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Physical and biogeochemical controls on seasonal iron, manganese, and cobalt distributions in Northeast Atlantic shelf seas

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1 Ocean circulation and biological cycles drive seasonal variations
2 of dissolved Al, Cd, Ni, Cu, and Zn on the Northeast Atlantic
3 continental margin
4

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20

21 **Key Points:**

- 22 ● Seasonal cycles of biological processes and fluvial inputs drive dissolved trace metal
23 variations in surface waters of Northeast (NE) Atlantic continental margin.
- 24 ● Dissolved Al, Cd, Ni, Cu, and Zn concentrations and metal:P ratios at depth are controlled
25 by the mixing of different water masses.
- 26 ● Mediterranean outflow waters provide a strong imprint on distributions of dissolved trace
27 metals and metal:P ratios in the NE Atlantic Ocean.
28

29 **Abstract**

30 We report the seasonal distributions of dissolved zinc (dZn), nickel (dNi), copper (dCu),
31 cadmium (dCd), aluminum (dAl), and nutrients (nitrate+nitrite (TN), phosphate (P), and silicic
32 acid (Si), as well as their relationships on the Northeast (NE) Atlantic continental margin (Celtic
33 Sea). Along the continental slope, surface dissolved trace metal (dTM) and nutrient concentrations
34 were controlled by seasonal cycling of enhanced phytoplankton uptake in summer,
35 remineralization of organic particles in autumn, and strong mixing in winter. Water columns on
36 the shelf received additional impact from a zero-salinity endmember, e.g., fluvial input from the
37 British Isles. The balance between fluvial input (especially for dCu and dZn) and seasonal cycling
38 of biogeochemical processes resulted in highly variable dTM:nutrient stoichiometry across the
39 shelf. Distributions of dTMs and nutrients at depth on the slope were regulated by the water mass
40 mixing driven by ocean circulation without invoking local remineralization process. The
41 Mediterranean Outflow Waters are especially important to transport Mediterranean-sourced
42 dTMs (e.g., dAl, dZn, and dNi) into the NE Atlantic Ocean and drive dAl:P and dCu:P kinks at a
43 depth of ~ 1000 m. These results highlight the importance of riverine input and ocean circulation
44 on the seasonal distributions of nutrients and nutrient-like dTMs in temperate continental margins,
45 which could further affect local biological carbon pump.

46

47 **Plain Language Summary**

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49

50

51 **1. Introduction**

52 Dissolved (< 0.2 μm) trace metals (dTMs) including zinc (Zn), nickel (Ni), copper (Cu) and
53 perhaps cadmium (Cd), are important micronutrients in marine systems. Low supply of dTMs
54 could potentially affect marine ecosystem structure and functioning (Lohan & Tagliabue, 2018;
55 Morel & Price, 2003; Twining & Baines, 2013). Specifically, Zn is connected to a series of
56 proteins, e.g., carbonic anhydrase and alkaline phosphatase, and Zn availability can influence
57 access of phytoplankton to the dissolved organic phosphorus pool (Lohan & Tagliabue, 2018;

58 Mahaffey et al., 2014). Nickel is primarily associated with urease, and superoxide dismutase has
59 a Ni-containing form. Copper is used in photosynthetic and respiratory electron transport chains
60 (La Fontaine et al., 2002; Twining & Baines, 2013). Cadmium can substitute Zn in carbonic
61 anhydrase in diatoms (Lane et al., 2005; Lane & Morel, 2000), or rather, Cd is mistakenly
62 assimilated into micro-organic cells with other divalent metals (Horner et al., 2013). Due to their
63 close association with biological activities, dissolved Zn (dZn), Ni (dNi), Cu (dCu) and Cd (dCd),
64 are classified as biogenic dTMs (bdTMs) and their vertical distributions resemble those of
65 nutrients (Nitrate+Nitrite (TN), phosphate (P), and silicic acid (Si)) (Bruland et al., 2014; Lohan
66 & Tagliabue, 2018). These dTMs typically exhibit seasonal depleted concentrations in surface
67 waters due to phytoplankton uptake (C. M. Moore et al., 2013; Morel & Price, 2003), and elevated
68 levels at depth due to remineralization of sinking organic particles (Boyd et al., 2017; Bruland et
69 al., 2014). Nutrient and bdTMs, therefore, show significant positive correlations with as examples
70 the dCd-P relationships in the global ocean (Boyle et al., 1976; Boyle, 1988; Middag et al., 2018;
71 Roshan & Wu, 2015; Wu & Roshan, 2015; Xie et al., 2015), dZn-P correlations in the South
72 Atlantic Ocean (Wyatt et al., 2014) and Southern Ocean (Saito et al., 2010), and dNi-P and dCu-
73 Si correlations in the Southern Ocean (e.g., Janssen et al., 2020).

74 However, the linear relationships between bdTMs and nutrients usually show pronounced
75 changes in slopes, e.g., P of $\sim 1.3 \mu\text{M}$ for Cd:P correlation (de Baar et al., 1994; Cullen, 2006;
76 Middag et al., 2018). The origin of such kinks (especially the Cd:P kink) has been scientifically
77 debated over the last decades. Some hypotheses point towards deeper regeneration of Cd relative
78 to P (Boyle, 1988; Roshan & DeVries, 2021), or enhanced Cd uptake due to the limitation of bio-
79 essential elements in surface waters (Cullen, 2006; Sunda & Huntsman, 2000). Kinks were also
80 assigned to a chemical replacement between Co, Zn, and Cd in carbonic anhydrase (Morel et al.,
81 1994; Price & Morel, 1990) or a change in bioavailability of Cd through organic complexation
82 (Bruland, 1992). Recent studies demonstrated that the mixing of water masses with different Cd:P
83 ratios could be a dominant factor accounting for the observed kinks (Baars et al., 2014; Middag
84 et al., 2018; Xie et al., 2015). In addition, external sources such as continental inputs and dust
85 deposition (Menzel Barraqueta et al., 2018; Middag et al., 2022), that can be traced by dissolved
86 aluminum (dAl) inputs (Han et al., 2008; Measures & Edmond, 1988), can affect bdTM
87 distributions in the ocean. Since there is a continued debate surrounding the drivers underpinning

88 bdTM distributions, further investigations regarding the occurrences of nutrients and bdTMs as
89 well as their relationships are crucial for understanding biogeochemical cycles in paleo – and
90 modern oceans.

