

Supplementary Figures:

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

5 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

10 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)

Table S1: Station information of the 55 core-top locations. Core types are abbreviated as follows: ‘MC’ = multi-core, ‘BC’ = box core, and ‘TC’ = trip core. Cruises 64PE410, 64PE406, and 64PE407 are conducted in 2016, 64PE418 in 2017, 63PE517 in 2023, and 64PE534 in 2024.

Area	Sample	Type core	Latitude (° N)	Longitude (° E)	Depth of water column (m)	Cruise-station
Baltic Sea	1	MC	57.21	19.95	220	64PE410-10
Baltic Sea	2	MC	55.47	15.48	93	64PE410-9
Baltic Sea	3	MC	54.85	13.36	45	64PE410-7
Baltic Sea	4	MC	55.82	12.76	27	64PE410-6
Baltic Sea	5	MC	55.93	12.71	45	64PE410-5
North Sea	6	MC	56.28	12.28	30	64PE410-4
North Sea	7	MC	56.60	11.78	38	64PE410-3
North Sea	8	MC	57.77	11.12	44	64PE410-2
North Sea	9	MC	58.50	9.60	550	64PE410-1
North Sea	10	MC	58.40	5.10	308	64PE534-5
North Sea	11	MC	58.90	5.29	124	64PE534-25
North Sea	12	MC	59.00	5.16	240	64PE534-21
North Sea	13	BC	59.13	4.45	259	64PE517-4
North Sea	14	MC	59.12	3.84	273	64PE517-11
North Sea	15	MC	59.09	3.47	209	64PE517-16
North Sea	16	MC	59.04	2.93	139	64PE517-22
North Sea	17	MC	59.09	2.48	126	64PE517-30
North Sea	18	MC	59.83	4.52	282	64PE534-34
North Sea	19	MC	60.15	4.74	346	64PE534-30
North Sea	20	MC	60.38	4.28	290	64PE517-62
North Sea	21	MC	60.37	3.81	297	64PE517-57
North Sea	22	MC	60.37	3.44	300	64PE517-49
North Sea	23	BC	60.36	3.12	131	64PE517-44
North Sea	24	BC	60.37	2.72	104	64PE517-37
North Sea	25	MC	60.75	4.14	318	64PE534-55
North Sea	26	MC	61.86	3.87	259	64PE517-122
North Sea	27	MC	61.71	3.52	369	64PE517-115
North Sea	28	MC	61.57	3.05	404	64PE517-79
North Sea	29	MC	61.42	2.65	378	64PE517-67
North Sea	30	BC	61.29	2.12	218	64PE517-73

Atlantic Ocean	31	MC	62.34	3.03	385	64PE517-84
Atlantic Ocean	32	BC	63.14	3.91	1012	64PE534-85
Atlantic Ocean	33	BC	62.72	3.35	494	64PE517-100
Atlantic Ocean	34	MC	62.76	2.88	601	64PE517-104
Atlantic Ocean	35	MC	62.62	2.38	574	64PE517-92
Atlantic Ocean	36	MC	62.48	1.89	542	64PE517-96
Atlantic Ocean	37	BC	62.20	0.60	604	64PE534-106
Black Sea	38	MC	42.94	30.03	1543	64PE418-3
Black Sea	39	MC	43.16	29.96	1970	64PE418-2
Black Sea	40	MC	42.83	29.59	2118	64PE418-4
Mediterranean Sea	41	MC	33.30	33.40	1760	64PE406-1
Mediterranean Sea	42	MC	33.73	30.60	2750	64PE406-2
Mediterranean Sea	43	MC	34.12	27.61	2494	64PE406-3
Mediterranean Sea	44	TC	38.42	24.82	346	64PE406-5
Mediterranean Sea	45	MC	35.05	20.64	2774	64PE406-6
Mediterranean Sea	46	MC	34.97	18.11	3609	64PE406-9
Mediterranean Sea	47	MC	34.77	14.18	370	64PE407-1
Mediterranean Sea	48	MC	37.00	13.48	610	64PE407-2
Mediterranean Sea	49	MC	37.99	11.51	467	64PE407-3
Mediterranean Sea	50	MC	38.50	9.00	1284	64PE407-4
Mediterranean Sea	51	MC	38.75	3.75	2391	64PE407-6
Mediterranean Sea	52	MC	38.00	0.75	1963	64PE407-7
Mediterranean Sea	53	MC	36.75	-1.50	1995	64PE407-8
Mediterranean Sea	54	MC	36.33	-3.98	720	64PE407-9
Mediterranean Sea	55	MC	36.25	-6.05	106	64PE407-10

