br_{org} determination. Because both cores were measured using the same XRF settings, the combined calibration was used to predict Br_{org} for both records. The MLC model was calibrated using 15 discrete ICP-MS-derived Br_{org} concentrations and their corresponding multi-element XRF intensities, resulting in a predicted downcore Br_{org} record ($Br_{org,MLC}$). Calibration samples were matched to XRF scan positions using a sample tolerance of 30 mm, with a significance level of 0.05. Although the calibration was generated using both cores, this study focuses on the piston-core application because it provides the main long-term sedimentary record for evaluating downcore Br_{org} -based paleoproductivity estimates.

3. Results and Discussion

3.1 Environmental controls on Br enrichment

TOC values vary from 0.07 to 6.9 wt% and Br_{org} concentrations range from 5.2 to 302.3 $\mu g\ g^{-1}$. Lowest values for both parameters occur offshore in the Atlantic Ocean, Mediterranean Sea, and North Sea, whereas the highest values are observed



in the Baltic and Black Seas. The measured Br_{org} concentrations are in the order of magnitude expected for marine sediments (Leri et al., 2010), and the Br/OC ratios ($2.7\text{--}13.8 \text{ mg g}^{-1}$) fall within the global range reported for marine core-top sediments (Table S2). The mean values of the sediment data per basin are summarized in Table 2.

In all basins, variations in Br_{org} largely reflect differences in OC content (Fig. 3a). The $\text{TOC}-\text{Br}_{\text{org}}$ relationships per basin are shown in Fig. S2. The best fit between TOC and Br_{org} shows a positive linear relationship, with an intercept close to the origin ($R^2 = 0.86$, $p < 0.05$; Fig. 3a). This implies that 86% of the variance observed in Br_{org} can be explained by variability in TOC. To explore the factors contributing to Br enrichment independent of OC content, and account for the remaining 14% of unexplained variance, we use the Br/OC ratio to evaluate environmental factors acting during production (Sect. 3.1.1), water-column transport (Sect. 3.1.2), and burial (Sect. 3.1.3) of OC_{mar} .

Table 2: Overview of the mean water-column conditions and sediment characteristics from the stations in each marine basin.

Area	SSS	Water depth (m)	BWO ($\mu\text{mol kg}^{-1}$)	NPP ($\text{gC m}^{-2} \text{ yr}^{-1}$)	TOC (wt%)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	C/N molar	Br_{org} ($\mu\text{g g}^{-1}$)	Br/OC (mg g^{-1})	OC_{mar} ($\delta^{13}\text{C}_{\text{org}}$) (wt%)	OC_{mar} (C/N) (wt%)
Baltic Sea	9.5	91.6	166.3	1080.8	3.6	-24.1	8.9	212.7	6.7	1.1	1.9
North Sea	33.8	241.4	269.8	452.1	1.1	-22.4	8.7	55.5	6.8	0.6	0.6
Atlantic Ocean	35.0	601.7	296.0	297.5	0.3	-22.3	7.6	16.6	6.3	0.2	0.2
Black Sea	18.3	1877.0	0.0	178.3	5.3	-24.9	10.6	200.6	3.6	1.0	1.4
Mediterranean Sea	38.0	575.9	193.9	197.7	0.5	-22.5	6.3	21.9	4.6	0.3	0.5

3.1.1 Surface-ocean conditions

The samples are taken from locations spanning major environmental gradients (Table 2). SST ($R^2 = 0.09$, $p < 0.05$; Fig. S3a), nitrate ($R^2 = 0.23$, $p < 0.05$; Fig. S3b), phosphate ($R^2 = 0.14$, $p < 0.05$; Fig. S3c), show weak correlations with Br/OC ratio. Other surface ocean variables exhibit no relationships with Br/OC ratio, including SSS (Fig. 4a), silicate, surface ocean oxygen, and NPP (Figs. S3d-f). These observations suggest that Br enrichment relative to OC is not directly controlled by large-scale differences in surface-ocean conditions, but rather by other factors such as the composition of the OM (Liu et al., 2015) and/or post-depositional processes (e.g., Berg & Solomon, 2016).

Among the surface-ocean parameters investigated, salinity is of particular interest because it directly influences dissolved Br^- availability, the ultimate source of Br. Our data show that at salinities > 7 (minimum value of dataset), dissolved Br^- availability is sufficient across all regions (Fig. 4a), meaning Br^- supply is not the limiting factor for bromination. In such environments, the degree of bromination shifts toward other controlling factors. Joe-Wong et al. (2019) demonstrate this shift in coastal wetland sediments along a salinity gradient, finding that Br_{org} production is initially dependent on Br^- supply at low to moderate salinity ($0.3\text{--}3.7$), but becomes decoupled from salinity under higher salinity conditions (~ 13.8 and higher). Here



bromination is instead controlled by OM reactivity, redox conditions, and hydrological processes. The salinity-Br_{salt} relationship is further explored by Zheng et al. (2026), who demonstrate that dissolved Cl and Br dominate total sedimentary Cl and Br pools and correlate with bottom-water salinity in environments with SSS < 30.4. Our results show that, once this dissolved fraction (Br_{salt}) is removed, the Br/OC ratio becomes largely decoupled from salinity (Fig. 4a), revealing that the salt correction has been effective. All studies combined, the Br/OC ratio may be a powerful tool for identifying major salinity transitions associated with shifts in OM sources in paleo-records (i.e., SSS < 7 vs SSS > 7). This may allow for a novel paleo-application to detect major salinity shifts, such as transitions from (terrestrial environment to) freshwater to brackish/marine conditions, which is an interesting topic for future work.