91 Continental margins with their shelves and slopes are junctions between terrestrial systems
92 and the ocean. The disproportionately high primary production and particulate organic carbon
93 export make continental margins important transition zones for the marine carbon cycle (Muller-
94 Karger et al., 2005; Simpson & Sharples, 2012; Zhang et al., 2019). Here, we report on the
95 seasonal distributions of bdTMs, dAl, and nutrients on the Northeast (NE) Atlantic continental
96 margin (Celtic Sea), which is characterized by large seasonal variations of biological activities
97 (Birchill et al., 2017), a complex bathymetry and a dynamic water circulation (Fig. 1a). A high
98 sampling resolution (Fig. 1b) offers us an ideal opportunity to study the influence of terrestrial
99 inputs, biogeochemical processes and ocean circulation on the seasonal variations of bdTMs and
100 their relationships with nutrients in this system.

101

102 **2. Methods**

103 The sampling procedures have been reported in detail by Rusiecka et al. (2018). We
104 conducted one transect on the continental shelf of the Celtic Sea, from Station A near the Bristol
105 channel to station CS2 near the shelf break (Fig. 1b). Two off-shelf transects were conducted
106 along a canyon (stations Fe01 - Fe07, Fe15) and a spur (stations Fe08 - Fe14) (Fig. 1b). Samples
107 were collected on board the *RRS Discovery* during three different seasons: an autumn cruise in
108 November 2014 (DY018), a spring cruise in April 2015 (DY029), and a summer cruise in July
109 2015 (DY033).

110 Seawater samples for dTM analyses were collected following GEOTRACES protocols
111 (Cutter et al., 2017). Samples were filtered immediately upon collection using a 0.2 μm filter
112 capsule (Acropack). Trace metals were pre-concentrated at GEOMAR using an automated system
113 (SC-4 DX SeaFAST pico; ESI) and analyzed by high-resolution inductively coupled plasma mass
114 spectrometry (HR-ICP-MS, Thermo Fisher Element XR) as per Rapp et al. (2017). Dissolved Al
115 concentrations were analyzed by a spectrofluorometer (Cary Eclipse) as per Hydes & Liss (1976).
116 Short-lived radium (Ra) isotopic activities, ^{223}Ra (half-life, $t_{1/2} = 11.4$ days) and ^{224}Ra (half-life,

117 $t_{1/2} = 3.66$ days), were counted from large volume samples using a Radium Delayed Coincidence
118 Counter (W. S. Moore, 2008). Radium isotope activities here are reported in excess of activity
119 supported by their parent isotopes in the water column. Nutrients, P, Si, and TN, were measured
120 on board using techniques described in Woodward & Rees (2001), according to the International
121 GO-SHIP nutrient manual recommendations (Hydes et al., 2010). Further details can be found in
122 the supporting information.

123

124 **3. Results and discussion**

125 Dissolved Cd, Zn, Ni, and Cu exhibited nutrient-like vertical distributions during all seasons
126 on the NE Atlantic continental margin (Fig. 2, Fig. 3), with the lowest concentrations observed in
127 surface waters due to biological utilization, and elevated concentrations at depth ascribed to
128 remineralization (Bruland et al., 2014; C. M. Moore et al., 2013). The canyon and spur transects
129 showed identical vertical profiles for dTMs and nutrients across all seasons. In the following
130 section, both transects on the slope were combined as a slope transect. While the deep bdTM and
131 nutrient concentrations on the continental slope were relatively constant throughout the year,
132 surface bdTM and nutrient levels on the continental shelf and slope showed pronounced seasonal
133 variations (Table S2, Fig. S2, Fig. S3). Kinks in dTM:nutrient ratios (e.g., dZn:P and dCu:P) ratios
134 were observed on the continental slope at a depth of ~ 100 m and ~ 1000 m (Fig. S4). The shelf
135 seas showed higher dCu, dNi, dZn, and Si concentrations than those on the slope (Fig. 3),
136 accompanied by varying dTM: nutrient correlations (Fig. S5).

137

138 **3.1 Biological influence on seasonal variations in surface dTM concentrations along** 139 **the continental slope**

140 A seasonal mixed layer (SML) covers the continental slope with a depth of $\sim < 100$ m from
141 spring to autumn (Supporting information: Hydrography). A reduction in dTM and nutrient levels
142 in the SML (especially at depths < 30 m) was observed between April 2015 and July 2015, due to
143 biological utilization and water column stratification (Birchill et al., 2017) (Fig. S6, Table S2).
144 The total drawdown of surface (depth < 30 m) dTMs and nutrients on the slope from April to July
145 were: dAl 2.68 ± 2.25 nM, dCd 79.5 ± 45.1 pM, dCu 0.08 ± 0.11 nM, dNi, 0.67 ± 0.31 nM, dZn