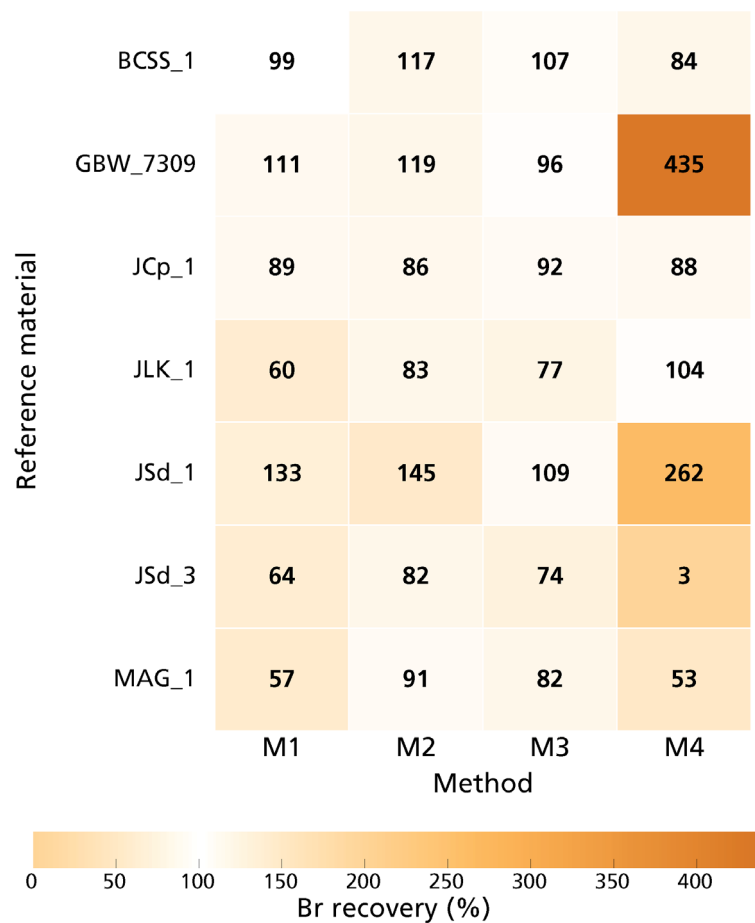


Figure S1: Bromine (Br) recovery rates (%) across the four analytical methods (M1-4) for certified reference materials. Values near 100% indicate high analytical accuracy, values above 100% represent overestimation, and values below 100% indicate underestimation.