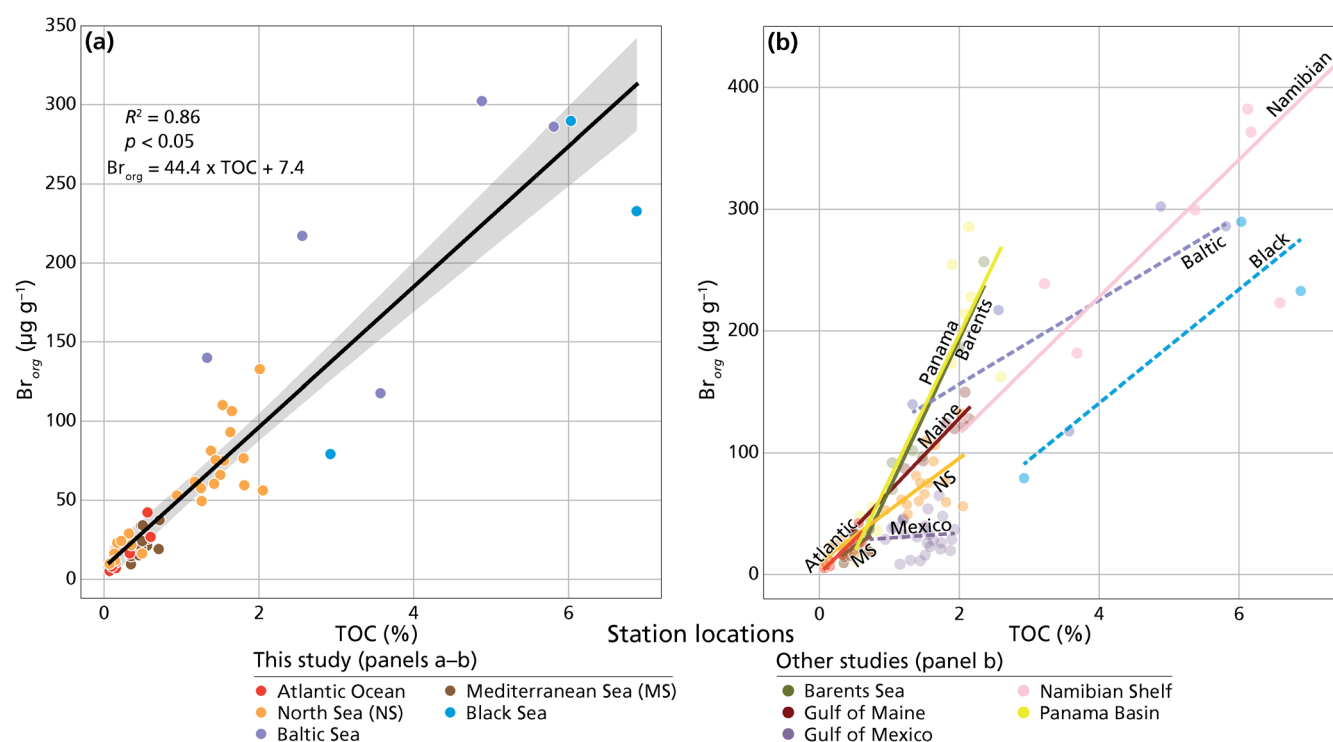


Figure 3: Cross-plots of total organic carbon (TOC) versus organic-associated bromine (Br_{org}) for this study (a) and available core-top datasets (b). In panel (a), the regression line is shown with a 95% confidence interval (gray shading). In panel (b), solid lines represent basin-specific linear regressions and symbols represent individual data points. Data for the Namibian Shelf and Panama Basin were derived from published figures, whereas raw data for the Barents Sea, Gulf of Maine, and Gulf of Mexico were obtained directly from published tables (Table S2). Note that the Namibian Shelf data extend beyond the x- and y-axis ranges shown here (see Price & Calvert, 1978). The dotted linear regression lines are not statistically significant ($p > 0.05$). Colors indicate the geographic region of each sample.

3.1.2 Marine organic matter through the water column

When OC_{mar} sinks to the seafloor it progressively degrades in the water column. The depth of the water column determines the oxygen exposure time. Consequently, sediments retrieved from greater depths contain a higher proportion of degraded, microbially processed OM (Burdige, 2007). Br/OC ratios are mostly lower at higher water-column depths (Fig. 4b). This



suggests preferential loss of Br-rich, labile OM during sinking (debromination), consistent with selective removal of Br during OM degradation in oxic sediments (Berg & Solomon, 2016; Leri et al., 2010; Leri & Myneni, 2012). Higher Br/OC ratios in shallower settings are consistent with water column observations (Carpenter et al., 2009; Liu et al., 2011; Quack & Wallace, 2003), showing higher concentrations of brominated compounds in coastal compared to open-ocean environments. Indeed, the degree of degradation seems to play a role in the Br contents of OC_{mar}, however, this process is difficult to disentangle from selective degradation occurring in the sediments (Berg & Solomon, 2016).

3.1.3 Burial in sediments

Sedimentation rate and oxygen availability are important controls for OM preservation in sediments and are thus compared to Br/OC ratios. The Br/OC ratio does not correlate with BWO ($R^2 = 0.11$, $p < 0.05$; Fig. S3g), confirming that bromination itself is largely independent of oxygen availability (Pedersen & Price, 1980), and that preservation primarily affects the absolute amount of retained OM and Br_{org} rather than the bromination state of OM. Therefore, Br/OC can retain information on marine OM source and composition despite changes in preservation, although absolute Br_{org} concentrations should still be interpreted considering preservation effects.

Using the sedimentation rate data from the North Sea and Atlantic Ocean (Hilgen et al., 2026b), Br_{org} shows a strong positive correlation with sedimentation rate ($R^2 = 0.66$, $p < 0.05$; Fig. 4c). Higher sedimentation rates promote OM preservation by facilitating faster OM burial and thereby reducing exposure to oxygen, the most efficient electron acceptor for OM oxidation (Middelburg, 2019). The increase of NPP with sedimentation rate here, as shown in Fig. 4c, suggests that higher sedimentation rates in this area are related to export and burial of biologically produced OC_{mar} in the surface ocean (Hilgen et al., 2026a), rather than higher input of OC_{ter}. The strong relationship between sedimentation rate and Br_{org} therefore supports the interpretation that Br_{org} tracks the increased primary production that results in greater production and export of Br-rich marine OM to the sediment, confirming Br_{org} close association with OC_{mar} production and export under oxic conditions.

Bottom water oxygenation has a major impact on OM preservation and thus exerts a major control on OM accumulation and thus also on Br_{org} and TOC (e.g., Hilgen et al., 2026a). This may hence influence potential proxy relationships we try to establish here and therefore, it is necessary to identify locations in which enhanced preservation potentially plays a role. Stations 1, 2, 38, 39, and 40 located within the hypoxic to anoxic zone (Fig. 4d) from the Baltic Sea and Black Sea have a high preservation potential and may bias proxy relationships by disproportionately retaining fresh, labile, Br-rich marine OM compared to other stations in our dataset. In such sediments, Br remains largely bound to organic compounds and has not yet been removed during early diagenesis (Berg & Solomon, 2016), resulting in high absolute Br_{org} concentrations. Consequently, we therefore remove these five stations from the NPP proxy calibrations, but data points are plotted as empty dots. Such an approach is similar to existing NPP calibrations based on sedimentary OC, which exclusively focused on oxic depositional settings (e.g., Sarnthein et al., 1992). Here, OC burial may be interpreted as a balance between export production, water-column transfer, sedimentation rate, and oxic degradation.