146 0.10 ± 0.25 nM, P 0.35 ± 0.11 μ M, TN 6.71 ± 1.83 μ M, and Si 2.44 ± 0.47 μ M (Table S2). The
 147 fraction of Cd, Ni, and TN removed over this period on the slope was higher, and drawdown of
 148 Cu was lower than reported for the study region between January 1994 and June 1995 (36% TN,
 149 41% Cd, 22% Cu, 14% Ni) (Cotté-Krief et al., 2002) and March – June 1987 (56% Cd, 12% Cu,
 150 4% Ni) (Kremling & Pohl, 1989). The decrease in dTM and nutrient concentrations was the
 151 consequence of phytoplankton uptake in summer, and the overall “uptake” ratio of phytoplankton
 152 normalized to P was:

$$153 \quad (N_{19}Si_7P_1)_{1000}Al_{7.5}Ni_{1.9}Zn_{0.34}Cu_{0.23}Cd_{0.23}$$

154 The surface dTM and nutrient concentrations on the continental slope increased from July
 155 to November, accompanied by comparable correlations between dTMs/nutrients and AOU at 20
 156 – 100 m (Fig. S7). Hence, the increase in surface dTM and nutrient concentrations in November
 157 was attributed to the remineralization of organic particles (Anderson & Sarmiento, 1994; Lohan
 158 & Tagliabue, 2018). Both surface and deep waters showed similar dTMs/nutrients – AOU
 159 correlations in April, likely reflecting water column mixing in winter (Fig. S7). Therefore, the
 160 increase in surface dTM and nutrient concentrations from November to April was attributed to
 161 resupply from subsurface waters. Using concentration differences between July and November
 162 (Table S2), we estimated the apparent “remineralization” ratio of dTMs and nutrients normalized
 163 to P as:

$$164 \quad (N_{15}Si_6P_1)_{1000}Al_{10.7}Ni_{1.9}Zn_{0.56}Cu_{0.49}Cd_{0.28}$$

165 and the “winter mixing” ratio estimated from the concentration differences between November
 166 and April observations as:

$$167 \quad (N_{21}Si_{7.5}P_1)_{1000}Al_{5.4}Ni_{1.8}Zn_{0.19}Cu_{0.06}Cd_{0.19}$$

168 The estimated Zn:P and Cu:P ratios between “uptake” and “remineralization” , but the
 169 “winter mixing” ratios varied strongly from these ratios, probably due to a relatively limited
 170 seasonal variations and large concentration ranges of both metals (Fig. S6; Table S2). The N:P,
 171 Si:P, Ni:P, and Cd:P ratios were relatively constant, indicating a close association of Ni and Cd
 172 with biological processes in surface waters across all seasons. The observed “uptake”,
 173 “remineralization”, and “winter mixing” ratios are close to the overall dTM:P ratios in the SML
 174 (depth of $< \sim 100$ m) (dAl:P of 8.68 mmol mol⁻¹, dCd:P of 214 μ mol mol⁻¹, dCu:P of 0.199 mmol
 175 mol⁻¹, dNi:P of 1.53 mmol mol⁻¹, and dZn:P of 0.37 mmol mol⁻¹) (Table S3). The dTM:P ratio

176 here is broadly consistent with metal:P ratios observed in full depth profiles in the North Atlantic
177 Ocean (Zn:P of 2.6 ± 1.0 mmol mol⁻¹, Ni:P of 1.6 ± 0.1 mmol mol⁻¹, Cu:P of 0.30 mmol mol⁻¹,
178 and Cd:P of 0.24 ± 0.12 mmol mol⁻¹) (Middag et al., 2018; Twining & Baines, 2013 and references
179 therein) and the extended Redfield ratio of phytoplankton cultures (Zn:P of 0.80 mmol mol⁻¹, Cu:P
180 of 0.38 mmol mol⁻¹, and Cd:P of 0.21 mmol mol⁻¹) (Ho et al., 2003). Therefore, the positive
181 correlations between dTMs and nutrients in the SML on the continental slope across all seasons
182 (Fig. S4) generally reflected the seasonal cycling of biological uptake in summer, remineralization
183 of organic particles in autumn, followed by winter mixing.

184 **3.2 Additional fluvial inputs of dTMs on the continental shelf**

185 Seasonal cycling of biological processes also affected the dTM and nutrient distributions on
186 the continental shelf of the NE Atlantic Ocean. Using station CCS (central Celtic Sea) as an
187 example (Fig. S8), surface dTM and nutrient concentrations decreased from April to July due to
188 phytoplankton uptake and slightly increased from July to November due to remineralization. The
189 gradual increase in nutrient concentrations from April to November at depths > 50 m was
190 attributed to the remineralization of sinking organic particles (Birchill et al., 2017; Lohan &
191 Tagliabue, 2018). Unlike similar dTM:P ratios at all stations on the slope, the overall dTM:P ratios
192 on the shelf varied greatly between sampling locations (Fig. S9). These variations were
193 accompanied by gradually decreasing dTM concentrations with increasing distance offshore (Fig.
194 S10), suggesting the dTM stocks on the shelf were determined by external sources. Benthic
195 sediments were likely not an important source for the enhanced dTMs, since dTM concentrations
196 did not change significantly with ²²³Ra_{xs} and ²²⁴Ra_{xs} activities (Fig. S11) which indicates minimal
197 benthic TM supply.