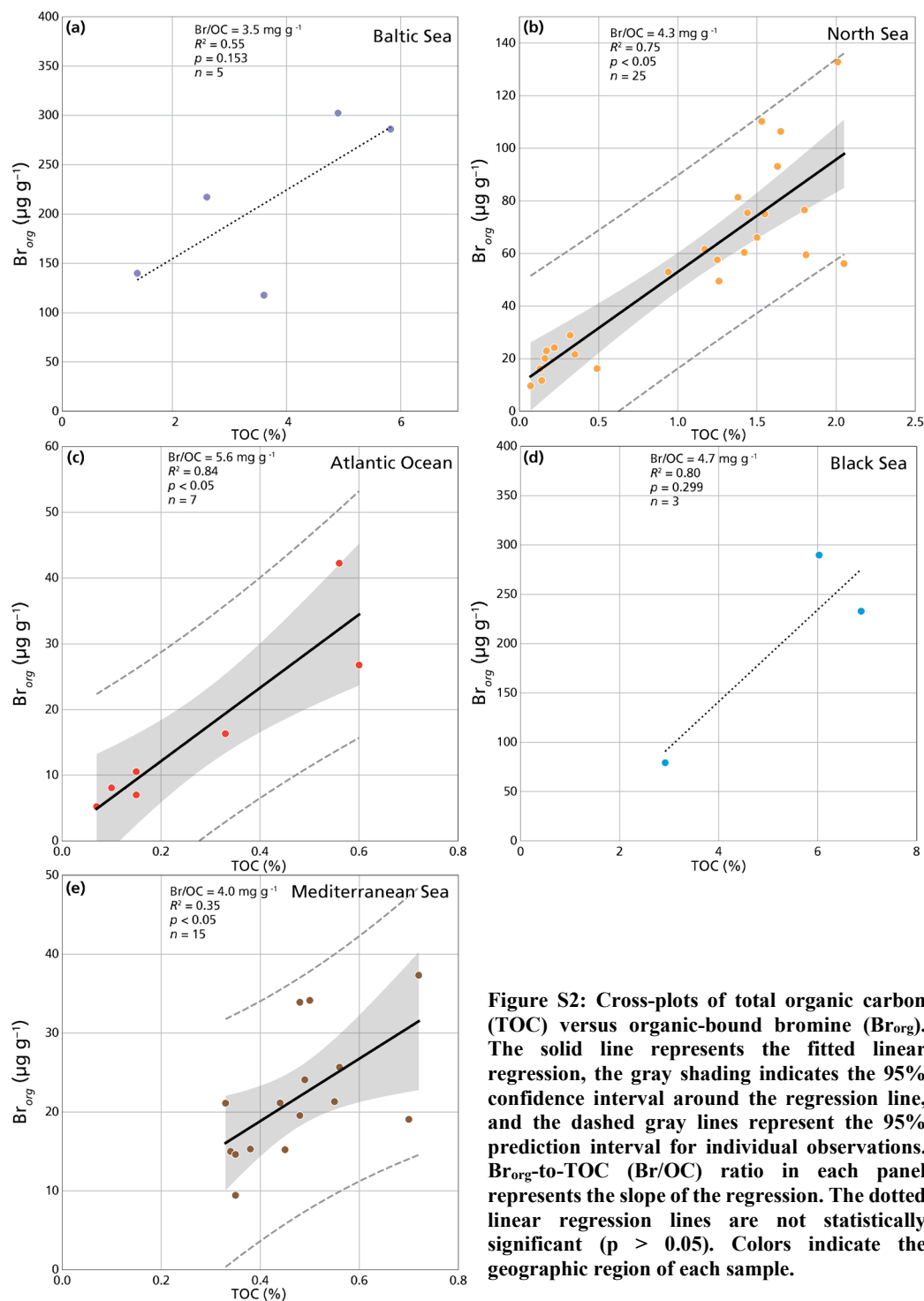


Figure S2: Cross-plots of total organic carbon (TOC) versus organic-bound bromine (Br_{org}). The solid line represents the fitted linear regression, the gray shading indicates the 95% confidence interval around the regression line, and the dashed gray lines represent the 95% prediction interval for individual observations. Br_{org} -to-TOC (Br/OC) ratio in each panel represents the slope of the regression. The dotted linear regression lines are not statistically significant ($p > 0.05$). Colors indicate the geographic region of each sample.