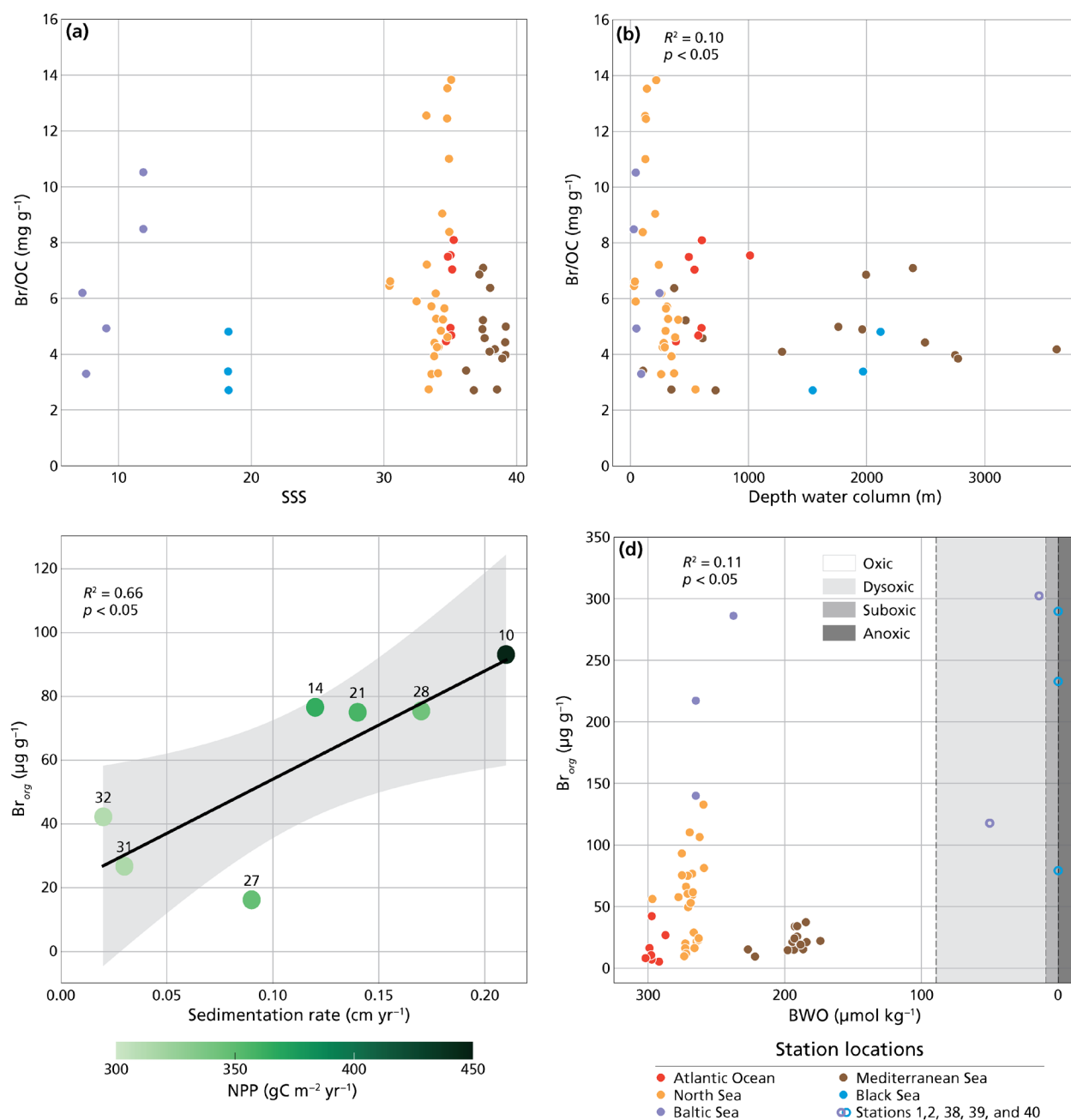


Figure 4: Cross-plots of sea surface salinity (SSS) (a) and water depth (b) versus sedimentary organic-bound bromine (Br_{org})-to-total organic carbon (Br/OC) ratio, and sedimentation rate (c) and bottom-water oxygen (BWO) (d) versus Br_{org}. In panel (c), the sedimentation rates are derived from Hilgen et al. (2026b), the numbers displayed above each data point indicate the corresponding station number (Fig. 1), the solid line represents the fitted linear regression, and the gray shading indicates the 95% confidence interval around the regression line. In panel (g), oxygen conditions are defined according to Tyson & Pearson (1991). In panels (a), (b), and (d) colors indicate the geographic region of each sample.



3.2 Br associated with marine organic matter

Br is primarily associated with marine organic compounds (Dembitsky, 2002; Leri et al., 2010, 2014, 2019; Leri & Myneni, 2012). Therefore, the strong positive linear relationship between TOC and Br_{org} (Fig. 3a) indicates that the sedimentary OC
385 pool is predominantly of marine origin across all studied basins and thus that absolute Br_{org} concentrations are closely linked to the amount of OM preserved in the sediment. The intercept of the linear regression is close to zero, reflecting no background Br signal from pore-water salts. This indicates that the rinsing procedure effectively removed Br_{salt} despite substantial differences in Br_{salt} contributions among basins (Fig. S4).

We compiled published TOC and Br_{org} datasets from marine core-top sediments (max 0-2 cm; number of samples in
390 dataset > 1) to place our data in a global context (Fig. 3b; Table S2). The compilation reveals that the positive TOC-Br_{org} relationship observed in this study is documented in previous studies from a range of marine environments (Malcolm & Price, 1984; Mayer et al., 1981; Pedersen & Price, 1980; Price & Calvert, 1978; Price et al., 1970), confirming the suitability of Br_{org} as indicator of the relative contribution of marine OM to the bulk OM inventory. We suggest that differences in the slope and strength of the TOC-Br_{org} relationship reflect variations in OC_{ter} input. Because terrestrial OM contributes to TOC but contains
395 little to no Br_{org}, increasing OC_{ter} input dilutes the marine Br signal, resulting in lower slopes and non-zero intercepts and, in some cases, the absence of a significant TOC-Br_{org} relationship. Accordingly, settings influenced by large amounts of terrestrial runoff, and therefore receiving substantial OC_{ter} inputs, such as the Gulf of Mexico (Mayer et al., 2007), exhibit no clear relationship between TOC and Br_{org}. These results show that distinguishing between carbon sources is essential for evaluating carbon cycles in different depositional settings and below we assess whether Br_{org} can be used for this purpose.

400 3.3 Productivity and relative contribution of marine organic matter

Accumulation of TOC in marine sediments is one of the most direct methods to estimate marine productivity, and many calibrations have been made during the last few decennia (e.g., Berger & Wefer, 1990; Müller & Suess, 1979; Sarnthein et al. 1992). Such calibrations generally work well when all OM is marine and when the preservation of the OM is not offset by enhanced preservation (Van der Weijden et al., 1999). In coastal and marginal seas, using TOC only for reconstructing NPP
405 is often unreliable as TOC reflects a complex mix of marine and terrestrial inputs. This is confirmed by our dataset and previous work (Hilgen et al., 2026a); no exceptionally strong relationship is observed between TOC and NPP ($R^2 = 0.43$, $p < 0.05$; Fig. 5a). The dilution from OC_{ter} obscures primary relations between TOC and NPP and thereby the application as a quantitative paleoproductivity proxy. Corrections for the potential admixing of terrestrial OM can be made using endmember mixing models based on $\delta^{13}\text{C}_{\text{org}}$ or the C/N ratio of OM (e.g., Seki et al., 2019).

410 The total pool of sedimentary OC consists of marine (*f_{mar}*) and terrestrial (*f_{ter}*) fractions, which can be estimated using two independent marine-terrestrial endmember mixing models based on $\delta^{13}\text{C}_{\text{org}}$ values and C/N ratios respectively:

$$f_{\text{mar}} = \frac{\text{sample measurement} - \text{terrestrial endmember}}{\text{marine endmember} - \text{terrestrial endmember}} \quad (6a)$$



$$f_{ter} = 1 - f_{mar} \quad (6b)$$

The proportion of marine organic carbon (OC_{mar}) and terrestrial organic carbon (OC_{ter}) per station can be calculated from these fractions and the TOC content:

$$OC_{mar} = f_{mar} * TOC \quad (6c)$$

$$OC_{ter} = TOC - OC_{mar} \quad (6d)$$

For the $\delta^{13}C_{org}$ model, terrestrial (-26.0 ‰) and marine (-20.0 ‰) endmembers are defined following Ziegler et al. (2008). For the C/N model, terrestrial (12) and marine (6.6) endmembers follow Lamb et al. (2006) and Redfield (1934). Br_{org} is primarily associated with reactive, marine-derived OM, making Br/OC (marine-derived / (marine-derived + terrestrial-derived)) also a potential tool to discriminate the OC source by using it in a two-endmember mixing model. Yet, in our study we do not apply a Br/OC endmember model like Mayer et al. (2007) in the core-top proxy comparison because TOC and Br_{org} show a strong linear relationship with an intercept close to zero (Fig. 3a) and OC_{ter} contributes little to no Br_{org} . As a result, Br/OC -derived OC_{mar} is mathematically proportional to Br_{org} and contains the same information. Nevertheless, the Br/OC approach remains useful for illustrating source partitioning in our downcore record, where the TOC- Br_{org} relationship has a non-zero intercept (Sect. 3.4).