198 Instead, a decreasing salinity with increasing distance offshore (Fig. 3) and strong negative
199 correlations between dTMs (especially for dAl, dCu, dNi, and dZn) and salinity suggest dTM
200 distributions on the shelf (Fig. S12) were augmented by a dTM-rich zero-salinity endmember e.g.,
201 riverine input from the British Isles through Irish Sea and/or the Bristol channel (Achterberg et
202 al., 1999; Kremling & Hydes, 1988). Based on the correlations between subsurface (depth of 50
203 – 200 m to exclude surface biological activities) dTMs, nutrients, and salinity in April when
204 significant correlations were observed, the apparent endmember concentrations of the freshwater

205 endmember at salinity of 0 were calculated as: dCd, 139 ± 1202 pM; dCu, 214 ± 26 nM; dNi, 26.1
206 ± 22.7 nM; dZn, 392 ± 63 nM; TN, 59.4 ± 79.2 μ M; P, 6.15 ± 4.67 μ M; and Si, 192 ± 37 μ M. The
207 enrichment of dCu, dZn, and Si relative to P in the fluvial endmember caused gradually decreasing
208 dCu:P and dZn:P ratios with increasing distance stretching from station A to CS2 (Fig. S9). Fluvial
209 input was not a major source of dCd and dNi, thereby resulting in increasing dCd:P and dNi:P
210 ratios with offshore distance. At station CS2, the dTM:P, TN:P, and Si:P ratios were close to those
211 on the continental slope.

212 The salinity in subsurface waters at station A gradually increased from ~ 34.9 in April to \sim
213 35.3 in November (Fig. 3), suggesting gradually decreasing fluxes of riverine waters or an
214 increasing contribution of North Atlantic waters, or a combination of both. For instance, the water
215 flow of River Severn, the longest river of the British Isles, shows decreasing flows from winter
216 to summer and autumn [website, Open WIMS data]. The estimated zero-salinity endmember
217 generally shows highest dTM concentrations in July and lowest values in November (Fig. S12),
218 possibly reflecting seasonal variations of the zero-salinity endmember. This phenomenon can
219 alternatively be explained by the enhanced influence of remineralization at stations away from
220 the fluvial source, evidenced by the gradually increased subsurface nutrient concentrations at
221 station CCS relative to other stations (Fig. S12). Therefore, the distributions of dTMs and
222 nutrients as well as their correlations on the NE Atlantic continental shelf were balanced by
223 sources and seasonal cycling of biogeochemical processes.

224

225 **3.3 Water mass mixing drive metal:P kinks at depth**

226 The waters on the NE Atlantic continental slope between the SML and ~ 1000 m are
227 characterized by the presence of East North Atlantic Central Waters (ENACW), Mediterranean
228 Outflow Waters (MOW), and Sub-Arctic Intermediate Waters (SAIW) (Fig. S13). The increasing
229 percentage contribution of MOW with depth is accompanied by increasing dTM and nutrient
230 concentrations. At depths of 950 – 1050 m with the highest MOW contribution ($\sim 60\%$), waters
231 showed strongly elevated dAl (20.1 ± 1.5 nM) compared with shallow waters (Table S4). Waters
232 below ~ 1000 m are characterized by a gradually decreasing MOW contribution, and increasing
233 contributions of Labrador Sea Water (LSW) and North East Atlantic Deep Waters (NEADW) (Fig.

234 S13). The concentrations of dTMs and nutrients continuously increased with depth, showing dAl
235 of ~ 18 nM, dCd of ~ 350 pM, dCu of ~ 2.2 nM, dNi of ~ 5 nM, dZn of ~ 2.7 nM in bottom waters
236 (Table S2). These concentrations are similar to the reported deep dCd (310 ± 26 pM), dNi ($4.1 \pm$
237 0.4 nM), and dCu (1.56 ± 0.33 nM) values for this region (Cotté-Krief et al., 2002) and consistent
238 with reported deep water concentrations of dTMs and nutrients in the North Atlantic Ocean
239 (Achterberg et al., 2021; Saager et al., 1997).

240 No apparent kinks were identified for ratios of dCd:P ($261 \mu\text{mol mol}^{-1}$), dNi:P (1.94 mmol
241 mol^{-1}), and dZn:P ($2.26 \text{ mmol mol}^{-1}$) in waters > 100 m (Table S3). The dCd:P ratio here is
242 consistent with the dCd:P ratio ($280 \mu\text{mol mol}^{-1}$, at P $0.5 - 1.5 \mu\text{M}$) from the north Atlantic Ocean
243 (GEOTRACES Intermediate Data Product Group, 2021; Middag et al., 2018; Roshan & Wu, 2015)
244 and the expected dCd:P ratio in the Atlantic Ocean using a Rayleigh model with a fractionation
245 factor ($\alpha_{\text{Cd/P}}$) of $1.6 - 2$ (Elderfield & Rickaby, 2000) (Fig. S14). The lack of dCd:P kink also
246 agrees with the linear dCd-P relationship at $P < 1.3 \mu\text{mol kg}^{-1}$ (de Baar et al., 1994; Cullen, 2006;
247 Frew & Hunter, 1992; Middag et al., 2018). The dNi - P and dZn - P correlations here were
248 similar to those reported for the North Atlantic Ocean with dNi:P of $2.01 \text{ mmol mol}^{-1}$ dZn:P of
249 $1.77 \text{ mmol mol}^{-1}$ at P of $0.5 - 1.5 \mu\text{M}$ (Fig. S14) (GEOTRACES Intermediate Data Product Group,
250 2021). In contrast, the dCu:P ratio on the continental slope increased from $0.31 \text{ mmol mol}^{-1}$ at 100
251 $- 1000$ m to $2.78 \text{ mmol mol}^{-1}$ at depths > 1000 m and the dAl concentrations showed pronounced
252 variations with increasing P levels. Considering the small variations of dCu concentrations in
253 surface waters (Table S2) and that Al is not a bio-essential element, the occurrence of changes in
254 dCu:P and dAl:P ratios should reflect physical (e.g., water mass mixing) rather than biological
255 processes. The importance of water mass mixing on the distributions of deep-water dTMs and
256 nutrients is further demonstrated by the significant positive loadings of dTMs, nutrients, depth,
257 density, and AOU in the same principal component (RC1, 55.9% of total variance) when using
258 principal component analysis (PCA) (Supporting information: PCA, Fig. S15).