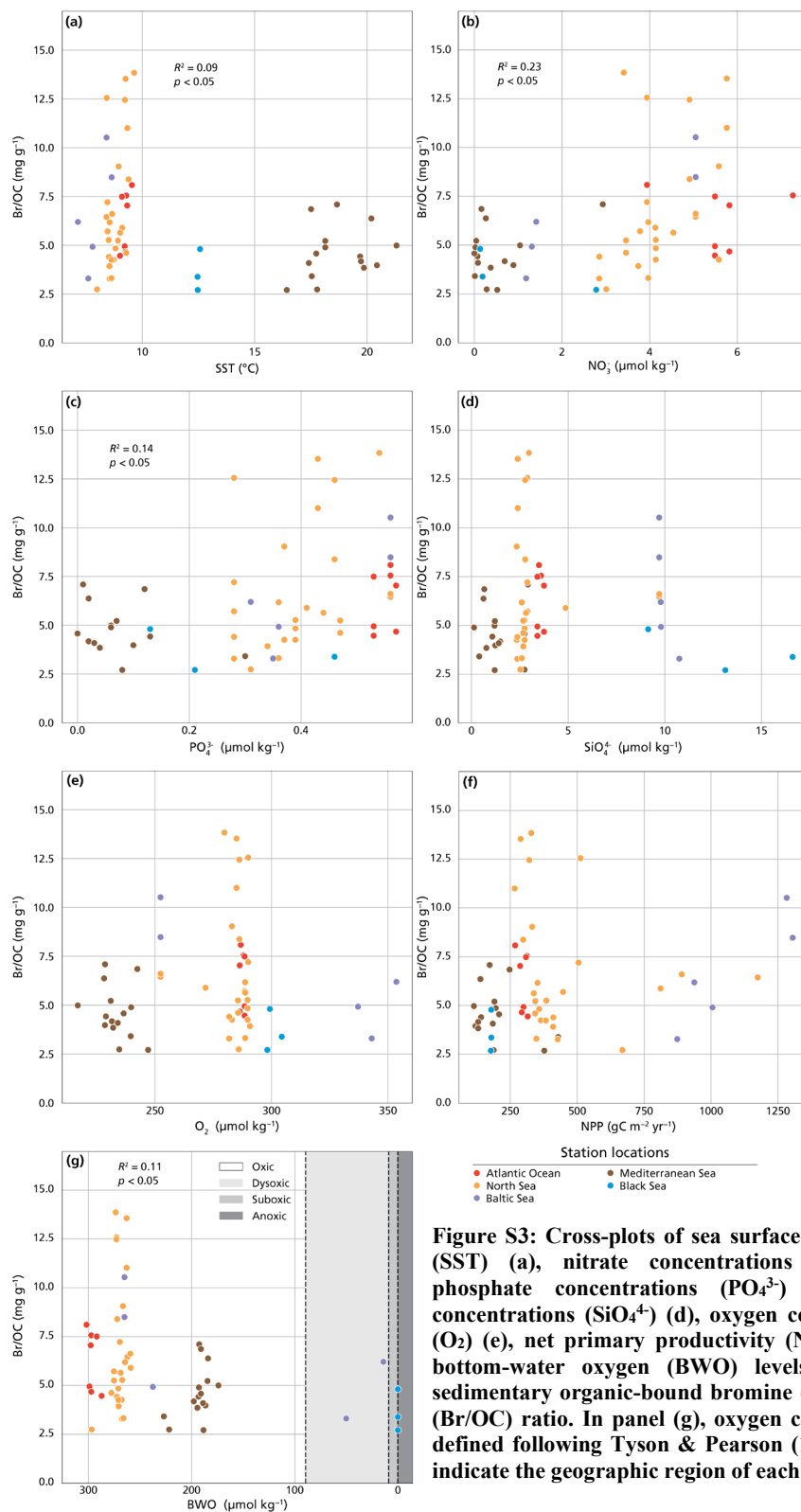


Figure S3: Cross-plots of sea surface temperature (SST) (a), nitrate concentrations (NO₃⁻) (b), phosphate concentrations (PO₄³⁻) (c), silicate concentrations (SiO₄⁴⁻) (d), oxygen concentrations (O₂) (e), net primary productivity (NPP) (f), and bottom-water oxygen (BWO) levels (g) versus sedimentary organic-bound bromine (Br_{org})-to-OC (Br/OC) ratio. In panel (g), oxygen conditions are defined following Tyson & Pearson (1991). Colors indicate the geographic region of each sample.

25 **Table S2: Overview of Br/OC ratios from core-top studies. The table is arranged chronologically from the oldest (top) to the most recent (bottom) publications. Italicized data are derived from river/estuary systems and are therefore not included in the compilation shown in Fig. 3b. All data are retrieved either from reported linear regression analyses or directly from published tables (average values reported).**

Area	Linear regression Br/OC (mg g ⁻¹)	Number of samples	Averaged Br/OC (mg g ⁻¹)	Number of samples	Reference	Data
Barents Sea	12.0	42	7.7	8	Price et al. (1970)	Fig. 4, Table 1
Namibian Shelf	6.0	15			Price & Calvert (1977)	Fig. 3
Massachusetts			9.0*	1	Harvey (1980)	Table 1
Wilkenson Basin			9.4*	1	Harvey (1980)	Table 1
SW Africa Shelf			0.8*	1	Harvey (1980)	Table 1
NW Atlantic Rise			5.0*	1	Harvey (1980)	Table 1
Hudson Canyon			4.1*	1	Harvey (1980)	Table 1
Buzzards Bay			9.0*	1	Harvey (1980)	Table 1
Panama Basin	14.6	11			Pedersen & Price (1980)	Fig. 2
<i>Damariscotta river</i>			4.0	10	<i>Mayer et al. (1981)</i>	<i>Table 1</i>
<i>Sheepscot river</i>			8.8	7	<i>Mayer et al. (1981)</i>	<i>Table 1</i>
Gulf of Maine			6.6	8	Mayer et al. (1981)	Table 1
<i>Estuary Scotland</i>	18.0**	18			<i>Malcolm & Price (1984)</i>	<i>Fig. 4</i>
Gulf of Mexico			2.3	27	Mayer et al. (2007)	Table 1
<i>Mississippi region</i>			0.3***	7	<i>Mayer et al. (2007)</i>	<i>Table 1</i>
Baltic Sea	3.5	5	6.7	5	This study	Fig. 3a, Table 2
North Sea	4.3	25	6.8	25	This study	Fig. 3a, Table 2
Atlantic Ocean	5.6	7	6.3	7	This study	Fig. 3a, Table 2
Black Sea	4.7	3	3.6	3	This study	Fig. 3a, Table 2
Mediterranean Sea	3.9	15	4.6	15	This study	Fig. 3a, Table 2