Where preservation conditions are comparable, OC_{mar} indicators can be related more directly to variations in their initial source, i.e. NPP. We therefore exclude stations indicative of high preservation potential (see Sect. 3.1.3). This step creates a refined dataset that minimizes this confounding factor and results in a selection of stations with similar depositional conditions. The separation of anoxic and oxic settings strengthens the correlations between TOC, OC_{mar} indicators, and NPP compared to the full dataset (Fig. 5). Moreover, it improves the agreement between the different OC_{mar} indicators (Fig. S5).

3.3.2 $\delta^{13}C_{org}$ and C/N ratio models

$\delta^{13}C_{org}$ values range from -25.7 to -20.8‰, and TOC and TN are strongly correlated ($R^2 = 0.98$, $p < 0.05$; Fig. S6). The $\delta^{13}C_{org}$ values and C/N ratios show a mix of terrestrial and refractory OM dominated (low SSS, low $\delta^{13}C_{org}$, high C/N ratio) to marine and fresh OM dominated (high SSS, high $\delta^{13}C_{org}$, low C/N ratio) stations (Table 2), confirming their indication for OM source and reflecting differences in the isotopic and elemental signatures of contributing sources. However, applying $\delta^{13}C_{org}$ - ($R^2 = 0.38$, $p < 0.05$; Fig. 5b) and C/N-based ($R^2 = 0.26$, $p < 0.05$; Fig. 5c) two-endmember mixing models to estimate OC_{mar} results in weaker correlations with NPP compared to TOC.

Although both traditional proxies show a positive correlation with NPP, they exhibit limited sensitivity across a larger range of productivity conditions. This limited sensitivity likely reflects mixing among potential marine and terrestrial sources (Fry, 2006; Lamb et al., 2006; Meyers, 1994), each with their own specific end-member values. The effect is particularly evident in productive nearshore regions ($NPP > 500 \text{ gC m}^{-2} \text{ yr}^{-1}$), such as parts of the coastal North Sea areas and Baltic Sea, where high NPP coincides with enhanced OC_{ter} input, promoting overlap between the isotopic signatures of for example C_3



terrestrial plants and marine algae (Lamb et al., 2006) and thereby reduces the ability of $\delta^{13}\text{C}_{\text{org}}$ and C/N ratios to resolve
 445 changes in NPP. Consequently, OM source and production are not necessarily fully coupled: the dominant OC source may
 remain marine, while the absolute amount of produced OC_{mar} and exported to the sediments can vary substantially. Moreover,
 $\delta^{13}\text{C}_{\text{org}}$ varies through time because isotopic fractionation during marine photosynthesis is strongly influenced by dissolved
 carbon dioxide (CO_2) concentrations, which are linked to local productivity as well as atmospheric $p\text{CO}_2$ (Jasper & Hayes,
 1990), making it a less suitable proxy. Likewise, although the TOC–TN relationship in our dataset exhibits a near-zero intercept
 450 (Fig. S6), indicating that nitrogen is predominantly organically bound, this assumption may not hold across different
 depositional environments or through time, and especially at low concentrations where inorganic nitrogen contributions can
 bias C/N ratios.

The end-member models discussed here have also other limitations. Endmembers defined in regional studies may not be
 globally applicable and can systematically over- or underestimate OC_{mar} . The lack of universal endmembers makes these
 455 models difficult to apply across different depositional environments, particularly when extending them to sedimentary records.
 Post-depositional degradation can modify OM derived parameters, thereby altering the endmember compositions and further
 increasing uncertainty in downcore interpretations of OM inventories. Therefore, using a proxy which does not rely on
 endmembers is more suitable and Br_{org} is such a proxy, as discussed below.

3.3.3 Br_{org} as proxy for marine net primary productivity

Br_{org} shows a substantially stronger correlation with NPP ($R^2 = 0.65$, $p < 0.05$; Fig. 5d) than TOC, $\delta^{13}\text{C}_{\text{org}}$ -derived OC_{mar} , and
 460 C/N-derived OC_{mar} (Fig. 5). The advantages of Br_{org} are particularly evident in highly productive nearshore regions, where
 OC_{ter} input of masks variations in $\delta^{13}\text{C}_{\text{org}}$ and C/N ratios. In these settings, Br_{org} yields a broader range of values over a
 comparable NPP range and continues to increase with NPP while other OC_{mar} indicators exhibit relatively limited variability.
 Nevertheless, Br_{org} also shows strong agreement with independently derived OC_{mar} estimates from the traditional parameters
 465 $\delta^{13}\text{C}_{\text{org}}$ ($R^2 = 0.78$, $p < 0.05$; Fig. S5b) and C/N ($R^2 = 0.71$, $p < 0.05$; Fig. S5c), indicating that Br_{org} primarily traces OC_{mar}
 across the investigated oxic environments. As Br_{org} does not rely on predefined source endmembers, it represents the best
 independent sedimentary indicator of NPP within our dataset.

The relationship between NPP and Br_{org} can be explained by the ability of freshly produced marine OM to react with
 active Br compounds in the photic zone, where light, Br^- , H_2O_2 , and enzymatic activity promote bromination (Leri et al., 2014;
 470 Méndez-Díaz et al., 2014). Consequently, Br_{org} directly tracks the fraction of marine OM after being freshly produced and thus
 water-column productivity. A wide range of marine organisms are known to produce reactive Br species, including
 cyanobacteria (Karlsson et al., 2008; Quack et al., 2007), diatoms (Hill & Manley, 2009; Moore et al., 1996; Quack et al.,
 2007), brackish-water algae (Abrahamsson et al., 2003), as well as heterotrophic bacteria (Liu et al., 2013), and macroalgae
 (La Barre et al., 2010). Unlike seawater measurements, which capture instantaneous or seasonal snapshots of OM bromination,
 475 the observed correlation between Br_{org} and NPP across different oxic oceanographic basins suggests that exported marine
 organisms-derived OM carries a brominated signature that is preserved during sedimentation. Although NPP varies seasonally



in response to changes in nutrient availability, light conditions, and species composition, sedimentary Br_{org} measured in core-tops integrates these processes over longer temporal and spatial scales, thereby reducing sensitivity to short-term variability in species composition and strengthening its relationship with multi-annual integrated NPP patterns.