259 Here, we estimated the elemental composition of each water mass using a three-step
260 calculation (Table S4). (1) At depths $< \sim 1000$ m, endmember concentrations of MOW were
261 calculated from the positive linear correlations with dTM concentrations as dTM levels decreased
262 with increasing contributions of ENACW and SAIW (Fig. S16). (2) Then, the dTM (and nutrient)
263 concentrations were corrected by removing the MOW contributions. At depths $> \sim 1000$ m, the

264 residual dTMs were contributed by LSW, NEADW, and SAIW, where the endmember SAIW
265 concentrations were calculated from the significant negative linear relationship between corrected
266 SAIW contribution and corrected dTM concentrations (Fig. S17). The endmember concentrations
267 of NEADW were evaluated at LSW < 1% (corresponding depth of 1000 – 1500 m) (Fig. S18a).
268 (3) Finally, the endmember concentrations of LSW and ENACW were estimated by removing the
269 contributions of MOW, SAIW, and NEADW (Fig. S18b and c).

270 All dTMs and nutrients showed significant correlations with percentage contributions of
271 LSW and ENACW at the final step, despite uncertainties propagating during each step in the
272 calculations. The predicted dTM concentrations, reconstructed by direct multiplication of water
273 mass fractions with their endmember values, illustrate almost identical values with the observed
274 concentrations (Fig. S19) with very low residuals (Fig. S20). In addition, the estimated
275 endmember dAl concentrations of MOW are consistent with the increased dAl concentrations of
276 MOW due to the dissolution of atmospherically deposited Saharan dust in the Mediterranean
277 Basin ($dAl = 35.6 \pm 6.8$ nM) (Table S4) (GEOTRACES Intermediate Data Product Group, 2021;
278 Measures et al., 2015; Rolison et al., 2015). The calculated endmember concentrations of
279 NEADW agree with deep water (> 4000 m) concentrations in the NE Atlantic Ocean
280 (GEOTRACES Intermediate Data Product Group, 2021; Liu & Tanhua, 2021), where NEADW
281 is a persistent feature (van Aken, 2000a; García-Ibáñez et al., 2015, 2018; Reinthaler et al., 2013).
282 Therefore, our estimations on the apparent endmember concentrations of each water mass are
283 robust to show their relative chemical compositions.

284 The correlations between reconstructed dTMs and nutrients corresponded to the observed
285 results, and no kinks were observed for the correlations between dCd, dNi, dZn, and P, while
286 dCu:P and dAl:P ratios showed deflections at ~ 1000 m (Fig. 4). Furthermore, the dTM:AOU and
287 nutrient:AOU ratios changed abruptly at depths of ~ 1000 m and ~ 2000 m across all seasons (Fig.
288 S7), coinciding with the variations of water mass fractions from MOW+SAIW+ENACW at 100
289 – 1000 m to MOW+NEADW+LSW at > 1000 m. Therefore, the AOU variations at depths > 100
290 m mostly reflect physical processes (e.g., water mass mixing) rather than local biological
291 processes. These observations indicate that the distributions of subsurface dTMs and nutrients
292 and their ratios on the NE Atlantic continental margin are mainly controlled by the mixing of
293 water masses driven by ocean circulation and local remineralization processes therefore make a

294 minor contribution.

295 **3.4 The influence of MOW on the dTM distributions on the NE Atlantic Ocean**

296 The appearances of dTM:nutrient and dTM:AOU kinks at ~ 1000 m and ~ 2000 m are closely
297 related to the maximum and diminished occurrence of MOW (Fig. 4, Fig. S7), probably ascribed
298 to the distinctive dTM and nutrient stoichiometry of MOW relative to other water masses (Table
299 S2). For instance, MOW shows much higher dAl:P but lower dCu:P ratios than LSW and
300 NEADW (Fig. S21), thus creating kinks of dCu:P and dAl:P ratios at the maximum occurrence
301 of MOW. Therefore, MOW provides an important imprint on dTM distributions on the continental
302 slope of the NE Atlantic Ocean.

303 The MOW is formed in the Mediterranean Sea and spreads across the NE Atlantic Ocean at
304 ~ 500 – 1500 m towards the Bay of Biscay and further along the shelf break of Celtic Sea (van
305 Aken, 2000b; Price et al., 1993). The occurrence of MOW in the NE Atlantic Ocean can be
306 observed in elevated dAl concentrations and salinity (Measures et al., 2015; Middag et al., 2022;
307 Rolison et al., 2015) at depths of 900 – 1400 m (Fig. S22). Similar to the long-distance transport
308 of anthropogenic Pb from MOW to the NE Atlantic continental margin (Rusiecka et al., 2018),
309 our results suggest that nutrient and dTM signals of MOW were transported from the Gibraltar
310 channel to the NE Atlantic continental margin. The significant correlations between dTMs and
311 salinity (Fig. S23) demonstrate that dTMs in the MOW core were predominantly controlled by
312 the conservative isopycnal mixing between MOW and lower salinity water masses (e.g., SAIW
313 with similar density range to MOW; Johnson & Gruber, 2007) during ocean circulation, rather
314 than scavenging removal. Specifically, the dAl, dZn, and dNi concentrations of the MOW core
315 decreased with decreasing salinity, suggesting the saline MOW is a net source to deliver
316 Mediterranean-sourced Al, Zn, and Ni into the NE Atlantic Ocean (Middag et al., 2022).