*not included in Fig. 3b **Br/OC = Br/OC_{mar} with OC_{mar} based on C/N ***data of suspended matter

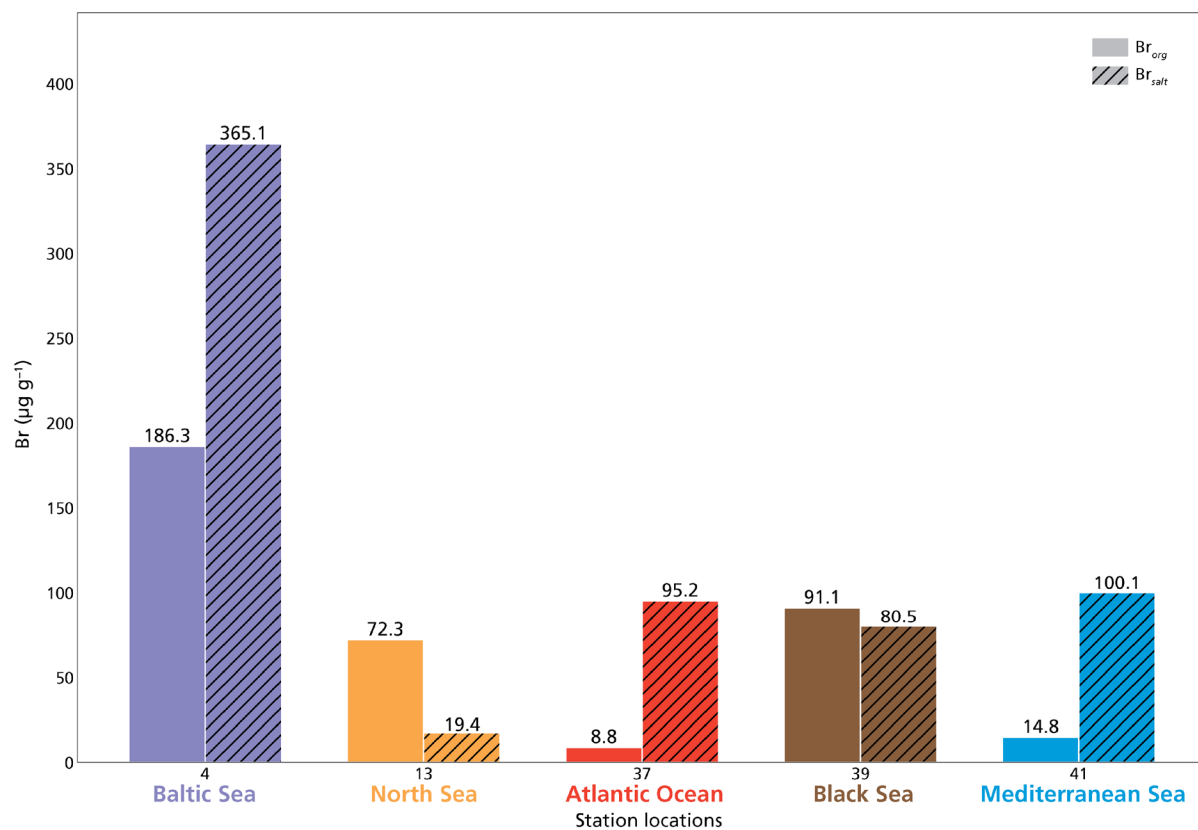


Figure S4: Comparison of salt-associated Br (Br_{salt}) dissolved in Milli-Q water and organic-bound Br (Br_{org}) dissolved in hydrogen peroxide (50 °C). For each basin, one sample has been analyzed of which the station number is written at the x-axis (Fig. 1).