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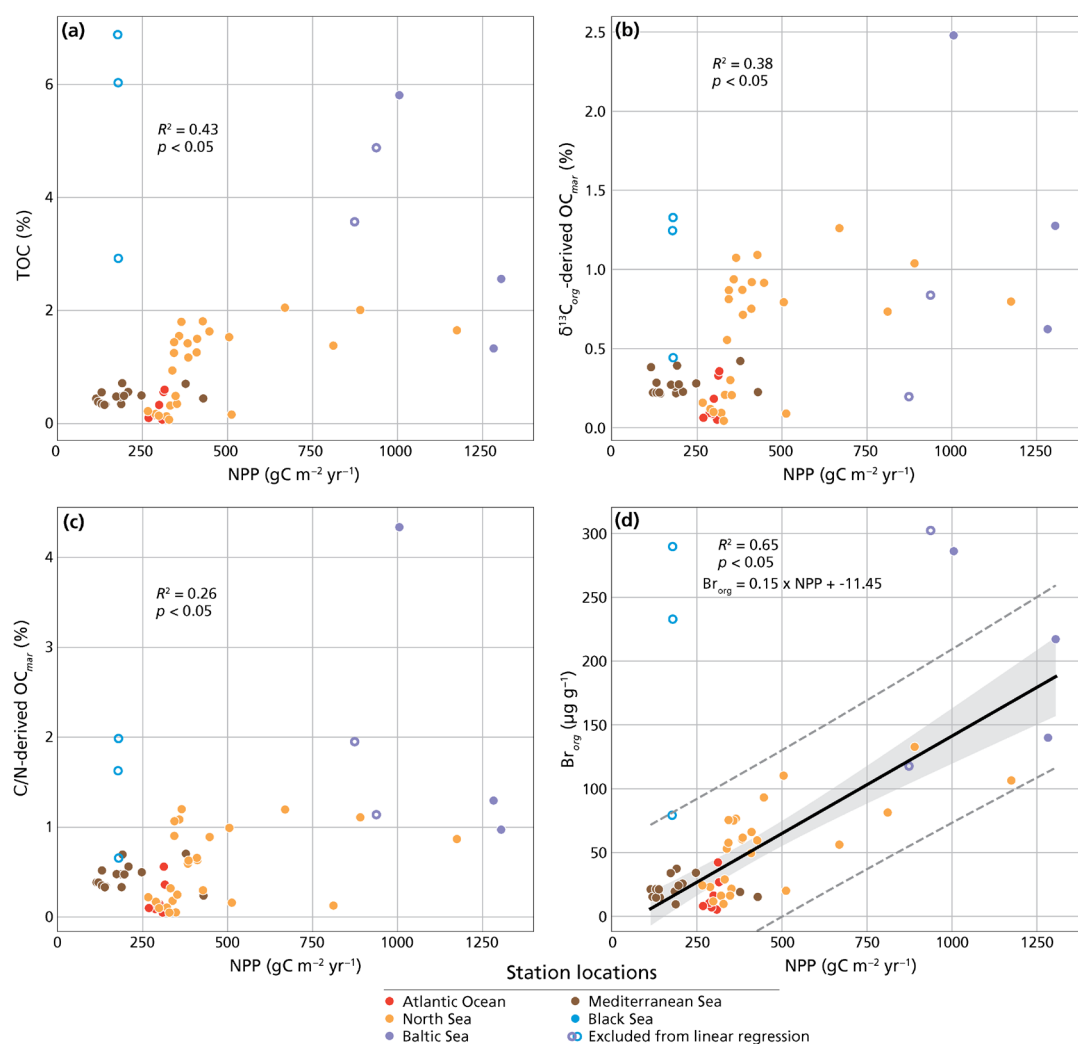


Figure 5: Cross-plots of net primary productivity (NPP) and potential indicators for marine organic carbon (OC_{mar}). R^2 values are shown for the subset of the dataset ($n = 50$) in which stations 1, 2, 38, 39, and 40 (bottom-water oxygen concentration $< 100 \mu\text{mol kg}^{-1}$; Fig. 4d) are excluded. In panel (d), the solid line represents the fitted linear regression, the gray shading indicates the 95% confidence interval around the regression line, and the dashed gray lines represent the 95% prediction interval for individual observations. Colors indicate the geographic region of each sample.



3.4 Organic Br using ICP-MS and XRF core-scanning

XRF core-scanning of sediment cores offers the possibility to generate continuous high-resolution records of OC_{mar} and, ultimately, past NPP (paleoproductivity), without measuring Br_{org} with expensive and time-demanding extraction methods at each depth. Our core-top dataset provides a basis for evaluating how Br_{xrf} is associated with the organic-bound fraction and
485 these samples were measured through XRF-scanning by the use of small cups. By comparing Br counts of untreated and rinsed samples, Br/Cl , $Br_{\%}$, and independently measured Br_{org} concentrations (see Sect. 2.6 for the details on their calculations), the core-tops allow us to test whether the pore-water Br contribution can be removed and whether the corrected XRF-scanning-derived Br signal can be quantitatively related to Br_{org} and subsequently, be used as a proxy for OC_{mar} and NPP.

Our core-top data reveal a substantial and variable pore-water Br component across the investigated marine basins. ICP-
490 MS based Br_{salt} varied significantly between basins (Fig. S4), likely reflecting differences in bottom-water salinity (Zheng et al., 2026) and pore-water volumes. This is confirmed by the $Br_{xrf,salt}$, calculated as the difference in percentage in total Br counts of a sample relative to Br counts of that sample when rinsed with Milli-Q water ((untreated Br counts – rinsed Br counts) / untreated Br counts * 100), which shows that up to 75% of total Br_{xrf} intensities can be salt-derived (median = 52%). These results, in line with those of Zheng et al. (2026), demonstrate that Br_{xrf} is definitely not only related to Br_{org} , especially
495 in recent and water-rich sediments. As such, the Br_{org} signal might be obscured in Br_{xrf} due to Br_{salt} .

This seems indeed to be reflected in the proxy relationships (Figs. 6; S7). Br_{xrf} shows a moderate relationship with Br_{org} ($R^2 = 0.66$, $p < 0.05$; Fig. S7a) and a weaker relationship with modern NPP ($R^2 = 0.41$, $p < 0.05$; Fig. 6a). After the rinsing step, the relationships improve for both Br_{org} ($R^2 = 0.69$, $p < 0.05$; Fig. S7b) and NPP ($R^2 = 0.67$, $p < 0.05$; Fig. 6b), confirming that removal of pore-water salt improves the correspondence between XRF-scanning-derived Br and the organic-bound,
500 productivity-related Br signal. However, Br_{rinsed} can only be obtained from discrete treated samples and is therefore not a proxy that can be obtained by doing continuous downcore measurements with an XRF scanner, which we aim for. The Br/Cl ratio is such a proxy, but this ratio is not correlated to marine organic enrichments, as it shows very weak relationships with both Br_{org} ($R^2 = 0.09$, $p < 0.05$; Fig. S7c) and NPP ($R^2 = 0.14$, $p < 0.05$; Fig. 6b). This indicates that this proxy is least suitable to reconstruct OC_{mar} through XRF scanning. In comparison, $Br_{\%}$ shows stronger relationships with both Br_{org} ($R^2 = 0.58$, $p < 0.05$;
505 Fig. S7d) and NPP ($R^2 = 0.65$, $p < 0.05$; Fig. 6d). This simple normalization step is an effective way to minimize the impact of physical sediment properties (Bertrand et al., 2024) in our sample cups, which clearly must have impacted our results (see the difference between Br_{xrf} and $Br_{\%}$ in Fig. 6) and serves therefore as the most suitable way to obtain information about Br_{org} from XRF scanning, even though Br_{salt} is not directly corrected for. The latter indicates that the Br_{salt} signal is apparently a relatively constant background signal in the core-top samples. Next, we will compare these different Br proxies also in sediments from
510 a wet North Sea core, for which we have results from both discrete measurements through ICP-MS and a near-continuous XRF-scanning dataset.