317 Furthermore, the minor seasonal variations of dTMs and nutrients in the MOW core possibly
318 reflect seasonal cycles of water mass circulation along the slope of the NE Atlantic continental
319 margin. Due to the wind-driven processes (Roque et al., 2019), the influence of SAIW in the NE
320 Atlantic Ocean declined in autumn. Hence, higher MOW signals (e.g., higher salinity) were
321 observed along the continental slope in November with respect to April and July. Accordingly,
322 the MOW core on the slope showed slightly higher dAl and dZn but lower dCd concentrations in

323 November than those in April and July (Fig. S23).

324

325 **4. Conclusions**

326 Our findings illustrate the seasonal variations of dTMs and nutrients in surface waters on the
327 continental margin of the NE Atlantic Ocean. The surface dTM concentrations on the shelf were
328 also influenced by a zero-salinity endmember, e.g., fluvial materials from the British Isles.
329 Therefore, temperate shelf sea ecosystems can be influenced by local biological processes and
330 external sources, where riverine inputs play an essential role to deliver terrestrial dTMs to the
331 ocean. The dTM concentrations and metal:P ratios at depth in the slope region can be explained
332 by mixing of water masses driven by ocean circulation without invoking local remineralization.
333 Specifically, the long-distance transportation of MOW delivers Mediterranean-sourced dTMs
334 (e.g., dAl, dZn, and Ni) into the NE Atlantic Ocean and drives dAl:P and dCu:P kinks at a depth
335 of ~ 1000 m along the NE Atlantic continental margin. Future climate change driven changes in
336 dust inputs into the Mediterranean and water mass characteristics in the subpolar gyre, therefore,
337 will have consequences for nutrient stoichiometry and the biological carbon cycles in the NE
338 Atlantic Ocean.

339

340 **Acknowledgments**

341

342 **Data availability**

343 Data are held at the British Oceanographic Data Centre (<http://www.bodc.ac.uk/>).

344 **Author contributions:**

345

346

347 **References**

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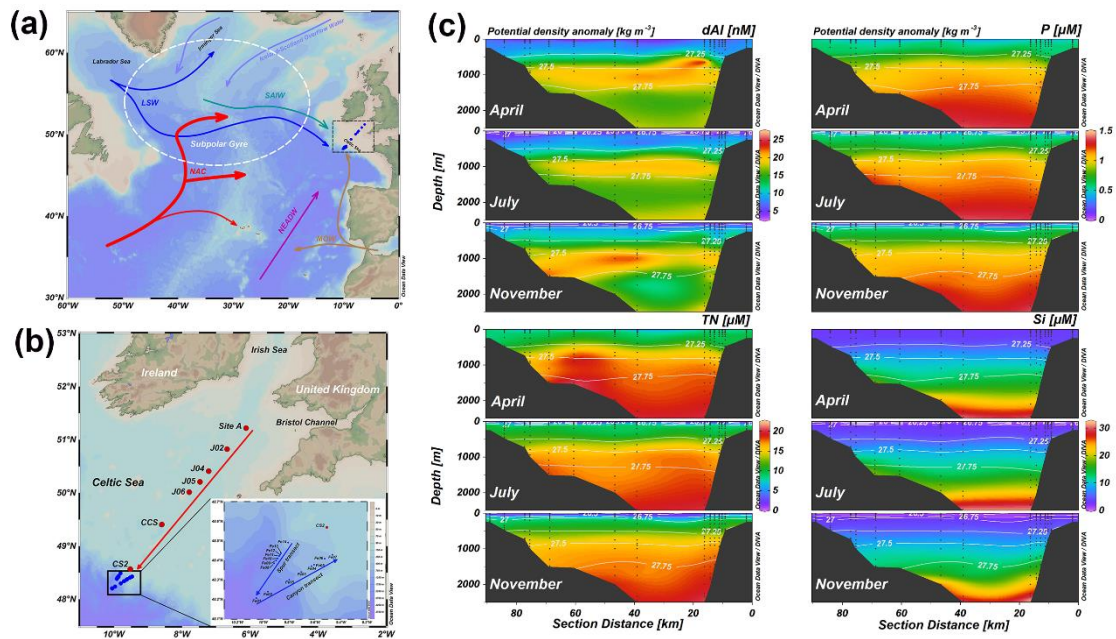
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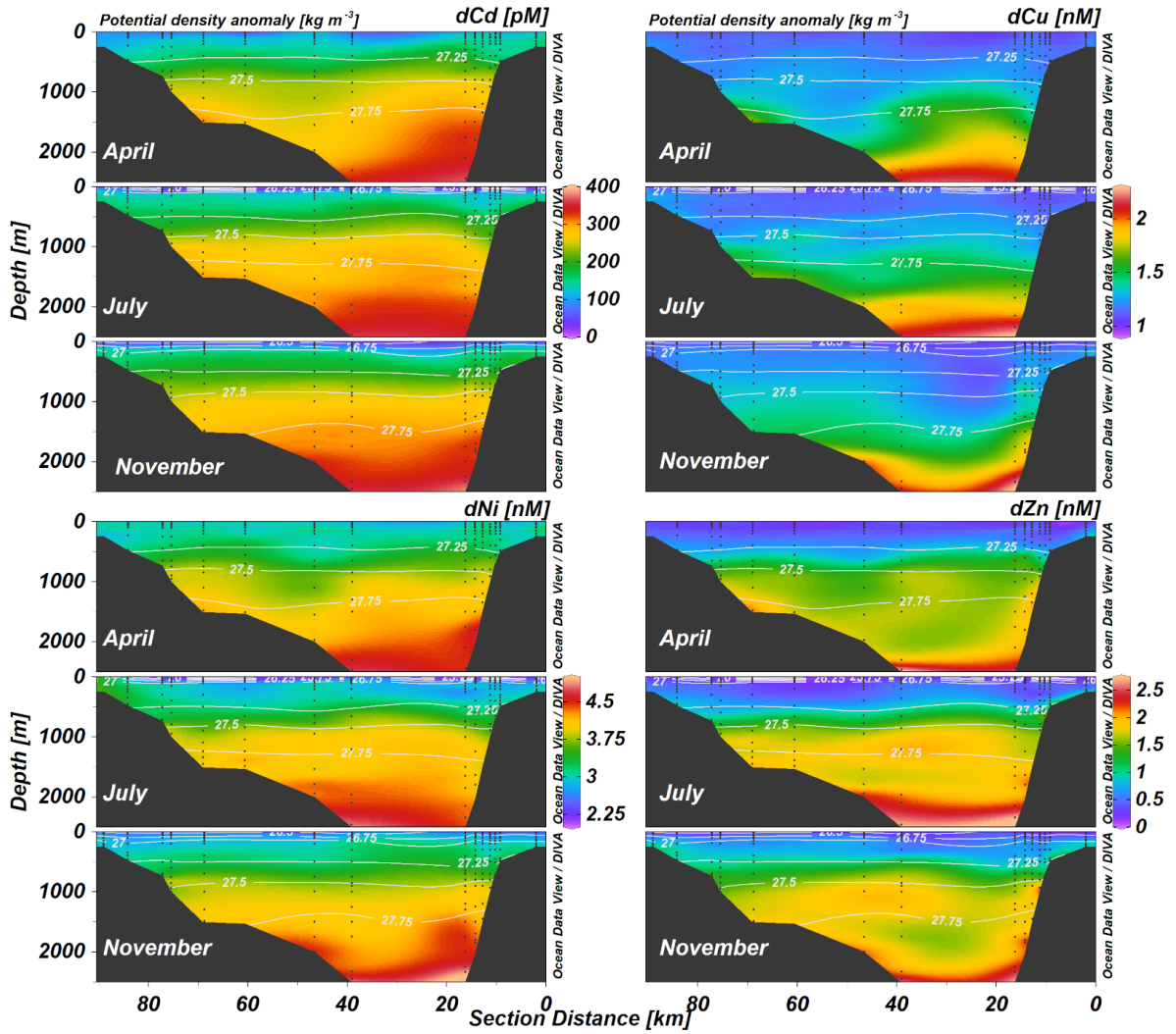
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548 **Figures**