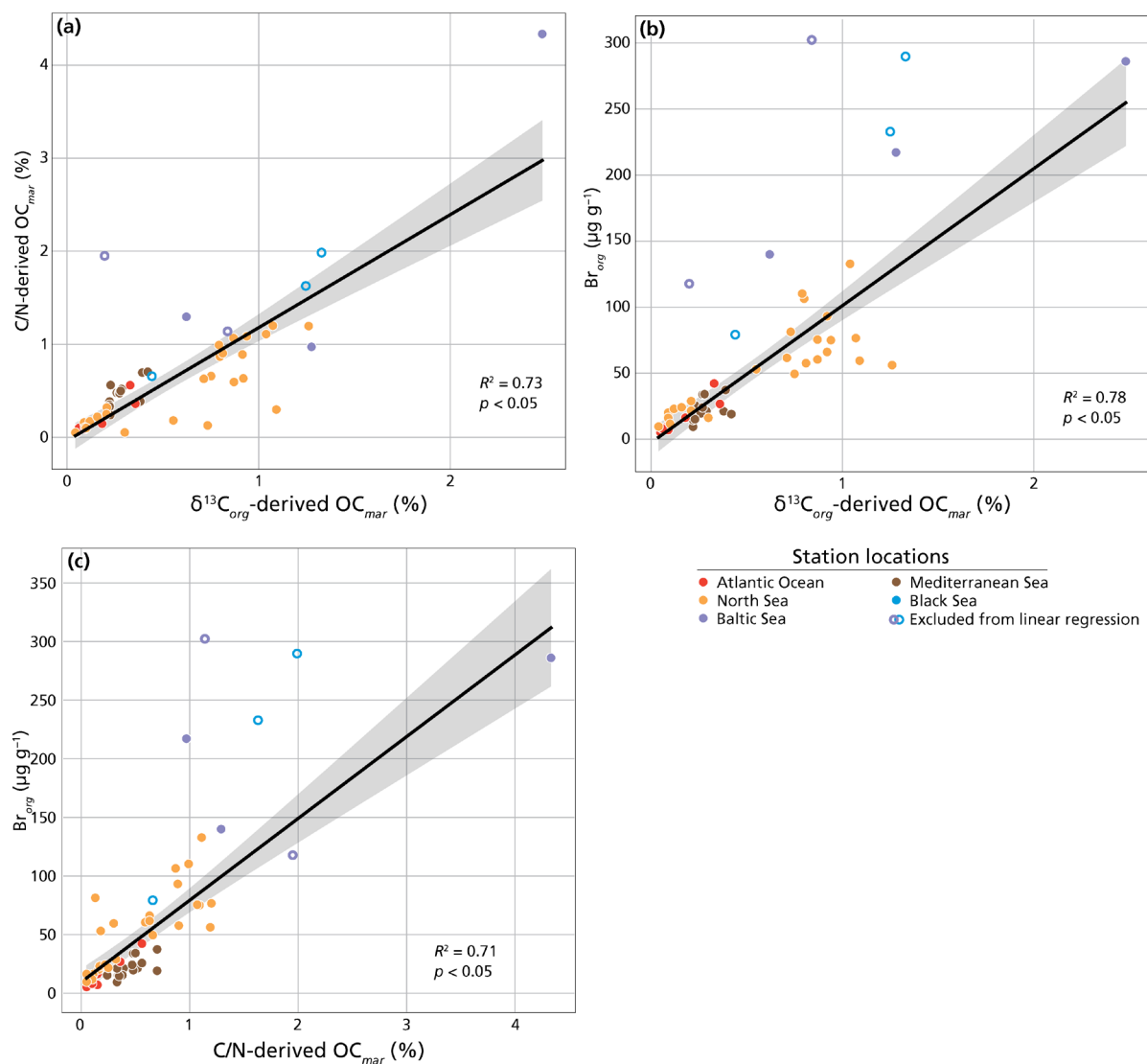
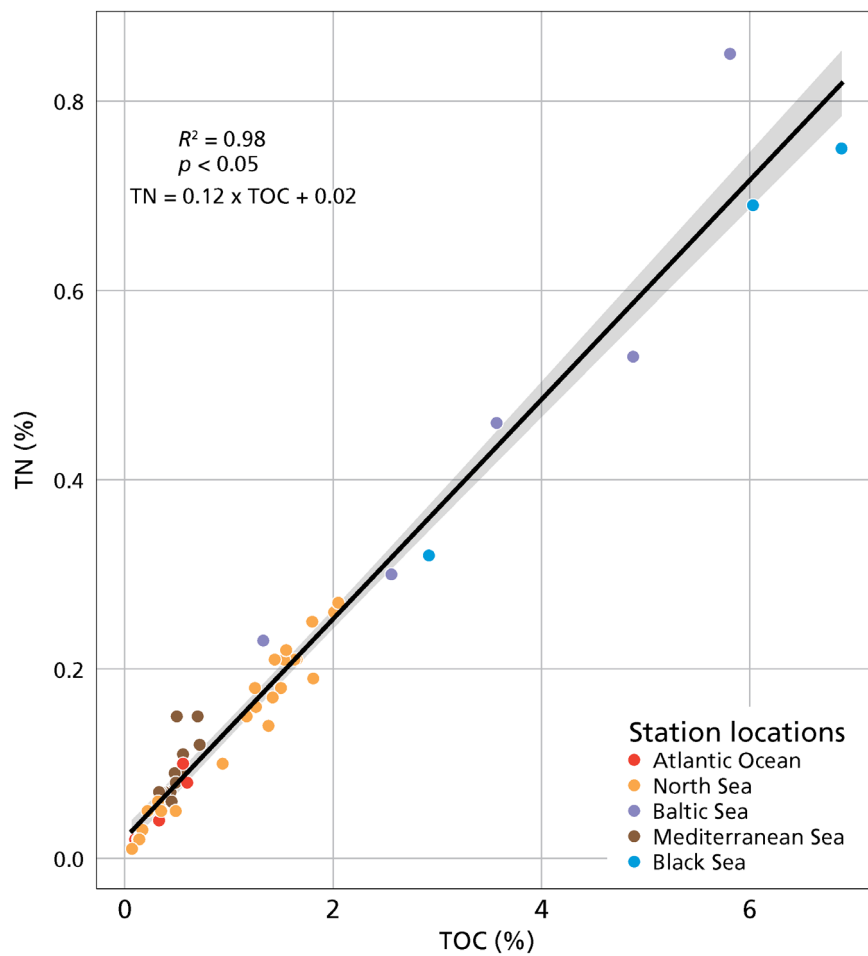