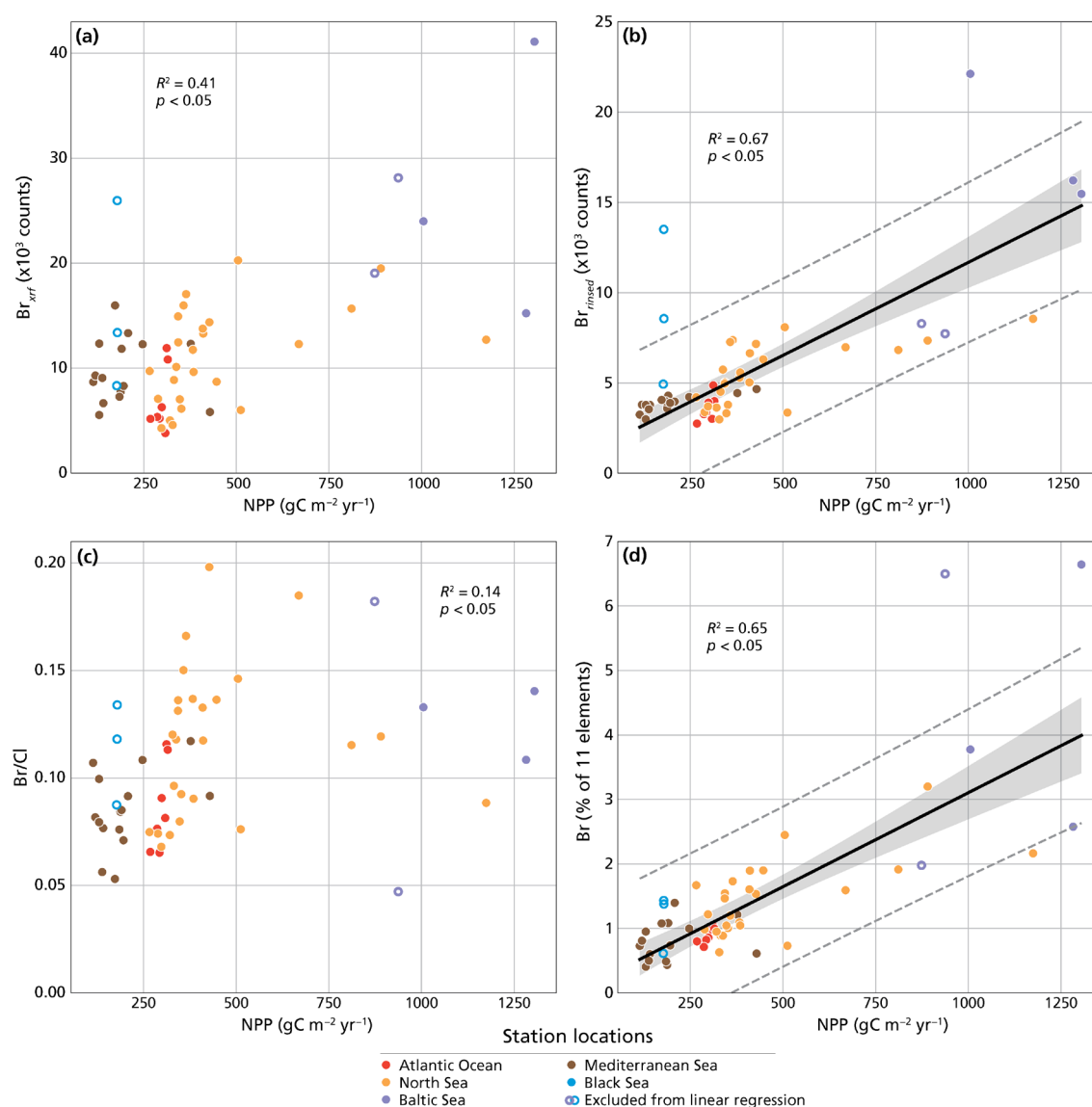


Figure 6: Cross-plots of net primary productivity (NPP) versus X-ray Fluorescence-scanning-based indicators: raw bromine (Br) counts from the untreated samples (Br_{xrf}) (a), Br counts from the rinsed samples (Br_{rinsed}) (b), bromine to chlorine (Cl) counts ratio (Br/Cl) (c), and total Br counts normalized to total counts of selected elements ($Br\%$) (d). R^2 values are shown for the subset of the dataset ($n = 50$) in which stations 1, 2, 38, 39, and 40 (bottom-water oxygen concentration $< 100 \mu\text{mol kg}^{-1}$; Fig. 4d) are excluded. In panel (b) and (d), the solid line represents the fitted linear regression, the gray shading indicates the 95% confidence interval around the regression line, and the dashed gray lines represent the 95% prediction interval for individual observations. Colors indicate the geographic region of each sample.