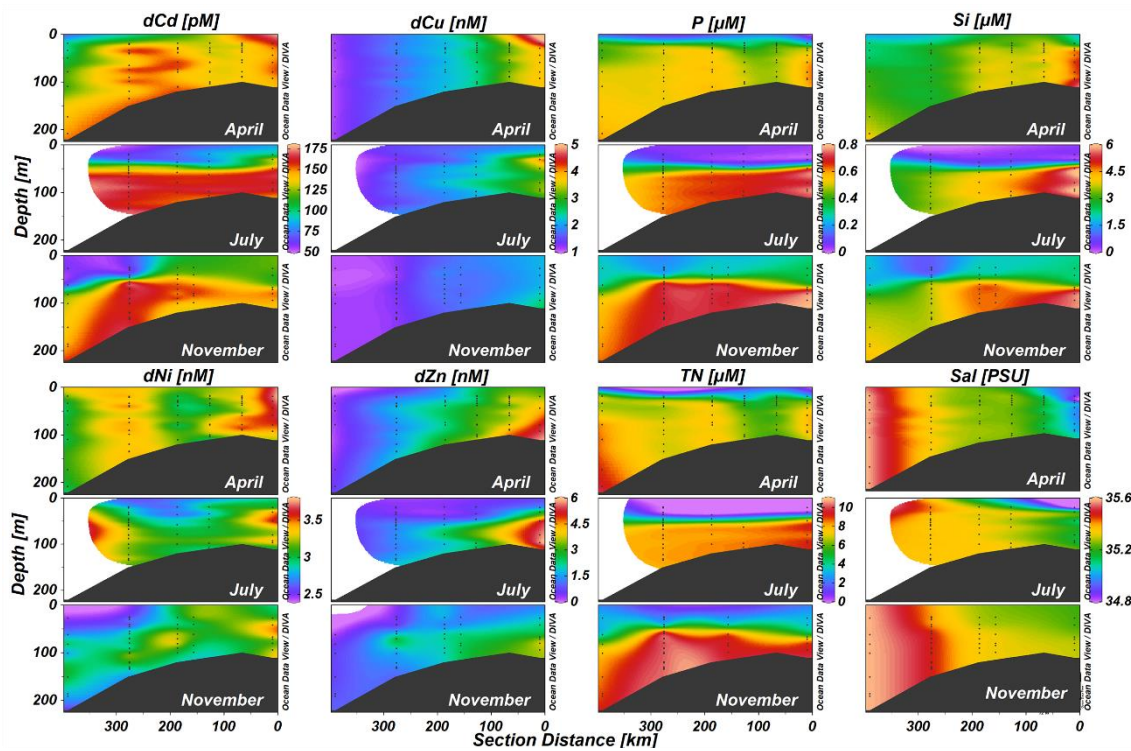
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 550 **Fig. 1** (a) The schematic circulation of water masses (NAC: North Atlantic Current; LSW:
 551 Labrador Sea waters; SAIW: Sub-Arctic Intermediate Waters; MOW: Mediterranean Outflow
 552 Waters; NEADW: Northeast Atlantic Deep Waters) in the North Atlantic Ocean; (b) Sampling
 553 transects and locations on the Northeast Atlantic continental margin (Celtic Sea). The red and blue
 554 arrows define the shelf and slope sections, respectively, for **Fig. 2** and **Fig. 3**. (c) Section plots of
 555 dissolved aluminum (dAl), phosphate (P), nitrate+nitrite (TN), and silicic acid (Si) along the slope
 556 transect during expeditions in November 2014 (DY018), April 2015 (DY029), and July 2015
 557 (DY033) in Celtic Sea.
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559