Figure S5: Comparison of marine organic carbon (OC_{mar}) derived from two-endmember models based on stable carbon isotope ratios of bulk organic matter ($\delta^{13}\text{C}_{\text{org}}$), carbon-to-nitrogen (C/N) ratio, and sedimentary organic-bound bromine (Br_{org}). R^2 values are shown for the 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. Regression lines are shown with 95% confidence intervals (gray shading). Colors indicate the geographic region of each sample.



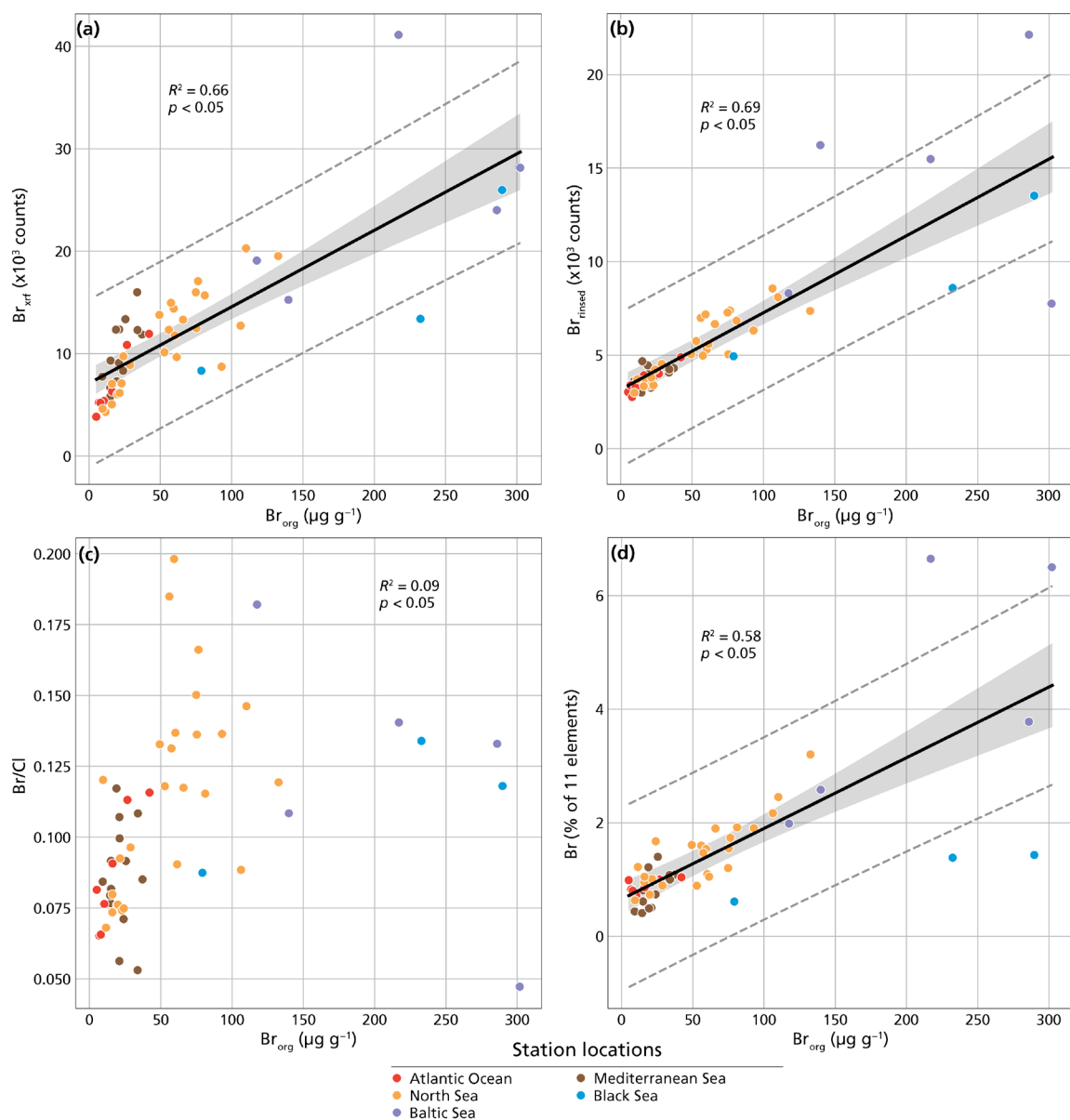


Figure S7: Cross-plots of organic-bound bromine (Br_{org}) versus X-ray Fluorescence-scanning-based indicators: raw bromine (Br) counts from the untreated samples (Br_{xrf}) (a), Br counts from the rinsed samples ($\text{Br}_{\text{rinsed}}$) (b), Br to chlorine (Cl) counts ratio (Br/Cl) (c), and total Br counts normalized to total counts of selected elements ($\text{Br}\%$) (d). R^2 values are shown for the full dataset ($n = 55$). 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.

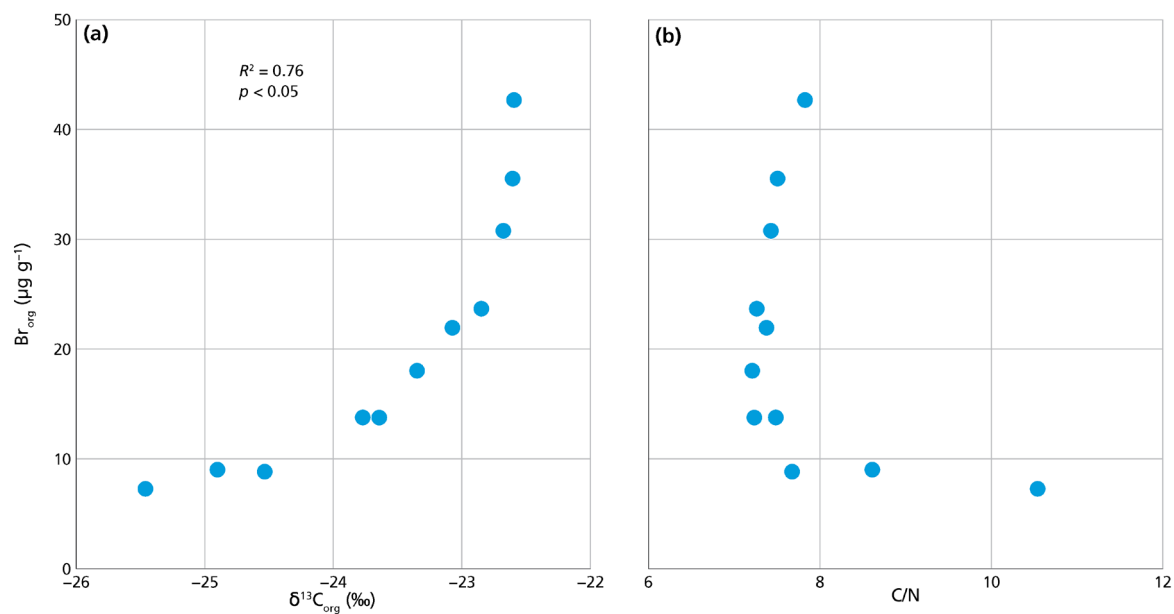


Figure S8: Downcore measurements of sedimentary organic-bound bromine (Br_{org}) versus stable carbon isotope ratios of bulk OM ($\delta^{13}\text{C}_{\text{org}}$) (a) and elemental carbon-to-nitrogen (C/N) ratio (b).