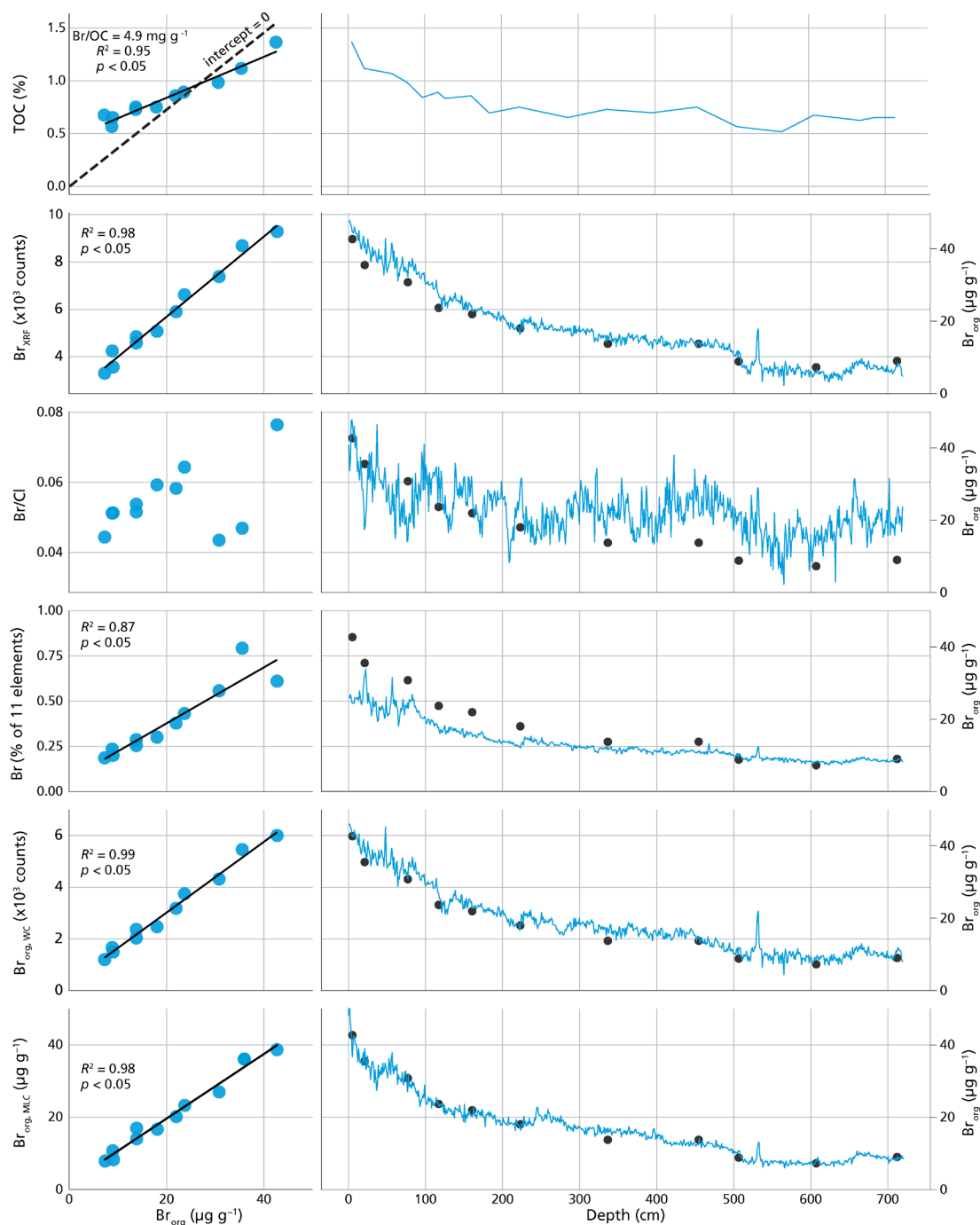


Figure 7: Downcore total organic carbon (TOC) and X-ray Fluorescence-scanning-derived bromine (Br) records. Rows from top to bottom: TOC, raw Br counts (Br_{XRF}), Br to chlorine (Cl) counts ratio (Br/Cl), total Br counts normalized to total counts of selected elements (Br%), Br corrected based on water content ($Br_{org,WC}$), and predicted sedimentary organic-bound Br (Br_{org}) based on multivariate log-ratio calibration (MLC) ($Br_{org,MLC}$). The left column shows the ICP-MS-derived Br_{org} versus the parameters and the right column shows the parameters over depth.



The strong linear relationships between Br_{org} and TOC ($R^2 = 0.95$, $p < 0.05$; Fig. 7) and Br_{xrf} ($R^2 = 0.98$, $p < 0.05$; Fig. 7) downcore indicate that most TOC and Br_{xrf} variability is linked to OC_{mar} . This likely reflects that the pore-water component has a much less pronounced impact downcore due to compaction. And it supports the idea that the primary Br signal is preserved over at least centennial to millennial timescales, consistent with relatively low debromination rates compared to other degradation pathways (Berg and Solomon, 2016). Thus, Br_{xrf} can provide a useful qualitative productivity signal (e.g., Bokhari-Friberg et al., 2025; Caley et al., 2011; Cartapanis et al., 2011), but quantitative conversion to Br_{org} and NPP requires accurate calibration. In contrast, Br/Cl does not show a significant relationship with Br_{org} ($p > 0.05$) and produces a different downcore pattern compared to the other XRF-scanning-derived Br indicators (Fig. 7), again showing that Br/Cl does not reliably isolate the Br_{org} signal. This might be due to the fact that Cl counts can be influenced by the thin seawater film that forms beneath the Ultralene foil during XRF core scanning of wet sediments (Hennekam and de Lange, 2012) and this water film might have a larger effect on the light element Cl compared to the heavier element Br. On the other hand, Br_{org} correlates strongly with Br_{org} ($R^2 = 0.87$, $p < 0.05$; Fig. 7), supporting the outcome of the core-top dataset calibration. Nevertheless, $\text{Br}_{\text{org,wc}}$ ($R^2 = 0.99$, $p < 0.05$; Fig. 7) and predicted $\text{Br}_{\text{org,MLC}}$ ($R^2 = 0.98$, $p < 0.05$; Fig. 7) show the strongest agreement with measured Br_{org} downcore. Both approaches reproduce the measured Br_{org} across the entire record well. However, the disadvantage of the water-content approach is that it requires besides Br_{org} measurements, both water-content and TOC data to determine the salt contribution per unit water content. The MLC approach, on the other hand, requires discrete Br_{org} calibration points only and is therefore the most optimal approach for generating a quantitative downcore Br_{org} record. This calibration approach renders units of the XRF-scanning data that are the same as those of ICP-MS, meaning that the $\text{Br}_{\text{org,MLC}}$ can directly be compared to NPP (by comparison of the Br_{org} relationship with NPP from core-top sediments).

The conversion of the $\text{Br}_{\text{org,MLC}}$ record to NPP using the core-top Br_{org} -NPP relationship (Fig. 5d) is shown in Fig. 8. Because this relationship is established for oxic settings, the resulting NPP reconstruction is interpreted under the assumption that the Norwegian Trench sediments are deposited under continuously oxic conditions. This is supported by the absence of exceptionally high TOC values (0.52 to 1.37 wt%; Fig. 7), compared with those observed in the anoxic basins Baltic and Black Seas (Table 2). In addition, the XRF-scanning-derived redox-sensitive element (e.g., V, U, and Mo; Hennekam et al., 2019) records from this core show no clear evidence for intervals during which anoxic depositional conditions prevailed.

The downcore TOC- Br_{org} relationship provides two additional constraints on the interpretation of the record. First, its slope (4.9 mg g^{-1}) is similar to the range observed in the core-top dataset ($3.5\text{--}5.6 \text{ mg g}^{-1}$; Fig. S2). This suggests that Br_{org} and OC are preserved in similar proportions downcore, with no clear evidence for strong selective preservation or degradation of Br-rich marine OM relative to total OC during (early) diagenesis. Therefore, the downcore Br_{org} signal mainly reflects changes in marine OM input rather than a strong diagenetic overprint on the Br/OC ratio. Second, the TOC- Br_{org} relationship has an intercept that is not close to zero (Fig. 7), indicating that a part of the TOC pool is not associated with Br_{org} and therefore interpreted as substantial OC_{ter} input signal.

Because of this non-zero intercept, we apply the aforementioned endmember approach (Eq. 6) based on Br/OC ratio as an example to partition TOC into OC_{mar} and OC_{ter} contributions downcore. The interpolated Br/OC record is scaled to the



Br/OC value of the core-top sample (5.24 mg g^{-1}) that is closest to the piston core location (station 28; Fig. 1), assuming a terrestrial endmember of zero. The modern NPP of this station is $343.3 \text{ gC m}^{-2} \text{ yr}^{-1}$ which is close to the NPP reconstructed from the top of the piston core record ($334.3 \text{ gC m}^{-2} \text{ yr}^{-1}$). This good correspondence suggests that the upper part of the piston core represents relatively recent depositional conditions.