560 **Fig. 2** Section plots of dissolved cadmium (dCd), copper (dCu), nickel (dNi), and zinc (dZn) on
 561 the slope of the Northeast Atlantic continental margin. Samples were taken in November 2014,
 562 April 2015, and July 2015, respectively. The section is defined in [Fig. 1b](#).

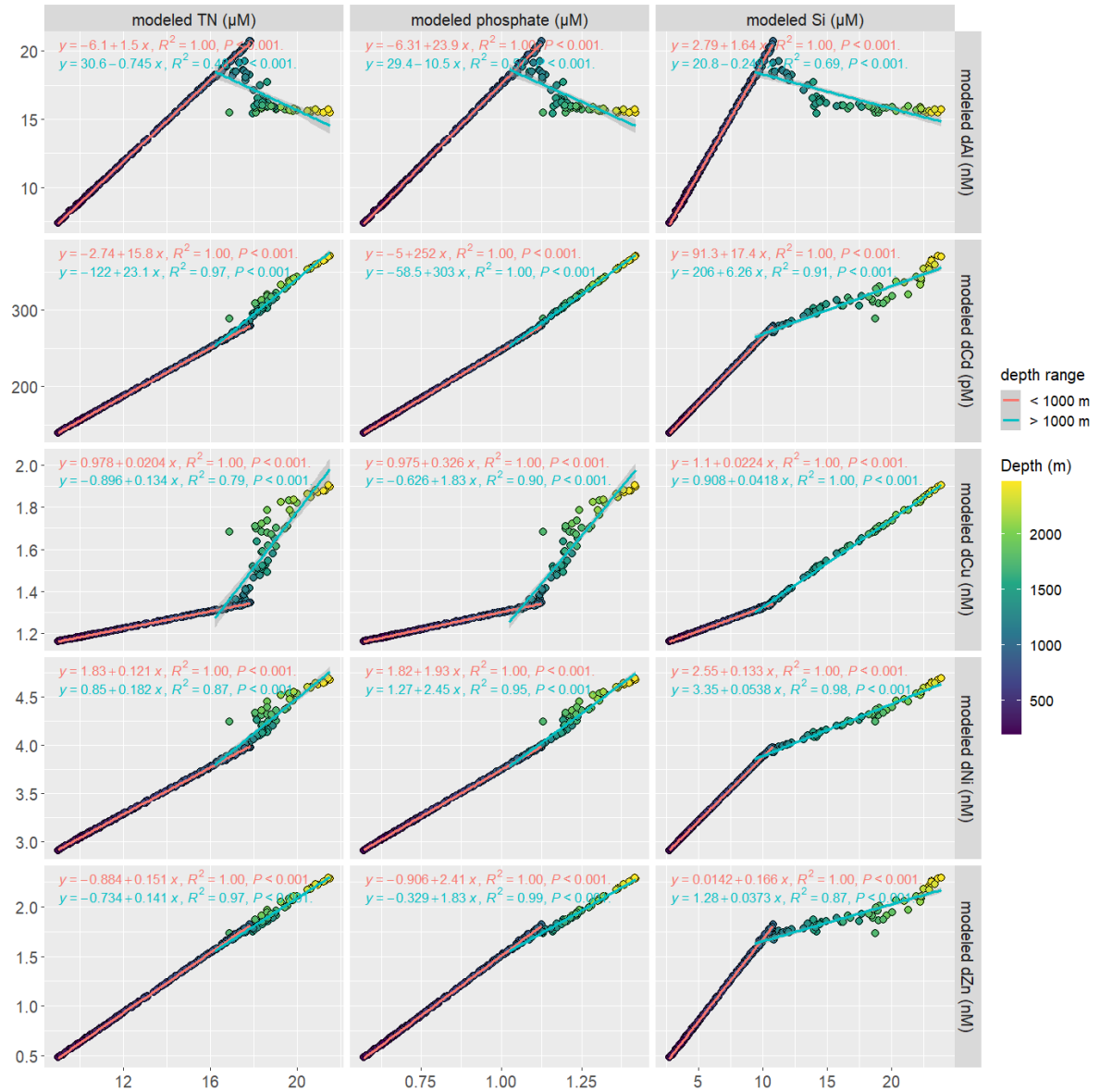
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564

565 **Fig. 3:** Section plots of dissolved trace metals (dCd, dCu, dNi, dZn), salinity, and nutrients
 566 (nitrate+nitrite (TN), phosphate (P), silicic acid (Si)) on the continental shelf of the Northeast
 567 Atlantic Ocean. The section is defined in Fig. 1b. Samples were taken in November 2014, April
 568 2015, and July 2015, respectively.

569



570

571 **Fig. 4:** Correlations between reconstructed dissolved trace metal (dTM: dAl, dCd, dCu, dNi, dZn)
 572 and nutrient (nitrate+nitrite (TN), phosphate (P), and silicic acid (Si)) concentrations on the
 573 Northeast Atlantic continental slope. Linear regression models were applied to depths < 1000 m
 574 and depths > 1000 m, respectively.

575