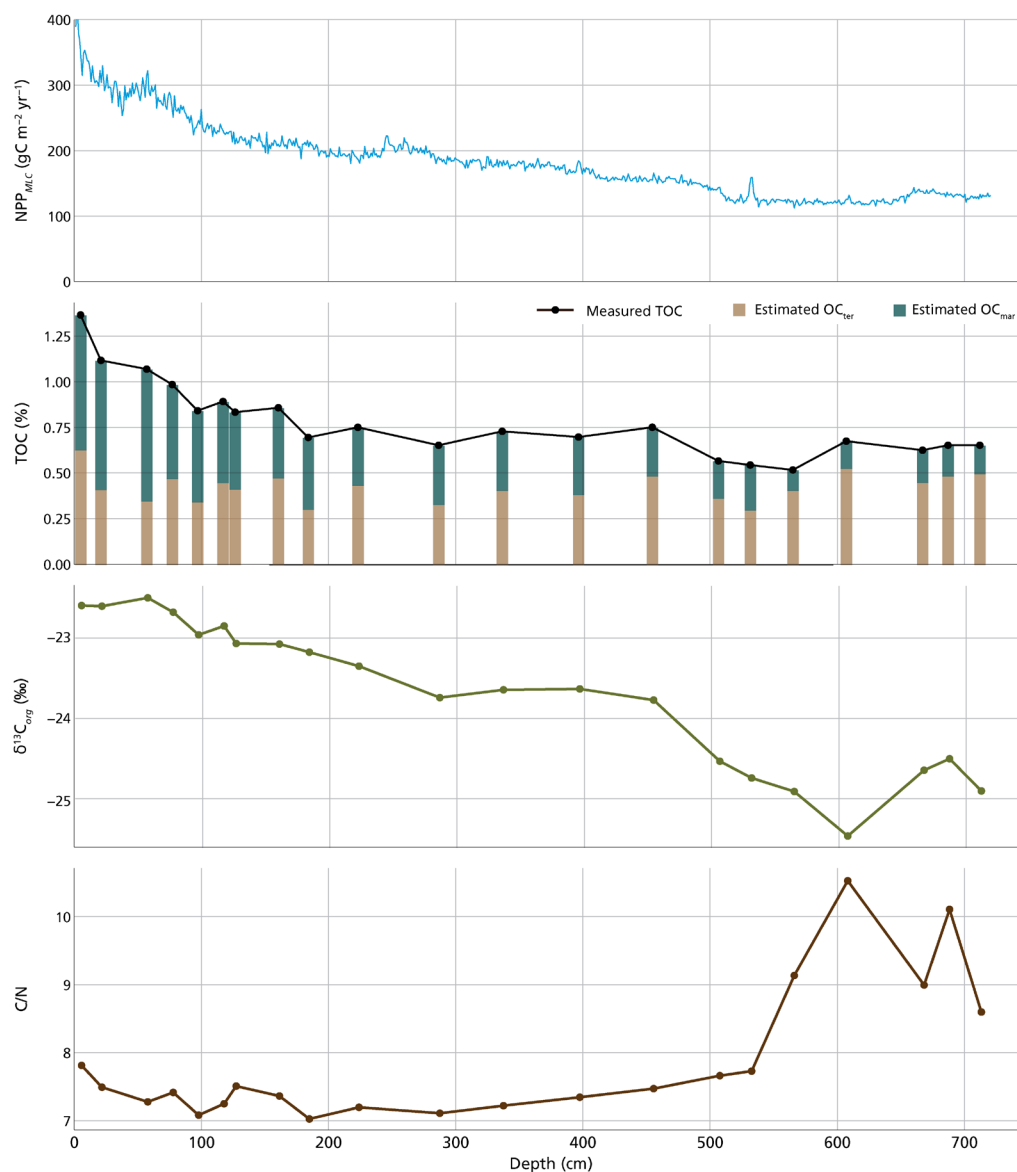


Figure 8: Downcore records of organic matter composition and net primary productivity (NPP). From top to bottom: NPP reconstructed based on multivariate log-ratio calibrated (MLC) organic-bound bromine (NPP_{MLC}), total organic carbon (TOC) together with the estimated relative contributions of marine organic carbon (OC_{mar}) and terrestrial organic carbon (OC_{ter}), bulk organic carbon isotopic composition ($\delta^{13}\text{C}_{\text{org}}$), and carbon-to-nitrogen (C/N) ratio.



555 The reconstructed OC_{mar} and NPP records show lower values in the deeper part of the piston core (400-700 cm), as also
indicated by lower $\delta^{13}C_{org}$ and higher C/N ratios (Fig. 8). Toward the younger sediments of the piston core (<200 cm) OC_{mar}
and NPP increase. The downcore ranges of Br_{org} values (5.7-50.2 ppm), $\delta^{13}C_{org}$ values (-22.5 to -25.5 ‰), C/N ratios (7.0-
10.5), and Br/OC ratios (1.1- 3.2 mg g⁻¹) overlap with those observed in the core-top dataset (Table 2; Fig. S8). This suggests
560 calibration, supporting the application of the Br_{org} -NPP relationship throughout the record.

4. Conclusion

We have shown that Br_{org} can be measured in marine sediments using several digestion methods, with H₂O₂ at 50-80 °C being
565 optimal for accuracy and efficiency. Among the four oxidative digestions conditions tested, the 50 °C condition provides both
chemical and practical advantages: it accelerates OM oxidation relative to lower temperatures while minimizing Br volatility
and safety issues (i.e., pressure build up in sample vials) observed at higher temperatures. Moreover, oxidizing at 50 °C
delivered the most accurate (best recoveries with least bias) and reproducible Br_{org} recoveries, which is why we think this is
the optimal digestion method for Br_{org} .

570 Using a multi-region dataset from the Baltic Sea, North Sea, Atlantic Ocean, Black Sea, and Mediterranean Sea, we have
been able to evaluate the potential of Br_{org} as quantitative proxy for marine productivity. Br_{org} shows a strong relationship with
TOC across all basins and correlates closely with independently derived OC_{mar} estimates based on $\delta^{13}C_{org}$ and C/N ratio,
demonstrating its ability to trace OC_{mar} contributions across a wide range of environmental conditions (e.g., salinity, OC_{ter}
input, BWO levels). Br/OC ratios show limited sensitivity to environmental gradients, indicating that Br enrichment is not
575 primarily controlled by surface-ocean conditions such as salinity. Compared to the traditional methods (i.e., TOC, $\delta^{13}C_{org}$ and
C/N ratio), Br_{org} show the strongest relationship with NPP, which highlights that it is the best OC_{mar} predictor as it best
captures the initial productivity of the typically used proxy methods. This proxy proves to be most sensitive to NPP, particularly
in near-shore higher productive regions, which suggests that Br_{org} is less susceptible to OC source mixing and more directly
reflects changes in OC_{mar} production. However, the application of Br_{org} as proxy for NPP requires careful consideration of the
580 preservation potential during deposition. When all stations are considered, NPP-proxy relationships are weaker, whereas
restricting the dataset to sites with comparable preservation conditions significantly improves NPP-proxy relationships. In oxic
environments, Br_{org} offers the most suitable proxy for OC_{mar} and NPP, as Br-rich labile OM might dominate sites with a high
preservation potential.

We provide a uniform workflow to reconstruct paleoproductivity using an XRF-scanner, which can be defined in three
585 steps. First, raw Br counts and normalized Br to a set of elements can provide quick and qualitative indications of OC_{mar} , and
hence, NPP. Second, for quantitative application, calibration against Br_{org} measured independently on discrete samples is
required. This can involve raw Br counts using MLC or corrected with water content and TOC measurements (Eq. 5) and



linear conversion to Br_{org} . Third, the resulting quantitative Br_{org} record can be used to infer past NPP using the Br_{org} –NPP relationship using the linear relationship presented in Fig. 5d, provided that the sediments are deposited under oxic conditions.

590 Data availability

Datasets for this paper will be deposited at Zenodo with a private access link for review. The dataset will be made public upon acceptance of the manuscript.

Sample availability

The surface samples from RV *Pelagia* cruise 64PE406 in 2016, 64PE407 in 2016, 64PE410 in 2016, 64PE418 in 2017,
595 64PE517 in 2023, and cruise 64PE534 in 2024 are stored at NIOZ, Texel.

Author contribution

The research was designed by GR, RH, and CSH. Sediment data are generated by CSH with help from WB. All authors helped with the data interpretation. CSH wrote the article. GR, WB, MTJM, FS, and RH reviewed and edited the article.

Competing interests

600 The authors declare that they have no conflict of interest.

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